

Chapter 16

Acids and Bases

Applications of equilibrium thermodynamics are developed further in Chapter 16, with its analysis of conjugate relationships in acid–base reactions. The accompanying exercises should provide ample opportunity to work through the various issues and operations introduced in the text.

The bulk of the chapter is concerned with Arrhenius acids and bases in aqueous solution. For an earlier treatment of acid–base phenomena, particularly of the Lewis kind, see Section 3-2, pages R3.4–R3.5, and Example 3-5 in PoC. The analogy with redox processes, first made in Chapter 3, will be completed in Chapter 17.

Ionization constants are compiled in Table C-20 of Appendix C (pages A98–A99). Help with the mathematics (mostly logarithms and quadratic equations) is available in Appendix B.

1. Although HI, HBr, and HCl are all strong acids in water, the species HF is an anomalously weak acid despite a strongly polarized $\text{H}^{\delta+}-\text{F}^{\delta-}$ bond—a feature that would otherwise facilitate the removal of H^+ from F^- . Contrasting with the favorable polarity, however, the small and highly electronegative fluorine atom produces a very *strong* bond between H and F, a bond harder to break than one between H and Cl. The intact structure HF is favored; the ionized structure $\text{H}^+ \cdots \text{F}^-$ is not.

In addition, the compact F^- ion (the conjugate base of HF) must accommodate its destabilizing negative charge in a comparatively small volume. The second-period fluoride ion is smaller and less stable than the third-period chloride ion, and consequently the acidic form is favored still further over the conjugate base. The effects of both a hard-to-break H–X bond and a hard-to-sustain X^- ion combine to make HF ($\text{p}K_{\text{a}} = 3.17$) a weaker acid than HCl.

See Section 16-2 and pages R16.1–R16.3 of *PoC* for a general discussion of acidic strength and weakness. Bond lengths and dissociation energies are collected in Table C-13 of Appendix C (page A82), and electronegativities are tabulated in Figure 7-18 (page 244).

2. Both HCl and HI are strong acids, but HI is stronger. The I^- anion is larger and easier to stabilize than the Cl^- anion, and the H–I bond is longer and weaker than the H–Cl bond as well (see Table C-13 in *PoC*, page A82).

3. An unstable acidic structure (HA) and a stable conjugate structure (A^-) tend to make an acid strong. See Section 16-2 and pages R16.1–R16.3 of *PoC*, as well as Examples 8-7 and 16-1.

Ionization constants, cited in support of the qualitative descriptions given below, are available in Table C-20 of *PoC* (pages A98–A99).

(a) CF_3COOH ($pK_a = 0.23$) is a stronger acid than CH_2FCOOH ($pK_a = 2.59$), because fluorine is more electronegative than hydrogen. Three electron-withdrawing fluoro groups, rather than only one, are better able to stabilize the negative charge on the anion.

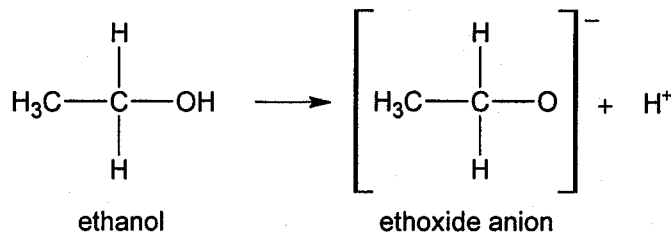
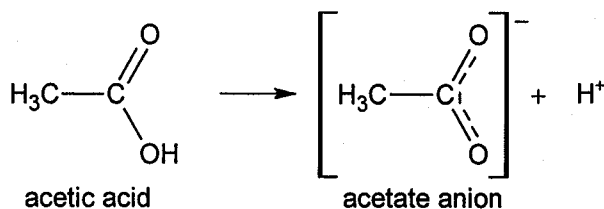
(b) The sulfur atom in H_2SO_4 is more electronegative than the boron atom in H_3BO_3 . Sulfuric acid is one of a relatively few *strong* acids, completely dissociated in aqueous solution. Boric acid ($pK_a = 9.27$) is a weak acid.

(c) Hypochlorous acid ($HClO$, $pK_a = 7.52$) is stronger than hypoiodous acid (HIO , $pK_a = 10.5$). The electron-withdrawing Cl atom in $H-O-Cl$ helps both to polarize the $O-H$ bond and to stabilize the anion that results. Chlorine is more electronegative than iodine.

(d) Phosphoric acid (H_3PO_4 , $pK_a = 2.12$) acts as a triprotic acid, releasing three H^+ ions in succession. The dihydrogen phosphate ion ($H_2PO_4^-$, $pK_a = 7.21$) is formed only after H_3PO_4 loses its first proton. To remove a second proton from an anion is always harder than to remove the first proton from a neutral molecule, and therefore H_3PO_4 is the stronger acid of the two.

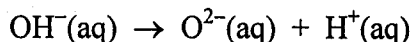
4. Use the same reasoning as in the preceding exercise.

(a) In the ethoxide ion, negative charge is concentrated on a single oxygen atom. The acetate anion, by contrast, is able to spread its negative charge over a three-atom π system, making CH_3COO^- a more stable structure than $CH_3CH_2O^-$:



Acetic acid ($pK_a = 4.75$) is a stronger acid than ethanol ($pK_a = 15.9$). One molecule is a carboxylic acid; the other is an alcohol.

(b) KOH, which releases OH^- in water, is an Arrhenius *base*, not an acid. Ionization of the hydroxide ion,



would produce the highly unstable oxide ion, O^{2-} , as its conjugate base.

The hydrogen sulfate ion, HSO_4^- , is the conjugate base of sulfuric acid:

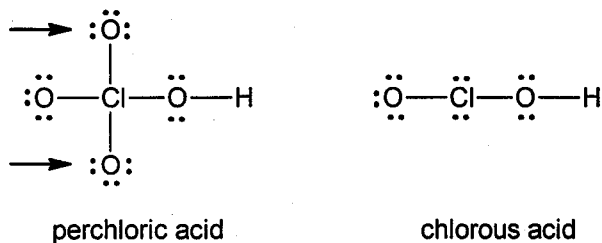


An Arrhenius acid in its own right, HSO_4^- dissociates to form the stable sulfate anion, SO_4^{2-} . Although weaker than sulfuric acid, the hydrogen sulfate ion ($pK_a = 1.92$) is a far stronger acid than the hydroxide ion in KOH.

See Figure 16.1(c) on page 464 below for Lewis diagrams of HSO_4^- and H_2SO_4 .

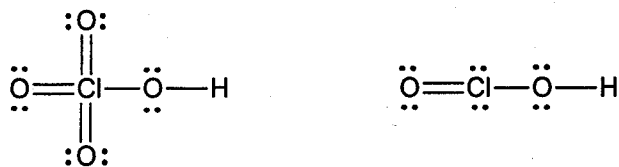
(c) Perchloric acid, HClO_4 , is a strong acid, completely ionized in aqueous solution. Chlorous acid, HClO_2 , ionizes with a pK_a of 1.96.

Perchloric acid draws its extra strength from the two additional oxygen atoms contained in the structure:



The O–H bond is more polarized in HClO_4 than in HClO_2 , and the negative charge is spread over more atoms in the perchlorate anion as well.

Note that other resonance forms also exist, notable among them diagrams such as

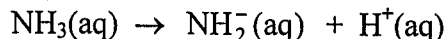


in which chlorine exhibits an expanded octet. The ability of a conjugate base to disperse its charge is reflected, in part, by the number of equivalent resonance structures that contribute to the system.

(d) Remember that a weak base is transformed into a strong conjugate acid, and remember also that the ammonium ion, NH_4^+ , is indeed the conjugate acid of a weak base: ammonia, NH_3 . With a ready proton to give, NH_4^+ is therefore a stronger acid than NH_3 . The ammonium ion produces the stable ammonia molecule as its conjugate base,

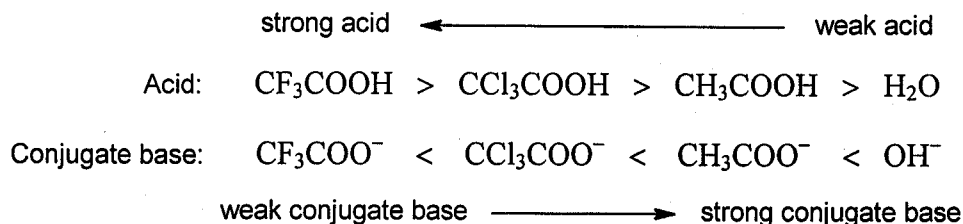


whereas the ammonia *molecule* produces NH_2^- , a far less stable species:



See Figure 16.1(a) on page 464 for Lewis structures of ammonia and the ammonium ion.

5. The weaker the acid HA, the stronger is its conjugate base A^- :

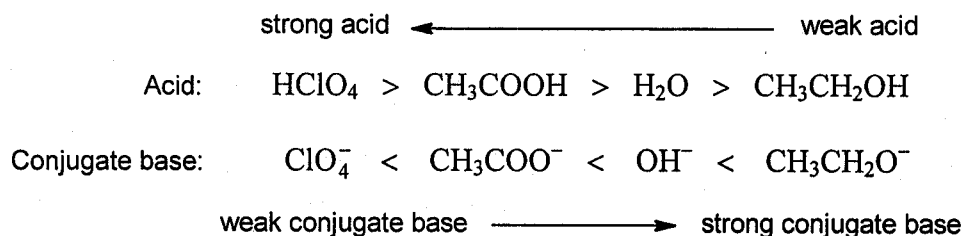


The rankings are justified as follows:

1. Water, with $\text{p}K_a = 14$, is the weakest acid of the four. Its conjugate base, OH^- , is best suited to accept a proton.
2. Acetic acid, CH_3COOH , is a carboxylic acid of moderate strength, falling between H_2O and CCl_3COOH . Its $\text{p}K_a$ is equal to 4.75.
3. The electron-withdrawing chlorine atoms in trichloroacetic acid make CCl_3COOH a better proton donor—and hence a stronger acid—than CH_3COOH . The CCl_3COO^- anion, a weaker base than CH_3COO^- , is better able to disperse its negative charge and thereby resist protonation.
4. Fluorine is more electronegative than chlorine, and consequently CF_3COOH is a stronger acid than CCl_3COOH . Weakest of the set, the trifluorinated conjugate base (CF_3COO^-) is highly stable and least likely to accept a proton.

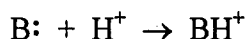
See Section 16-2 and pages R16.1–R16.3 of *PoC* for a more extended discussion of conjugate strength and weakness.

6. Again, the weakest acid produces the strongest conjugate base:



Perchloric acid is the strongest acid owing to the four oxygen atoms that stabilize negative charge in the ClO_4^- anion. The perchlorate species is therefore the weakest conjugate base. Next in basic strength is the acetate anion, which arises from the ionization of a carboxylic acid with $\text{p}K_a = 4.75$. The OH^- ion is produced by H_2O ($\text{p}K_a = 14$), and the $\text{CH}_3\text{CH}_2\text{O}^-$ ion is produced by ethanol ($\text{p}K_a = 15.9$). See Exercises 4 and 5 for additional details concerning the structure and acidity of these species.

7. Add H^+ to the base $\text{B}:$ to obtain the conjugate acid BH^+ , as in the generic reaction below:



Lewis structures are shown in Figure 16.1 (overleaf).

8. Similar to Exercise 7. See Figure 16.2 for the Lewis structures.

Exercises 9 through 23 provide straightforward drill in manipulating logarithms. All are solved in substantially the same way.

The specified ranges typically span either 14 powers of 10 in large steps or just a single decade in small steps.

9. We define pH as the negative logarithm of the hydronium ion concentration, expressing $[\text{H}_3\text{O}^+]$ in moles per liter:

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

For example, the pH of a solution 0.1 M in H_3O^+ is 1.0:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 0.1 = -\log(1 \times 10^{-1}) = -(-1.0) = 1.0$$

Digits in the mantissa (the decimal portion of the logarithm) are significant, whereas those in the characteristic (the integral portion) are not. See pages R16.8 and A42–A45 for more information about base-10 logarithms.

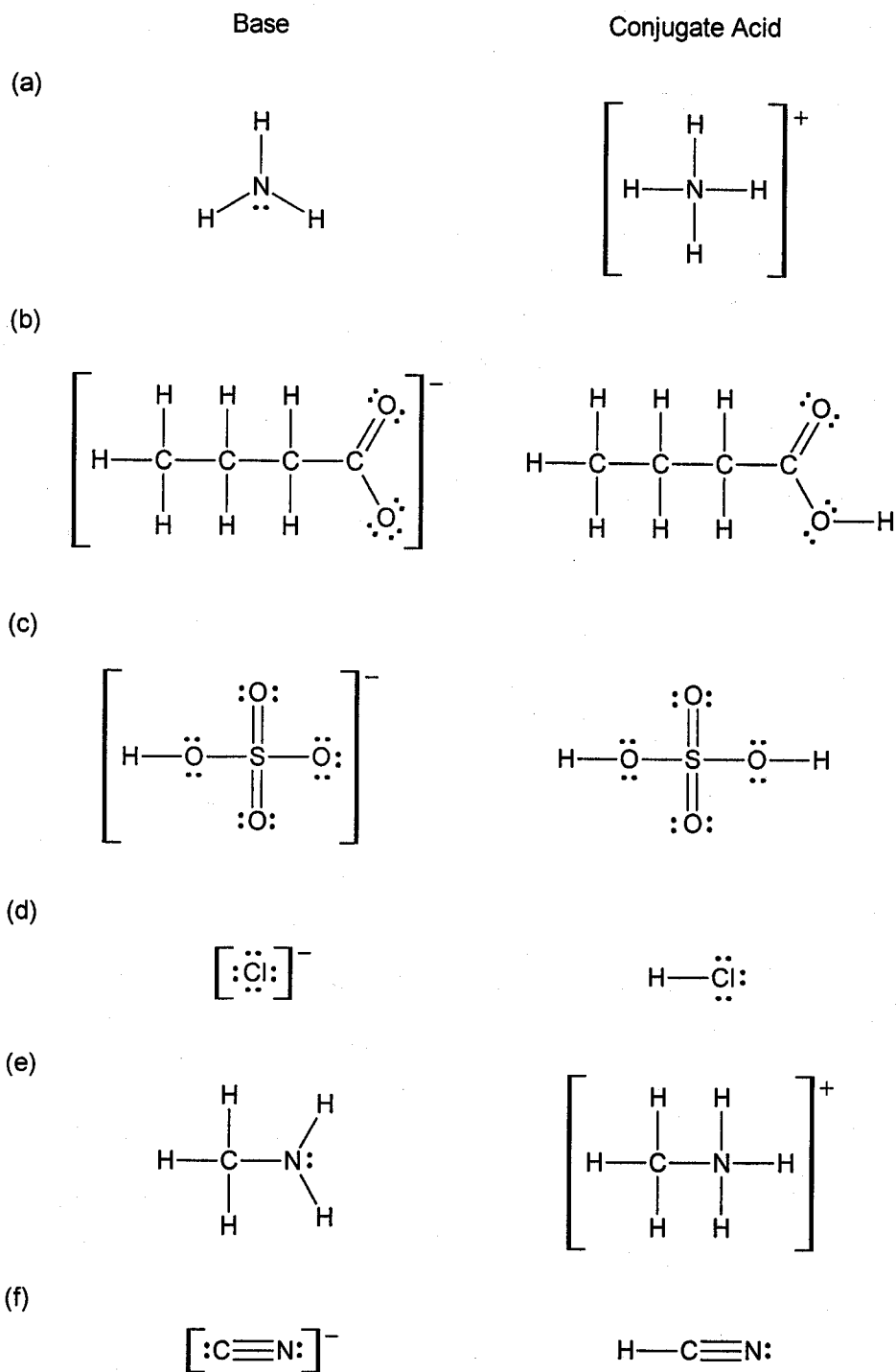


FIGURE 16.1 Principal Lewis diagrams of the conjugate pairs requested in Exercise 7. In (b), the anion is stabilized by a delocalized π system that spans the carboxylate carbon and two oxygens. Only one of two equivalent resonance forms is shown. In (c), the expanded octet about the sulfur atoms (resulting in both S–O and S=O bonds) is consistent with the known structure of sulfuric acid. Other resonance forms are possible as well.

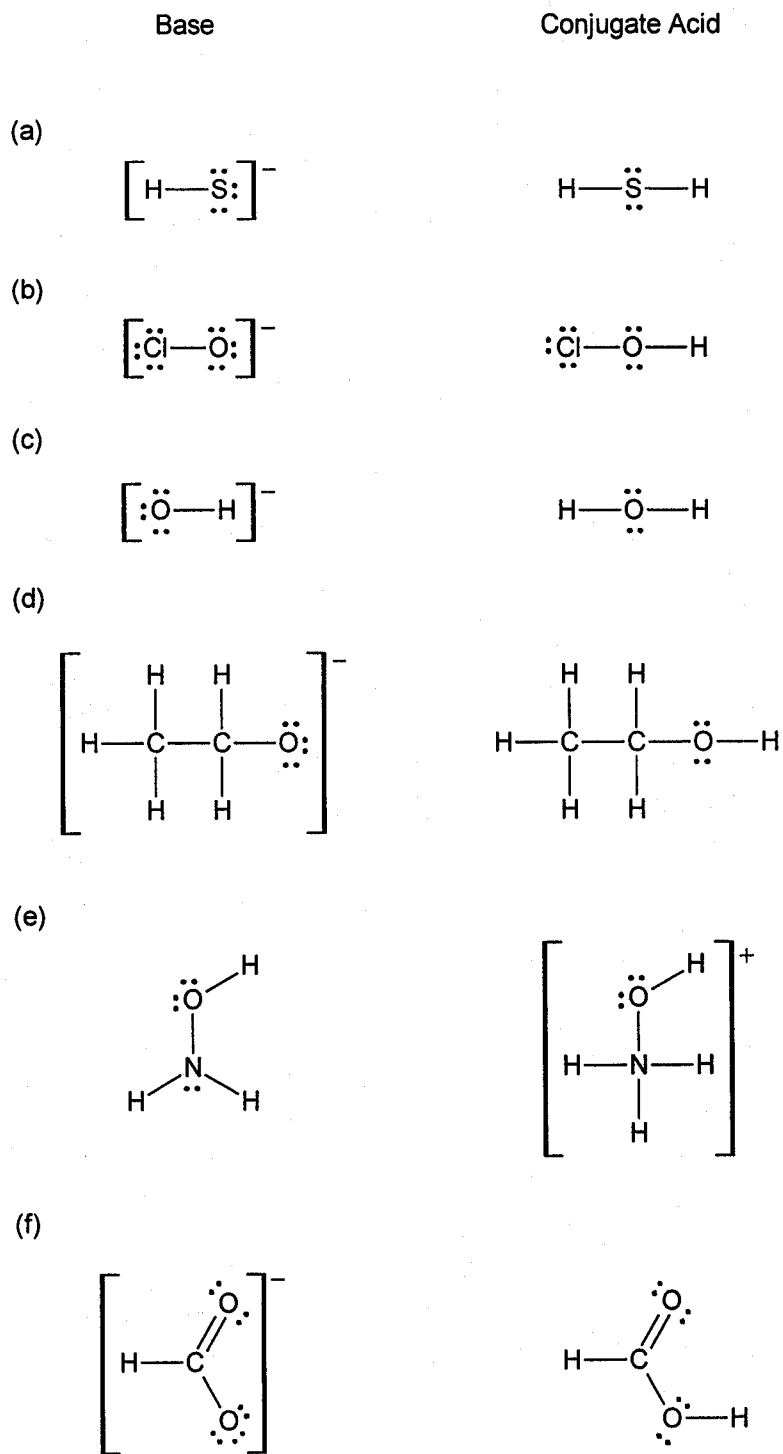


FIGURE 16.2 Principal Lewis diagrams for the conjugate species in Exercise 8. In (f), the formate anion is stabilized by a delocalized π system in the COO^{-} group. Only one of two equivalent resonance structures is shown.

Values of $[\text{H}_3\text{O}^+]$ and pH are tabulated below. Each number is stated to just one significant figure:

	$[\text{H}_3\text{O}^+]$ (M)	pH
(a)	1	0.0
(b)	0.1	1.0
(c)	0.01	2.0
(d)	0.001	3.0
(e)	0.0001	4.0
(f)	0.00001	5.0
(g)	0.000001	6.0
(h)	0.0000001	7.0

10. Each molar concentration is alternatively expressed in the general form

$$[\text{H}_3\text{O}^+] = 5 \times 10^{-n}$$

with the corresponding pH following straightforwardly from the definition:

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ &= -\log(5 \times 10^{-n}) \\ &= -\log 5 - \log(10^{-n}) \\ &= -0.6990 + n \end{aligned}$$

A 0.5 M solution of H_3O^+ , for example, has a pH equal to 0.3:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 0.5 = -\log(5 \times 10^{-1}) = -0.6990 + 1 = 0.3010$$

The other values are all calculated in the same way:

	$[\text{H}_3\text{O}^+]$ (M)	pH
(a)	0.5	0.3
(b)	0.05	1.3
(c)	0.005	2.3
(d)	0.0005	3.3
(e)	0.00005	4.3
(f)	0.000005	5.3
(g)	0.0000005	6.3

Note that the mantissas are limited to one significant figure.

11. The molar concentrations are all given here in the form

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

No explicit computation is necessary. We simply read the exponent to obtain the pH:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(10^{-\text{pH}}) = -(-\text{pH}) = \text{pH}$$

Since each concentration is reported only as a power of 10, the pH values show no significant figures past the decimal point:

	$[\text{H}_3\text{O}^+] (M)$	pH
(a)	10^{-8}	8
(b)	10^{-9}	9
(c)	10^{-10}	10
(d)	10^{-11}	11
(e)	10^{-12}	12
(f)	10^{-13}	13
(g)	10^{-14}	14

12. Similar to Exercise 10. Each $[\text{H}_3\text{O}^+]$ is given as 5×10^{-n} , and each pH is therefore equal to $n - \log 5$:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(5 \times 10^{-n}) = -\log 5 - \log(10^{-n}) = -0.6990 + n$$

Results (to one significant figure) are tabulated below:

	$[\text{H}_3\text{O}^+] (M)$	pH
(a)	5×10^{-8}	7.3
(b)	5×10^{-9}	8.3
(c)	5×10^{-10}	9.3
(d)	5×10^{-11}	10.3
(e)	5×10^{-12}	11.3
(f)	5×10^{-13}	12.3
(g)	5×10^{-14}	13.3

13. Each hydronium concentration is equivalently expressed as

$$[\text{H}_3\text{O}^+] = n \times 10^{-3} \quad (n = 1, 2, \dots, 10)$$

The associated pH is equal to $3 - \log n$, as demonstrated below for a concentration of $0.005 M$ (part e):

$$\begin{aligned}\text{pH} &= -\log(5 \times 10^{-3}) = -\log 5 - \log(10^{-3}) \\ &= -0.6990 - (-3) = 2.3010\end{aligned}$$

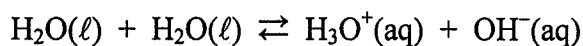
Logarithms of the first few prime numbers will be useful to readers who wish to forgo a calculator:

$$\log 2 = 0.3010 \quad \log 3 = 0.4771 \quad \log 5 = 0.6990 \quad \log 7 = 0.8451$$

The resulting pH values are limited to one significant figure in the mantissa:

	$[\text{H}_3\text{O}^+]$ (M)	pH
(a)	0.001	3.0
(b)	0.002	2.7
(c)	0.003	2.5
(d)	0.004	2.4
(e)	0.005	2.3
(f)	0.006	2.2 (2.22)
(g)	0.007	2.2 (2.15)
(h)	0.008	2.1 (2.10)
(i)	0.009	2.0 (2.046)
(j)	0.01	2.0

14. Concentrations of H_3O^+ and OH^- are linked by the ion-product constant for water:



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad (\text{at } 25^\circ\text{C})$$

Taking $[\text{H}_3\text{O}^+] = 1 M$, for example, we calculate pH, $[\text{OH}^-]$, and pOH as follows:

$$[\text{H}_3\text{O}^+] = 1 M$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 1 = 0.0$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1} = 1 \times 10^{-14} M$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1 \times 10^{-14}) = 14.0$$

The remaining values are all determined in the same way, with the product of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ always equal to K_w . In turn, the sum of pH and pOH is equal to $\text{p}K_w$ (14.00 at 25°C):

	$[\text{H}_3\text{O}^+]$ (M)	pH	$[\text{OH}^-]$ (M)	pOH
(a)	1×10^0	0.0	1×10^{-14}	14.0
(b)	1×10^{-1}	1.0	1×10^{-13}	13.0
(c)	1×10^{-2}	2.0	1×10^{-12}	12.0
(d)	1×10^{-3}	3.0	1×10^{-11}	11.0
(e)	1×10^{-4}	4.0	1×10^{-10}	10.0
(f)	1×10^{-5}	5.0	1×10^{-9}	9.0
(g)	1×10^{-6}	6.0	1×10^{-8}	8.0
(h)	1×10^{-7}	7.0	1×10^{-7}	7.0

15. Since each hydronium concentration is specified as 1×10^{-n} , the corresponding pH (with a one-digit mantissa) is simply n :

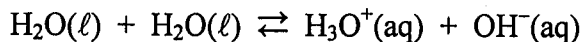
$$\text{pH} = -\log(1 \times 10^{-n}) = -\log 1 - \log(10^{-n}) = 0.0 + n$$

mantissa
characteristic

Taking $[\text{H}_3\text{O}^+] = 1 \times 10^{-8} \text{ M}$, for instance, we quickly determine that the pH is equal to 8.0:

$$\text{pH} = -\log(1 \times 10^{-8}) = -\log 1 - \log(10^{-8}) = 0.0 + 8 = 8.0$$

We obtain, next, the concentration of hydroxide ion required to sustain the ion-product constant of water (continuing with $[\text{H}_3\text{O}^+] = 1 \times 10^{-8} \text{ M}$ as a specific example):



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad (\text{at } 25^\circ\text{C})$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1 \times 10^{-8}} = 1 \times 10^{-6} \text{ M}$$

The pOH is defined, by analogy to pH, as the negative logarithm of the hydroxide concentration:

$$\text{pOH} = -\log [\text{OH}^-] = -\log(1 \times 10^{-6}) = 6.0$$

Note that the equivalent numerical relationships

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00$$

are valid at 25°C. See below:

	$[\text{H}_3\text{O}^+] (M)$	pH	$[\text{OH}^-] (M)$	pOH
(a)	1×10^{-8}	8.0	1×10^{-6}	6.0
(b)	1×10^{-9}	9.0	1×10^{-5}	5.0
(c)	1×10^{-10}	10.0	1×10^{-4}	4.0
(d)	1×10^{-11}	11.0	1×10^{-3}	3.0
(e)	1×10^{-12}	12.0	1×10^{-2}	2.0
(f)	1×10^{-13}	13.0	1×10^{-1}	1.0
(g)	1×10^{-14}	14.0	1×10^0	0.0

16. Start with the mass-action expression for the autoionization of water,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

and take the negative logarithm of both sides:

$$-\log K_w = -\log\{[\text{H}_3\text{O}^+][\text{OH}^-]\} = -\log [\text{H}_3\text{O}^+] - \log [\text{OH}^-]$$

Then define the quantities pH, pOH, and $\text{p}K_w$ as

$$\text{pH} = -\log [\text{H}_3\text{O}^+] \quad \text{pOH} = -\log [\text{OH}^-] \quad \text{p}K_w = -\log K_w$$

to obtain the desired result:

$$\text{p}K_w = \text{pH} + \text{pOH}$$

At 25°C, the values of K_w and $\text{p}K_w$ are 1.0×10^{-14} and 14.00, respectively. See pages 577–584 and R16.3–R16.5 in *PoC*.

17. Consider the case where $\text{pH} = 1.0$. Taking the antilogarithm of $-\text{pH}$, we immediately have the concentration of hydronium ion:

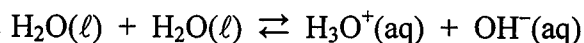
$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-1.0} = 1 \times 10^{-1} \text{ M}$$

The equilibrium concentration of hydroxide ion is linked with $[\text{H}_3\text{O}^+]$ through the mass-action expression

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

that governs the autoionization of water:



At 25°C ($K_w = 1.0 \times 10^{-14}$), we therefore have an OH^- concentration of $1 \times 10^{-13} \text{ M}$ to balance the H_3O^+ concentration of $1 \times 10^{-1} \text{ M}$:

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1 \times 10^{-1}} = 1 \times 10^{-13} \text{ M}$$

Another method, equally valid, is to use the relationship between pH , pOH , and $\text{p}K_w$ at 25°C :

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00 \quad (25^\circ\text{C})$$

$$\text{pOH} = -\log [\text{OH}^-] = 14.00 - \text{pH} = 14.00 - 1.0 = 13.0$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-13.0} = 1 \times 10^{-13} \text{ M}$$

Antilogarithms of nonintegral exponents are easily computed on most scientific calculators. Note, however, that *half*-integral values ($n + \frac{1}{2}$) may be handled analytically:

$$10^{-(n+\frac{1}{2})} = 10^{-\frac{1}{2}} \times 10^{-n} = \frac{1}{\sqrt{10}} \times 10^{-n} = 0.3162 \times 10^{-n}$$

Results are collected on the next page.

	pH	$[\text{H}_3\text{O}^+] (M)$	$[\text{OH}^-] (M)$	pOH
(a)	1.0	1×10^{-1}	1×10^{-13}	13.0
(b)	1.5	$\frac{1}{\sqrt{10}} \times 10^{-1}$	$\frac{1}{\sqrt{10}} \times 10^{-12}$	12.5
(c)	2.0	1×10^{-2}	1×10^{-12}	12.0
(d)	2.5	$\frac{1}{\sqrt{10}} \times 10^{-2}$	$\frac{1}{\sqrt{10}} \times 10^{-11}$	11.5
(e)	3.0	1×10^{-3}	1×10^{-11}	11.0
(f)	3.5	$\frac{1}{\sqrt{10}} \times 10^{-3}$	$\frac{1}{\sqrt{10}} \times 10^{-10}$	10.5
(g)	4.0	1×10^{-4}	1×10^{-10}	10.0
(h)	4.5	$\frac{1}{\sqrt{10}} \times 10^{-4}$	$\frac{1}{\sqrt{10}} \times 10^{-9}$	9.5
(i)	5.0	1×10^{-5}	1×10^{-9}	9.0
(j)	5.5	$\frac{1}{\sqrt{10}} \times 10^{-5}$	$\frac{1}{\sqrt{10}} \times 10^{-8}$	8.5
(k)	6.0	1×10^{-6}	1×10^{-8}	8.0
(l)	6.5	$\frac{1}{\sqrt{10}} \times 10^{-6}$	$\frac{1}{\sqrt{10}} \times 10^{-7}$	7.5
(m)	7.0	1×10^{-7}	1×10^{-7}	7.0

18. The calculations are the same as in the preceding exercise. See the tabulation of results on the next page.

	pH	$[\text{H}_3\text{O}^+] (M)$	$[\text{OH}^-] (M)$	pOH
(a)	7.5	$\frac{1}{\sqrt{10}} \times 10^{-7}$	$\frac{1}{\sqrt{10}} \times 10^{-6}$	6.5
(b)	8.0	1×10^{-8}	1×10^{-6}	6.0
(c)	8.5	$\frac{1}{\sqrt{10}} \times 10^{-8}$	$\frac{1}{\sqrt{10}} \times 10^{-5}$	5.5
(d)	9.0	1×10^{-9}	1×10^{-5}	5.0
(e)	9.5	$\frac{1}{\sqrt{10}} \times 10^{-9}$	$\frac{1}{\sqrt{10}} \times 10^{-4}$	4.5
(f)	10.0	1×10^{-10}	1×10^{-4}	4.0
(g)	10.5	$\frac{1}{\sqrt{10}} \times 10^{-10}$	$\frac{1}{\sqrt{10}} \times 10^{-3}$	3.5
(h)	11.0	1×10^{-11}	1×10^{-3}	3.0
(i)	11.5	$\frac{1}{\sqrt{10}} \times 10^{-11}$	$\frac{1}{\sqrt{10}} \times 10^{-2}$	2.5
(j)	12.0	1×10^{-12}	1×10^{-2}	2.0
(k)	12.5	$\frac{1}{\sqrt{10}} \times 10^{-12}$	$\frac{1}{\sqrt{10}} \times 10^{-1}$	1.5
(l)	13.0	1×10^{-13}	1×10^{-1}	1.0
(m)	13.5	$\frac{1}{\sqrt{10}} \times 10^{-13}$	$\frac{1}{\sqrt{10}} \times 10^0$	0.5
(n)	14.0	1×10^{-14}	1×10^0	0.0

19. Here the pH values range over just one decade, spanning H_3O^+ concentrations from 0.01 M to 0.001 M. The general method is otherwise the same as in Exercise 17.

Strictly speaking, the numbers are limited to one significant figure. An extra (nonsignificant) digit is occasionally shown, however, where necessary to demonstrate

that the ion product $[\text{H}_3\text{O}^+][\text{OH}^-]$ is properly equal to 1.0×10^{-14} at 25°C . See the tabulation below:

	pH	$[\text{H}_3\text{O}^+]$ (M)	$[\text{OH}^-]$ (M)	pOH
(a)	2.0	1×10^{-2}	1×10^{-12}	12.0
(b)	2.1	7.9×10^{-3}	1.3×10^{-12}	11.9
(c)	2.2	6.3×10^{-3}	1.6×10^{-12}	11.8
(d)	2.3	5×10^{-3}	2×10^{-12}	11.7
(e)	2.4	4×10^{-3}	2.5×10^{-12}	11.6
(f)	2.5	3.2×10^{-3}	3.2×10^{-12}	11.5
(g)	2.6	2.5×10^{-3}	4×10^{-12}	11.4
(h)	2.7	2×10^{-3}	5×10^{-12}	11.3
(i)	2.8	1.6×10^{-3}	6.3×10^{-12}	11.2
(j)	2.9	1.3×10^{-3}	7.9×10^{-12}	11.1
(k)	3.0	1×10^{-3}	1×10^{-11}	11.0

20. Analogous to pH, we have the logarithmic quantity p*K*:

$$\text{p}K = -\log K$$

Results are tabulated below:

	<i>K</i>	p <i>K</i>		<i>K</i>	p <i>K</i>
(a)	1×10^{-1}	1.0	(g)	1×10^{-4}	4.0
(b)	5×10^{-2}	1.3	(h)	5×10^{-5}	4.3
(c)	1×10^{-2}	2.0	(i)	1×10^{-5}	5.0
(d)	5×10^{-3}	2.3	(j)	5×10^{-6}	5.3
(e)	1×10^{-3}	3.0	(k)	1×10^{-6}	6.0
(f)	5×10^{-4}	3.3	(l)	5×10^{-7}	6.3

For more detail, see Exercise 21.

21. Use the same method as in Exercises 9 through 13, this time substituting *K* and p*K* in place of $[\text{H}_3\text{O}^+]$ and pH:

$$\text{p}K = -\log K$$

Note that the logarithms in this exercise are all obtained from just two key relationships:

$$-\log(1 \times 10^{-n}) = n \quad -\log(5 \times 10^{-n}) = n - \log 5 = n - 0.6990$$

The results below show one significant figure in the mantissa:

	K	pK		K	pK
(a)	1×10^{-7}	7.0	(f)	5×10^{-10}	9.3
(b)	5×10^{-8}	7.3	(g)	1×10^{-10}	10.0
(c)	1×10^{-8}	8.0	(h)	5×10^{-11}	10.3
(d)	5×10^{-9}	8.3	(i)	1×10^{-11}	11.0
(e)	1×10^{-9}	9.0			

22. Both here and in Exercise 23 we obtain K by inverting the definition of pK :

$$pK = -\log K$$

$$K = 10^{-pK}$$

The requested values are as follows:

	pK	K		pK	K
(a)	1.0	1×10^{-1}	(h)	4.5	3×10^{-5}
(b)	1.5	3×10^{-2}	(i)	5.0	1×10^{-5}
(c)	2.0	1×10^{-2}	(j)	5.5	3×10^{-6}
(d)	2.5	3×10^{-3}	(k)	6.0	1×10^{-6}
(e)	3.0	1×10^{-3}	(l)	6.5	3×10^{-7}
(f)	3.5	3×10^{-4}	(m)	7.0	1×10^{-7}
(g)	4.0	1×10^{-4}			

23. The method is the same as in Exercises 17 and 19, with pK and K used in place of pH and $[H_3O^+]$:

$$pK = -\log K$$

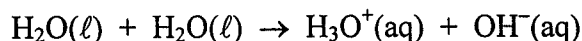
$$K = 10^{-pK}$$

Values of pK and K are tabulated on the next page.

	pK	K		pK	K
(a)	2.0	1×10^{-2}	(g)	2.6	2.5×10^{-3}
(b)	2.1	7.9×10^{-3}	(h)	2.7	2×10^{-3}
(c)	2.2	6.3×10^{-3}	(i)	2.8	1.6×10^{-3}
(d)	2.3	5×10^{-3}	(j)	2.9	1.3×10^{-3}
(e)	2.4	4×10^{-3}	(k)	3.0	1×10^{-3}
(f)	2.5	3.2×10^{-3}			

Where indicated, a second (nonsignificant) digit is included to show the relative magnitudes more clearly.

24. The constraints governing $\text{H}_2\text{O}(\ell)$, $\text{H}_3\text{O}^+(\text{aq})$, and $\text{OH}^-(\text{aq})$ at equilibrium are covered in Section 16-3 of *PoC* and reviewed on pages R16.3–R16.5. Our frame of reference is the autoionization of water,



with its associated equilibrium constant:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad (\text{at } 25^\circ\text{C})$$

The pH, a convenient substitute for $[\text{H}_3\text{O}^+]$, is defined as a negative logarithm:

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

See also Example 16-2.

(a) Potassium hydroxide is a strong base, producing one mole of OH^- per mole of KOH dissolved in water:

$$\begin{aligned} [\text{OH}^-] &= \frac{0.345 \text{ g KOH}}{57.2 \text{ mL}} \times \frac{1 \text{ mol KOH}}{56.1056 \text{ g KOH}} \times \frac{1 \text{ mol OH}^-}{\text{mol KOH}} \times \frac{1000 \text{ mL}}{\text{L}} = 0.1075 \text{ M} \\ &= 0.108 \text{ M} \quad (3 \text{ sig fig}) \end{aligned}$$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.1075} = 9.30 \times 10^{-14} \text{ M} \\ &= 9.3 \times 10^{-14} \text{ M} \quad (2 \text{ sig fig}) \end{aligned}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(9.30 \times 10^{-14}) = 13.03 \quad (2 \text{ sig fig})$$

The solution is basic: $\text{pH} > 7$.

(b) HCl is a strong acid, completely ionized in dilute aqueous solution:

$$[\text{H}_3\text{O}^+] = \frac{0.107 \text{ mol HCl}}{0.898 \text{ L}} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HCl}} = 0.119 \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 0.119 = 0.924 \quad (\text{acidic, pH} < 7)$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{0.119} = 8.4 \times 10^{-14} \text{ M}$$

(c) Potassium chloride is the salt of a strong acid (HCl) and a strong base (KOH). Any solution of KCl is neutral:

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M} \quad [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M} \quad \text{pH} = 7.00$$

See pages 584–589 in *PoC*.

(d) HBr, a strong acid, yields one mole of hydronium ions per mole of dissolved compound:

$$[\text{H}_3\text{O}^+] = \frac{0.000100 \text{ mol HBr}}{100.0 \text{ mL}} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HBr}} \times \frac{1000 \text{ mL}}{\text{L}} = 1.00 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.00 \times 10^{-3}) = 3.000 \quad (\text{acidic, pH} < 7)$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.00 \times 10^{-3}} = 1.0 \times 10^{-11} \text{ M}$$

The mixture is weakly acidic, with a pH of 3. HBr is a strong acid—it dissociates completely in dilute solution—but the amount of acid introduced into this particular volume is comparatively small.

25. Use the same methods as in the preceding exercise.

(a) HNO_3 is a strong acid, yielding one mole of hydronium ions per mole of dissolved acid:

$$[\text{H}_3\text{O}^+] = \frac{1.00 \text{ mol HNO}_3}{1.00 \text{ L}} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HNO}_3} = 1.00 \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 1.00 = 0.000 \quad (\text{acidic, pH} < 7)$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.00} = 1.0 \times 10^{-14} \text{ M}$$

(b) Similar. HClO_4 is a strong acid:

$$[\text{H}_3\text{O}^+] = \frac{22.7 \text{ g HClO}_4}{40.9 \text{ L}} \times \frac{1 \text{ mol HClO}_4}{100.459 \text{ g HClO}_4} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HClO}_4} = 5.5248 \times 10^{-3} \text{ M}$$

$$= 5.52 \times 10^{-3} \text{ M} \quad (3 \text{ sig fig})$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 2.258 \quad (3 \text{ sig fig})$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{5.525 \times 10^{-3}} = 1.8 \times 10^{-12} \text{ M} \quad (2 \text{ sig fig})$$

The solution is acidic: $\text{pH} < 7$.

(c) Sodium hydroxide is a strong base, producing one mole of OH^- per mole of NaOH dissolved in water:

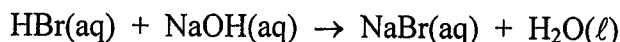
$$[\text{OH}^-] = \frac{1.0 \text{ g NaOH}}{0.100 \text{ L}} \times \frac{1 \text{ mol NaOH}}{39.9971 \text{ g NaOH}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} = 0.25 \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.25} = 4.0 \times 10^{-14} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(4.0 \times 10^{-14}) = 13.40$$

The solution is basic: $\text{pH} > 7$.

(d) Sodium bromide is the salt of a strong acid and a strong base:



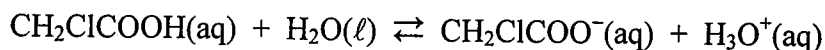
Any solution of NaBr is neutral, with $\text{pH} = 7$ at 25°C :

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M} \quad [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M} \quad \text{pH} = 7.00$$

See pages 584–589 in *PoC*.

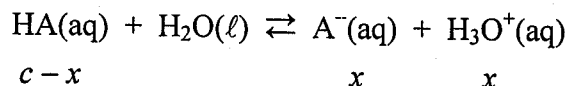
At this point we introduce a set of three weak acids—chloroacetic, benzoic, and hydrocyanic—to explore the effects of acidic strength and initial concentration on a series of equilibrium mixtures. First to be considered (in Exercises 26 through 28) is the unbuffered ionization of HA, followed (in Exercises 29 through 31) by an analysis of relative strength and weakness.

26. Let the reaction treated in this exercise



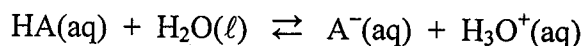
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_2\text{ClCOO}^-]}{[\text{CH}_2\text{ClCOOH}]} = 1.4 \times 10^{-3}$$

serve as a specific example of a general ionization equilibrium in aqueous solution:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Given an initial concentration of acid, $c = [\text{HA}]_0$, we thus have a symbolic template for the equilibrium concentrations of HA, A^- , and H_3O^+ in any comparable system:



Initial concentration	c	0	0
Change	$-x$	x	x
Equilibrium concentration	$c - x$	x	x

From the mass-action equation,

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{c - x}$$

we then go on to determine x in either of two ways:

1. By expanding the expression for K_a and solving the quadratic equation that results:

$$x^2 = K_a(c - x)$$

$$0 = x^2 + K_a x - K_a c$$

$$x_{\pm} = \frac{-K_a \pm \sqrt{(K_a)^2 - 4(1)(-K_a c)}}{2(1)}$$

Of the two possible roots, x_+ and x_- , only one will be physically valid. See pages A50–A54 in *PoC* (Appendix B) for a derivation of the quadratic formula.

2. By assuming that x is exceedingly small relative to c , such that $c - x \approx c$:

$$K_a = \frac{x^2}{c-x} \approx \frac{x^2}{c} \quad \text{if } x \ll c$$

$$x^2 = K_a c$$

$$x = \sqrt{K_a c}$$

The validity of this approximation will depend on the relative magnitudes of c and x , which in turn will be determined by the magnitude of K_a .

We shall follow either this procedure or a suitably modified variant when solving many of the subsequent exercises. For similar calculations, see pages 592–594 and also Examples 16-3 and 16-4.

(a) The initial concentration of weak acid, c , is 1.000 M :

$$K_a = 0.0014 \quad c = 1.000 \text{ M}$$

$$\frac{x^2}{1.000 - x} = 0.0014$$

Assume first that $1 - x \approx 1$:

$$x^2 \approx 0.0014$$

$$x = 0.0374 = 0.037 \text{ M} \quad (2 \text{ sig fig})$$

To be sure, compare this approximate x with the result obtained by solving the full quadratic equation:

$$0 = x^2 + 0.0014x - 0.0014$$

$$x = \frac{-0.0014 \pm \sqrt{(0.0014)^2 - 4(1)(-0.0014)}}{2(1)} = 0.0367, -0.0381$$

The approximate solution (0.0374) is in error by 1.9% relative to the more accurate value ($x_+ = 0.0367$), but both agree to two significant figures: 0.037 M .

Note that the second root ($x_- = -0.0381$) makes no physical sense, since it would demand that the concentration of undissociated acid *increase* from its initial value:

$$c - x_- = 1.000 - (-0.038) = 1.038$$

Accordingly, we reject x_- and use

$$x_+ = [\text{H}_3\text{O}^+] = 0.0367 \text{ M}$$

to calculate the pH and the ratio $[\text{A}^-]/[\text{HA}]$:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 0.0367 = 1.44$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{x}{c-x} = \frac{0.0367}{1.000 - 0.0367} = 0.038$$

Final results are limited to two significant figures by the accuracy of K_a . For pH, only the decimal portion of the logarithm (the mantissa) is significant.

The remaining calculations are all done in the same way.

(b) The initial concentration of chloroacetic acid is 0.500 M:

$$\frac{x^2}{0.500 - x} = 0.0014$$

$$x = 0.0265 \text{ M} \quad (\text{approximate solution})$$

$$x = 0.0258 \text{ M} \quad (\text{exact solution})$$

The pH and anion-to-acid ratio follow directly:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 0.0258 = 1.59$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{x}{c-x} = \frac{0.0258}{0.500 - 0.0258} = 0.054$$

(c) Insert $c = 0.100 \text{ M}$ and solve:

$$\frac{x^2}{0.100 - x} = 0.0014$$

$$x = 0.0118 \text{ M} \quad (\text{approximate solution})$$

$$x = 0.0112 \text{ M} \quad (\text{exact solution})$$

At equilibrium, the relative amount of ionized species (A^-) increases as the initial concentration of acid decreases:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 0.0112 = 1.95$$

$$\frac{[A^-]}{[\text{HA}]} = \frac{x}{c-x} = \frac{0.0112}{0.100 - 0.0112} = 0.13$$

The stated value of K_a (1.4×10^{-3}) restricts both the pH and the ratio $[A^-]/[\text{HA}]$ to two significant figures.

(d) The initial concentration is 0.010 M:

$$\frac{x^2}{0.010 - x} = 0.0014$$

$$x = 0.00374 \text{ M} \quad (\text{approximate solution})$$

$$x = 0.00311 \text{ M} \quad (\text{exact solution})$$

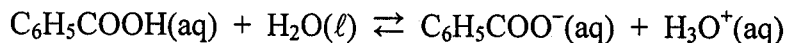
An approximate solution clearly becomes unacceptable as c approaches K_a (and hence becomes closer in magnitude to x).

The pH and anion-to-acid ratio are computed below:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 0.00311 = 2.51$$

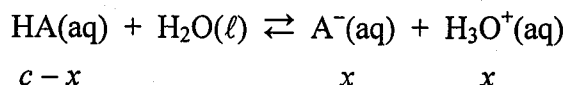
$$\frac{[A^-]}{[\text{HA}]} = \frac{x}{c-x} = \frac{0.00311}{0.010 - 0.00311} = 0.45$$

27. Follow the same procedure as in Exercise 26, this time taking the process



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = 6.5 \times 10^{-5}$$

as a specific member of the general class:



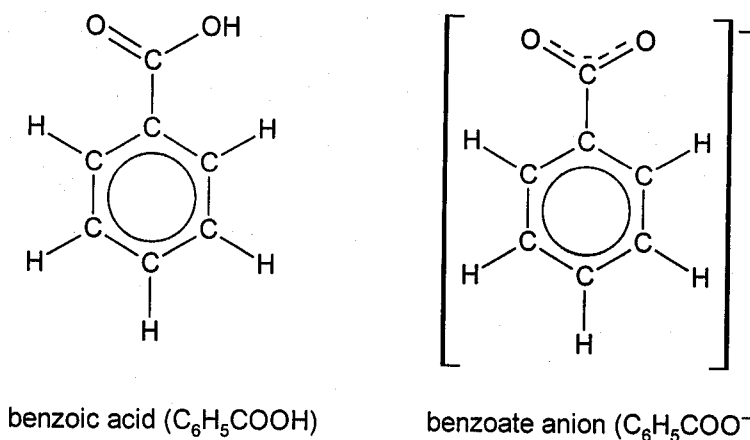
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{c-x}$$

The symbol c denotes the initial concentration of acid, $[\text{HA}]_0$ —in the present example, $[\text{C}_6\text{H}_5\text{COOH}]_0$.

Results obtained by approximation are compared below with those obtained from the full quadratic equation:

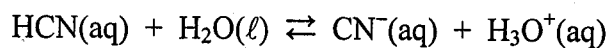
	c (M)	APPROXIMATE		EXACT	
		pH	$\frac{[\text{A}^-]}{[\text{HA}]}$	pH	$\frac{[\text{A}^-]}{[\text{HA}]}$
(a)	1.000	2.09	0.0081	2.10	0.0081
(b)	0.500	2.24	0.012	2.25	0.011
(c)	0.100	2.59	0.026	2.60	0.026
(d)	0.010	3.09	0.088	3.11	0.084

For reference, the structures of benzoic acid and the benzoate anion are shown below:



See pages 284 and 575–576 of *PoC*, together with Example 8-7, for further discussion of carboxylic acids.

28. The ionization of hydrocyanic acid,



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = 6.2 \times 10^{-10}$$

is handled as described in the preceding two exercises. Refer to Exercise 26 for explicit details of the calculation.

Solutions obtained both by approximation and from the full quadratic expression agree to better than two significant figures. In each case, the approximation

$$c - x \approx c$$

is valid since $K_a \ll c$ in the mass-action equation:

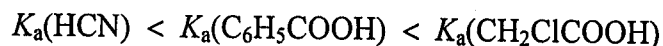
$$K_a = \frac{x^2}{c - x}$$

Results are collected in the following table:

	c (M)	pH	$\frac{[A^-]}{[HA]}$
(a)	1.000	4.60	0.000025
(b)	0.500	4.75	0.000035
(c)	0.100	5.10	0.000079
(d)	0.010	5.60	0.00025

29. Acid strength, a reflection of the equilibrium mass-action ratio, is measured by the one number K_a —a fixed value. The pH of an acidic solution varies with the particular conditions, but the equilibrium constant does not. See Examples 16-3 and 16-4, as well as Exercise 54.

(a) The strength of acidity tracks the ionization constants:

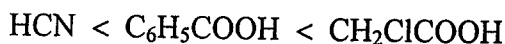


For each initial concentration considered, chloroacetic acid is ionized to a greater extent than benzoic acid. Benzoic acid, too, is ionized to a greater extent than hydrocyanic acid:

c (M)	$\frac{[\text{CN}^-]}{[\text{HCN}]}$	$\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$	$\frac{[\text{CH}_2\text{ClCOO}^-]}{[\text{CH}_2\text{ClCOOH}]}$
1.000	0.000025	0.0081	0.038
0.500	0.000035	0.011	0.054
0.100	0.000079	0.026	0.13
0.010	0.00025	0.084	0.45

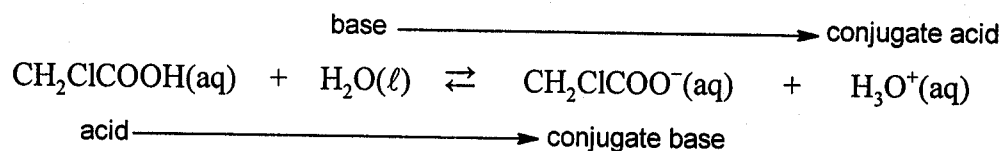
(b) The lower the initial concentration of acid, the higher is the fraction ionized at equilibrium. Relatively *more* acid must dissociate to reach equilibrium in a very dilute solution, but the total concentration of H_3O^+ is small nevertheless. The pH is higher (less acidic), even though a smaller fraction of the acid remains unionized in the form HA.

30. The three acids are ranked according to strength in Exercise 29:

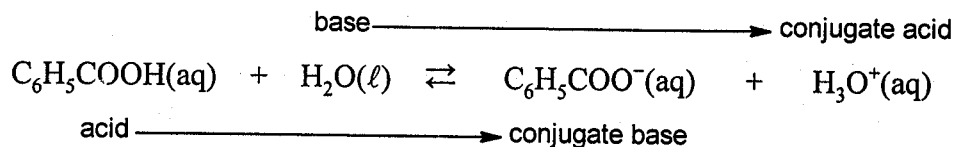


See Section 16-2 and pages R16.1–R16.3 of *PoC* for a general discussion of conjugate acid–base pairs.

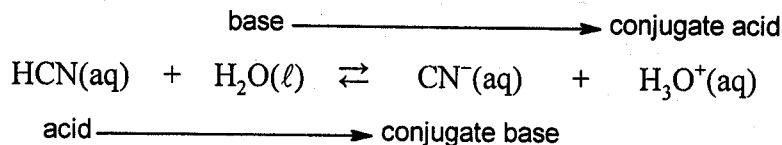
(a) The chloroacetate anion is the conjugate base of chloroacetic acid:



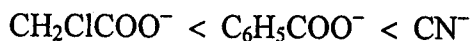
(b) The benzoate anion is the conjugate base of benzoic acid:



(c) The cyanide anion is the conjugate base of hydrocyanic acid:

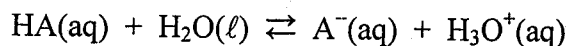


The strength of a conjugate base is inversely related to the strength of its partner acid. A strong acid is matched with a relatively weak conjugate base; a weak acid is matched with a relatively strong conjugate base. The cyanide ion, CN^- , originates from a weaker acid and hence is a stronger base than $\text{C}_6\text{H}_5\text{COO}^-$. Likewise, $\text{C}_6\text{H}_5\text{COO}^-$ is a stronger base than $\text{CH}_2\text{ClCOO}^-$:



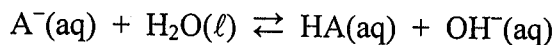
The base ionization constants, K_b , are calculated in the next exercise.

31. We combine the ionization of a weak acid



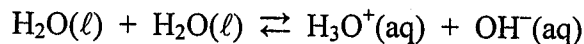
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

with the hydrolysis of its conjugate base



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

to obtain, as the net reaction, the autoionization of water:



$$K_a K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

Substituting $K_w = 1.0 \times 10^{-14}$ at 25°C , we then have a numerical value for K_b :

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{K_a}$$

See pages 583–584 and R16.3–R16.5 in *PoC*.

$$\text{(a)} \quad K_b = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-3}} = 7.1 \times 10^{-12}$$

$$\text{(b)} \quad K_b = \frac{1.0 \times 10^{-14}}{6.5 \times 10^{-5}} = 1.5 \times 10^{-10}$$

$$\text{(c)} \quad K_b = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$

The weaker the acid, the stronger the conjugate base:

