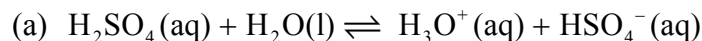


CHAPTER 10

ACIDS AND BASES

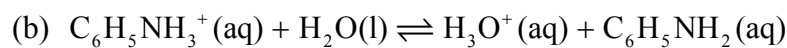
- 10.1** (a) CH_3NH_3^+ (b) NH_2NH_3^+ (c) H_2CO_3 (d) CO_3^{2-}
(e) $\text{C}_6\text{H}_5\text{O}^-$ (f) CH_3CO_2^-

10.3 For all parts (a) – (e), H_2O and H_3O^+ form a conjugate acid-base pair in which H_2O is the base and H_3O^+ is the acid



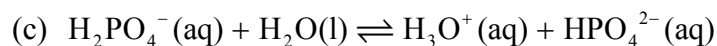
H_2SO_4 and $\text{HSO}_4^-(\text{aq})$ form a conjugate acid-base pair in which

H_2SO_4 is the acid and $\text{HSO}_4^-(\text{aq})$ is the base.



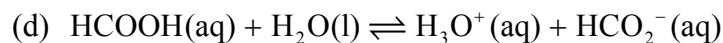
$\text{C}_6\text{H}_5\text{NH}_3^+$ and $\text{C}_6\text{H}_5\text{NH}_2(\text{aq})$ form a conjugate acid-base pair in which

$\text{C}_6\text{H}_5\text{NH}_3^+$ is the acid and $\text{C}_6\text{H}_5\text{NH}_2(\text{aq})$ is the base.



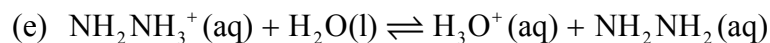
$\text{H}_2\text{PO}_4^-(\text{aq})$ and $\text{HPO}_4^{2-}(\text{aq})$ form a conjugate acid-base pair in which

$\text{H}_2\text{PO}_4^-(\text{aq})$ is the acid and $\text{HPO}_4^{2-}(\text{aq})$ is the base.



$\text{HCOOH}(\text{aq})$ and $\text{HCO}_2^-(\text{aq})$ form a conjugate acid-base pair in which

$\text{HCOOH}(\text{aq})$ is the acid and $\text{HCO}_2^-(\text{aq})$ is the base.



$\text{NH}_2\text{NH}_3^+(\text{aq})$ and $\text{NH}_2\text{NH}_2(\text{aq})$ form a conjugate acid-base pair in

which $\text{NH}_2\text{NH}_3^+(\text{aq})$ is the acid and $\text{NH}_2\text{NH}_2(\text{aq})$ is the base.

10.5 (a) Brønsted acid: HNO_3

Brønsted base: HPO_4^{2-}

(b) conjugate base to HNO_3 : NO_3^-

conjugate acid to HPO_4^{2-} : H_2PO_4^-

10.7 (a) HCO_3^- , as an acid: $\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$.

HCO_3^- and CO_3^{2-} form a conjugate acid-base pair in which HCO_3^- is the acid and CO_3^{2-} is the base.

HCO_3^- , as a base: $\text{H}_2\text{O}(\text{l}) + \text{HCO}_3^-(\text{aq}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) + \text{OH}^-(\text{aq})$.

HCO_3^- and H_2CO_3 form a conjugate acid-base pair in which HCO_3^- is the base and H_2CO_3 is the acid. H_2O and OH^- form a conjugate acid-base pair in which H_2O is the acid and OH^- is the base.

(b) HPO_4^{2-} , as an acid:

$\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$.

$\text{HPO}_4^{2-}(\text{aq})$ and $\text{PO}_4^{3-}(\text{aq})$ form a conjugate acid-base pair in which

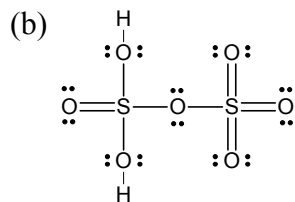
$\text{HPO}_4^{2-}(\text{aq})$ is the acid and $\text{PO}_4^{3-}(\text{aq})$ is the base. H_2O and H_3O^+ form a conjugate acid-base pair in which H_2O is the base and H_3O^+ is the acid.

HPO_4^{2-} , as a base: $\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{PO}_4^-(\text{aq}) + \text{OH}^-(\text{aq})$.

HPO_4^{2-} and H_2PO_4^- form a conjugate acid-base pair in which HPO_4^{2-} is the base and H_2PO_4^- is the acid. H_2O and OH^- form a conjugate acid-base pair in which H_2O is the acid and OH^- is the base.

10.9 (a) basic; (b) acidic; (c) amphoteric; (d) basic

10.11 (a) $\text{SO}_3(\text{g}) + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_7(\text{l})$;



(c) sulfuric acid acts as the Lewis base while SO_3 acts as a Lewis acid.

10.13 In each case, use $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$, then

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

$$(a) [\text{OH}^-] = \frac{1.0 \times 10^{-14}}{0.02} = 5.0 \times 10^{-13} \text{ mol} \cdot \text{L}^{-1}$$

$$(b) [\text{OH}^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.0 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$$

$$(c) [\text{OH}^-] = \frac{1.0 \times 10^{-14}}{3.1 \times 10^{-3}} = 3.2 \times 10^{-12} \text{ mol} \cdot \text{L}^{-1}$$

10.15 (a) $K_w = 2.1 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-] = x^2$, where $x = [\text{H}_3\text{O}^+] = [\text{OH}^-]$

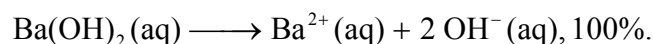
$$x = \sqrt{2.1 \times 10^{-14}} = 1.4 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 6.80$$

$$(b) [\text{OH}^-] = [\text{H}_3\text{O}^+] = 1.4 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log[\text{OH}^-] = 6.80$$

10.17 Because $\text{Ba}(\text{OH})_2$ is a strong base,



Then

$[\text{Ba}(\text{OH})_2]_0 = [\text{Ba}^{2+}]$, $[\text{OH}^-] = 2 \times [\text{Ba}(\text{OH})_2]_0$, where $[\text{Ba}(\text{OH})_2]_0$ = nominal concentration of $\text{Ba}(\text{OH})_2$.

$$\text{moles of Ba}(\text{OH})_2 = \frac{0.25 \text{ g}}{171.36 \text{ g} \cdot \text{mol}^{-1}} = 1.5 \times 10^{-3} \text{ mol}$$

$$[\text{Ba}(\text{OH})_2]_0 = \frac{1.5 \times 10^{-3} \text{ mol}}{0.100 \text{ L}} = 1.5 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} = [\text{Ba}^{2+}]$$

$$[\text{OH}^-] = 2 \times [\text{Ba}(\text{OH})_2]_0 = 2 \times 1.5 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} = 2.9 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-2}} = 3.4 \times 10^{-13} \text{ mol} \cdot \text{L}^{-1}$$

10.19 Because if $\text{pH} = -\log[\text{H}_3\text{O}^+]$, $\log[\text{H}_3\text{O}^+] = -\text{pH}$. Taking the antilogs of both sides gives $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} \text{ mol} \cdot \text{L}^{-1}$

(a) $[\text{H}_3\text{O}^+] = 10^{-3.3} = 5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$

(b) $[\text{H}_3\text{O}^+] = 10^{-6.7} \text{ mol} \cdot \text{L}^{-1} = 2 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$

(c) $[\text{H}_3\text{O}^+] = 10^{-4.4} \text{ mol} \cdot \text{L}^{-1} = 4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$

(d) $[\text{H}_3\text{O}^+] = 10^{-5.3} \text{ mol} \cdot \text{L}^{-1} = 5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$

10.21 (a) $[\text{HNO}_3] = [\text{H}_3\text{O}^+] = 0.0146 \text{ mol} \cdot \text{L}^{-1}$

$$\text{pH} = -\log(0.0146) = 1.84, \quad \text{pOH} = 14.00 - (-1.84) = 12.16$$

(b) $[\text{HCl}] = [\text{H}_3\text{O}^+] = 0.11 \text{ mol} \cdot \text{L}^{-1}$

$$\text{pH} = -\log(0.11) = 0.96, \quad \text{pOH} = 14.00 - 0.96 = 13.04$$

(c) $[\text{OH}^-] = 2 \times [\text{Ba}(\text{OH})_2] = 2 \times 0.0092 \text{ M} = 0.018 \text{ mol} \cdot \text{L}^{-1}$

$$\text{pOH} = -\log(0.018) = 1.74, \quad \text{pH} = 14.00 - 1.74 = 12.26$$

(d) $[\text{KOH}]_0 = [\text{OH}^-]$

$$[\text{OH}^-] = \left(\frac{2.00 \text{ mL}}{500 \text{ mL}} \right) \times (0.175 \text{ mol} \cdot \text{L}^{-1}) = 7.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log(7.0 \times 10^{-4}) = 3.15, \quad \text{pH} = 14.00 - 3.15 = 10.85$$

(e) $[\text{NaOH}]_0 = [\text{OH}^-]$

$$\text{number of moles of NaOH} = \frac{0.0136 \text{ g}}{40.00 \text{ g} \cdot \text{mol}^{-1}} = 3.40 \times 10^{-4} \text{ mol}$$

$$[\text{NaOH}]_0 = \frac{3.40 \times 10^{-4} \text{ mol}}{0.350 \text{ L}} = 9.71 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} = [\text{OH}^-]$$

$$\text{pOH} = -\log(9.71 \times 10^{-4}) = 3.01, \quad \text{pH} = 14.00 - 3.01 = 10.99$$

(f) $[\text{HBr}]_0 = [\text{H}_3\text{O}^+]$

$$[\text{H}_3\text{O}^+] = \left(\frac{75.0 \text{ mL}}{500 \text{ mL}} \right) \times (3.5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}) = 5.3 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

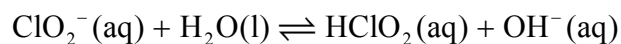
$$\text{pH} = -\log(5.3 \times 10^{-5}) = 4.28, \quad \text{pOH} = 14.00 - 4.28 = 9.72$$

10.23 $\text{p}K_{\text{a1}} = -\log K_{\text{a1}}$; therefore, after taking antilogs, $K_{\text{a1}} = 10^{-\text{p}K_{\text{a1}}}$

Acid	$\text{p}K_{\text{a1}}$	K_{a1}
(a) H_3PO_4	2.12	7.6×10^{-3}
(b) H_3PO_3	2.00	1.0×10^{-2}
(c) H_2SeO_3	2.46	3.5×10^{-3}
(d) HSeO_4^-	1.92	1.2×10^{-2}
(e) The larger K_{a1} , the stronger the acid; therefore		
$\text{H}_2\text{SeO}_3 < \text{H}_3\text{PO}_4 < \text{H}_3\text{PO}_3 < \text{HSeO}_4^-$		

10.25 (a) $\text{HClO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{ClO}_2^-(\text{aq})$

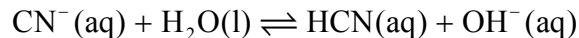
$$K_{\text{a}} = \frac{[\text{H}_3\text{O}^+][\text{ClO}_2^-]}{[\text{HClO}_2]}$$



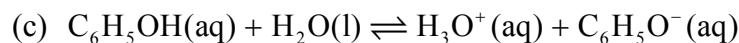
$$K_{\text{b}} = \frac{[\text{HClO}_2][\text{OH}^-]}{[\text{ClO}_2^-]}$$

(b) $\text{HCN}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CN}^-(\text{aq})$

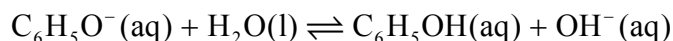
$$K_{\text{a}} = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$$



$$K_{\text{b}} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$



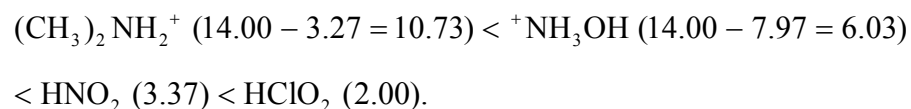
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]}$$



$$K_b = \frac{[\text{C}_6\text{H}_5\text{OH}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{O}^-]}$$

10.27 Decreasing $\text{p}K_a$ will correspond to increasing acid strength because

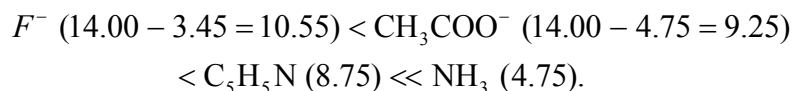
$\text{p}K_a = -\log K_a$. The $\text{p}K_a$ values (given in parentheses) determine the following ordering:



Remember that the $\text{p}K_a$ for the conjugate acid of a weak base will be given by $\text{p}K_a + \text{p}K_b = 14$.

10.29 Decreasing $\text{p}K_b$ will correspond to increasing base strength because

$\text{p}K_b = -\log K_b$. The $\text{p}K_b$ values (given in parentheses) determine the following ordering:



Remember that the $\text{p}K_b$ for the conjugate base of a weak acid will be given by $\text{p}K_a + \text{p}K_b = 14$.

10.31 Any acid whose conjugate base lies above water in Table 10.3 will be a strong acid; that is, the conjugate base of the acid will be a weaker base than water, and so water will accept the H^+ preferentially. Based upon this information, we obtain the following analysis: (a) HClO_3 , strong; (b) H_2S , weak; (c) HSO_4^- , weak (Note: even though H_2SO_4 is a

strong acid, HSO_4^- is a weak acid. Its conjugate base is SO_4^{2-}); (d) CH_3NH_3^+ , weak acid; (e) HCO_3^- , weak; (f) HNO_3 , strong; (g) CH_4 , weak.

10.33 For oxoacids, the greater the number of highly electronegative O atoms attached to the central atom, the stronger the acid. This effect is related to the increased oxidation number of the central atom as the number of O atoms increases. Therefore, HIO_3 is the stronger acid, with the lower $\text{p}K_{\text{a}}$.

- 10.35** (a) HCl is the stronger acid, because its bond strength is much weaker than the bond in HF , and bond strength is the dominant factor in determining the strength of binary acids.
- (b) HClO_2 is stronger; there is one more O atom attached to the Cl atom in HClO_2 than in HClO . The additional O in HClO_2 helps to pull the electron of the H atom out of the H—O bond. The oxidation state of Cl is higher in HClO_2 than in HClO .
- (c) HClO_2 is stronger; Cl has a greater electronegativity than Br, making the H—O bond in HClO_2 more polar than in HBrO_2 .
- (d) HClO_4 is stronger; Cl has a greater electronegativity than P.
- (e) HNO_3 is stronger. The explanation is the same as that for part (b). HNO_3 has one more O atom.
- (f) H_2CO_3 is stronger; C has greater electronegativity than Ge. See part (c).

10.37 (a) The $-\text{CCl}_3$ group that is bonded to the carboxyl group, $-\text{COOH}$, in trichloroacetic acid, is more electron withdrawing than the $-\text{CH}_3$ group in acetic acid. Thus, trichloroacetic acid is the stronger acid.

(b) The —CH_3 group in acetic acid has electron-donating properties, which means that it is less electron withdrawing than the —H attached to the carboxyl group in formic acid, HCOOH . Thus, formic acid is a slightly stronger acid than acetic acid. However, it is not nearly as strong as trichloroacetic acid. The order is $\text{CCl}_3\text{COOH} \gg \text{HCOOH} > \text{CH}_3\text{COOH}$.

10.39 (a) Nitrous acid is a stronger acid than acetic acid and, therefore, the acetate ion is a stronger base than the nitrite ion. Since the definition of a strong acid is one that favors products in the deprotonation reaction, the presence of acetate ions will shift the nitrous acid deprotonation reaction toward products by consuming protons making nitrous acid behave like a strong acid. Carbonic acid is a weaker acid and, therefore, will not behave like a strong acid in the presence of acetic acid.

(b) Ammonia will act like a strong base because its conjugate acid, the ammonium ion, is a weaker acid than acetic acid. The presence of acetic acid will shift the reaction: $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ toward products.

10.41 The larger the K_a , the stronger the corresponding acid. 2,4,6-

Trichlorophenol is the stronger acid because the chlorine atoms have a greater electron-withdrawing power than the hydrogen atoms present in the unsubstituted phenol.

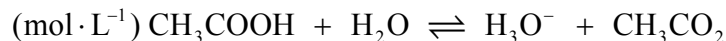
10.43 The larger the $\text{p}K_a$ of an acid, the stronger the corresponding conjugate base; hence, the order is aniline < ammonia < methylamine < ethylamine. Although we should not draw conclusions from such a small data set, we might suggest the possibility that

(1) arylamines < ammonia < alkylamines

(2) methyl < ethyl < etc.

(Arylamines are amines in which the nitrogen of the amine is attached to a benzene ring.)

10.45 (a) Concentration



initial	0.29	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.29 - x$	—	x	x

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{0.29 - x} \approx \frac{x^2}{0.29}$$

$$x = [\text{H}_3\text{O}^+] = 2.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(1.6 \times 10^{-3}) = 2.64, \text{pOH} = 14.00 - 2.64 = 11.36$$

(b) The equilibrium table for (b) is similar to that for (a).

$$K_a = 3.0 \times 10^{-1} = \frac{[\text{H}_3\text{O}^+][\text{CCl}_3\text{CO}_2^-]}{[\text{CCl}_3\text{COOH}]} = \frac{x^2}{0.29 - x}$$

$$\text{or } x^2 + 3.0 \times 10^{-1}x - 0.087 = 0$$

$$x = \frac{-3.0 \times 10^{-1} \pm \sqrt{(3.0 \times 10^{-1})^2 - (4)(-0.087)}}{2} = 0.18, -0.48$$

The negative root is not possible and can be eliminated.

$$x = [\text{H}_3\text{O}^+] = 0.18 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(0.18) = 0.74, \text{pOH} = 14.00 - 0.74 = 13.26$$

(c) Concentration $(\text{mol} \cdot \text{L}^{-1})$ $\text{HCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_2^-$

initial	0.29	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.29 - x$	—	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCO}_2^-]}{[\text{HCOOH}]} = \frac{x \cdot x}{0.29 - x} \approx \frac{x^2}{0.29} = 1.8 \times 10^{-4}$$

$$x = [\text{H}_3\text{O}^+] = \sqrt{0.29 \times 1.8 \times 10^{-4}} = 7.2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(7.2 \times 10^{-3}) = 2.14, \text{pOH} = 14.00 - 2.14 = 11.86$$

10.47 (a) Concentration

(mol · L ⁻¹)	H ₂ O	+	NH ₃	⇌	NH ₄ ⁺	+	OH ⁻
initial	—		0.057		0		0
change	—		-x		+x		+x
equilibrium	—		0.057 - x		x		x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x \cdot x}{0.057 - x} \approx \frac{x^2}{0.057} = 1.8 \times 10^{-5}$$

$$x = [\text{OH}^-] = \sqrt{0.057 \times 1.8 \times 10^{-5}} = 1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log(1.0 \times 10^{-3}) = 3.00, \text{pH} = 14.00 - 3.00 = 11.00$$

$$\text{percentage protonation} = \frac{1.0 \times 10^{-3}}{0.057} \times 100\% = 1.8\%$$

(b) Concentration

(mol · L ⁻¹)	NH ₂ OH	+	H ₂ O	⇌	⁺ NH ₃ OH	+	OH ⁻
initial	0.162		—		0		0
change	-x		—		+x		+x
equilibrium	0.162 - x		—		x		x

$$K_b = 1.1 \times 10^{-8} = \frac{x^2}{0.162 - x} \approx \frac{x^2}{0.162}$$

$$x = [\text{OH}^-] = 4.2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log(4.2 \times 10^{-5}) = 4.38, \text{pH} = 14.00 - 4.38 = 9.62$$

$$\text{percentage protonation} = \frac{4.2 \times 10^{-5}}{0.162} \times 100\% = 0.026\%$$

(c) Concentration

(mol · L ⁻¹)	(CH ₃) ₃ N	+	H ₂ O	⇌	(CH ₃) ₃ NH ⁺	+	OH ⁻
initial	0.35		—		0		0
change	-x		—		+x		+x
equilibrium	0.35 - x		—		+x		+x

$$6.5 \times 10^{-5} = \frac{x^2}{0.35 - x}$$

Assume $x \ll 0.35$

$$\text{Then } x = 4.8 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{OH}^-] = 4.8 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log(4.8 \times 10^{-3}) = 2.32, \text{ pH} = 14.00 - 2.32 = 11.68$$

$$\text{percentage protonation} = \frac{4.8 \times 10^{-3}}{0.35} \times 100\% = 1.4\%$$

$$(d) \text{ p}K_b = 14.00 - \text{p}K_a = 14.00 - 8.21 = 5.79, K_b = 1.6 \times 10^{-6}$$

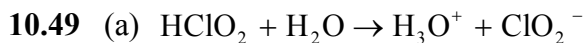


$$K_b = 1.6 \times 10^{-6} = \frac{x^2}{0.073 - x} \approx \frac{x^2}{0.073}$$

$$x = [\text{OH}^-] = 1.1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log(1.1 \times 10^{-4}) = 3.96, \text{ pH} = 14.00 - 3.96 = 10.04$$

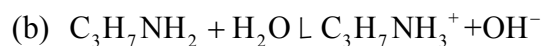
$$\text{percentage protonation} = \frac{1.1 \times 10^{-4}}{0.0073} \times 100\% = 2.5\%$$



$$[\text{H}_3\text{O}^+] = [\text{ClO}_2^-] = 10^{-\text{pH}} = 10^{-1.2} = 0.06 \text{ mol} \cdot \text{L}^{-1}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}_2^-]}{[\text{HClO}_2]} = \frac{(0.06)^2}{0.10 - 0.06} = 0.09 \text{ (1 sf)}$$

$$\text{p}K_a = -\log(0.09) = 1.0$$

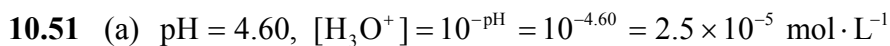


$$\text{pOH} = 14.00 - 11.86 = 2.14$$

$$[\text{C}_3\text{H}_7\text{NH}_3^+] = [\text{OH}^-] = 10^{-2.14} = 7.2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$K_b = \frac{[\text{C}_3\text{H}_7\text{NH}_3^+][\text{OH}^-]}{[\text{C}_3\text{H}_7\text{NH}_2]} = \frac{(7.2 \times 10^{-3})^2}{0.10 - 7.2 \times 10^{-3}} = 5.6 \times 10^{-4}$$

$$\text{p}K_b = -\log(5.6 \times 10^{-4}) = 3.25$$



Let x = nominal concentration of HClO , then

Concentration

(mol · L ⁻¹)	HClO	+	H ₂ O	⇌	H ₃ O ⁺	+	ClO ⁻
nominal	x		—		0		0
equilibrium	$x - 2.5 \times 10^{-5}$		—		2.5×10^{-5}		2.5×10^{-5}

$$K_a = 3.0 \times 10^{-8} = \frac{(2.5 \times 10^{-5})^2}{x - 2.5 \times 10^{-5}}$$

$$\begin{aligned} \text{Solve for } x; x &= \frac{(2.5 \times 10^{-5})^2 + (2.5 \times 10^{-5})(3.0 \times 10^{-8})}{3.0 \times 10^{-8}} \\ &= 2.1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} = 0.021 \text{ mol} \cdot \text{L}^{-1} \end{aligned}$$

(b) $\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.20 = 3.80$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-3.80} = 1.6 \times 10^{-4}$$

Let x = nominal concentration of NH_2NH_2 , then

Concentration

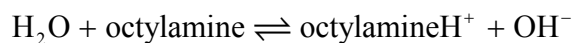
(mol · L ⁻¹)	NH_2NH_2	+	H_2O	⇌	NH_2NH_3^+	+	OH^-
nominal	x		—		0		0
equilibrium	$x - 1.6 \times 10^{-4}$		—		1.6×10^{-4}		1.6×10^{-4}

$$K_b = 1.7 \times 10^{-6} = \frac{(1.6 \times 10^{-4})^2}{x - 1.6 \times 10^{-4}}$$

$$\text{Solve for } x; x = 1.5 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

10.53 Concentration

(mol · L ⁻¹)	$\text{C}_6\text{H}_5\text{COOH}$	+	H_2O	⇌	H_3O^+	+	$\text{C}_6\text{H}_5\text{CO}_2^-$
initial	0.110		—		0		0
change	$-x$		—		$+x$		$+x$
equilibrium	$0.110 - x$		—		x		x



$$x = 0.024 \times 0.110 \text{ mol} \cdot \text{L}^{-1} = [\text{H}_3\text{O}^+] = [\text{C}_6\text{H}_5\text{CO}_2^-]$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{(0.024 \times 0.110)^2}{(1 - 0.024) \times 0.110} = 6.3 \times 10^{-5}$$

$$\text{pH} = -\log(2.6 \times 10^{-3}) = 2.58$$

10.55 The change in the concentration of octylamine is

$$x = 0.067 \times 0.10 = 0.0067 \text{ mol} \cdot \text{L}^{-1}. \text{ Thus the equilibrium table is}$$

Concentration

(mol · L ⁻¹)	H ₂ O	+ octylamine	⇌	octylamineH ⁺	+ OH ⁻
initial	—	0.100		0	0
change	—	-0.0067		+0.0067	+0.0067
equilibrium	—	0.100 - 0.0067		0.0067	0.0067

The equilibrium concentrations are

$$[\text{octylamine}] = 0.100 - 0.067 \times 0.10 = 0.093 \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{OH}^-] = [\text{octylamineH}^+] = 0.0067 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log(0.0067) = 2.17, \text{ pH} = 14.00 - 2.17 = 11.83$$

$$K_b = \frac{[\text{octylamineH}^+][\text{OH}^-]}{[\text{octylamine}]} = \frac{(6.7 \times 10^{-3})^2}{0.093} = 4.8 \times 10^{-4}$$

10.57 $\text{CH}_3\text{CH}_2\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

Concentration (mol · L⁻¹)

initial	0.0147	—	0	0
change	-x	—	+x	+x
equilibrium	0.0147 - x	—	x	x

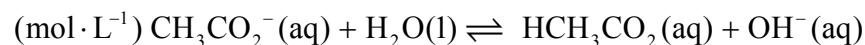
$$K_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]} = 1.3 \times 10^{-5} = \frac{x^2}{0.0147 - x} \approx \frac{x^2}{0.0147}$$

$$x = 4.4 \times 10^{-4}, \text{ Percent deprotonated} = \frac{4.4 \times 10^{-4}}{0.0147} \times 100\% = 3.0\%$$

- 10.59** (a) less than 7, $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq})$
 (b) greater than 7, $\text{H}_2\text{O}(\text{l}) + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq})$
 (c) greater than 7, $\text{H}_2\text{O}(\text{l}) + \text{F}^-(\text{aq}) \rightleftharpoons \text{HF}(\text{aq}) + \text{OH}^-(\text{aq})$
 (d) neutral
 (e) less than 7,
 $\text{Al}(\text{H}_2\text{O})_6^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{Al}(\text{H}_2\text{O})_5\text{OH}^{2+}(\text{aq})$
 (f) less than 7,
 $\text{Cu}(\text{H}_2\text{O})_6^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{Cu}(\text{H}_2\text{O})_5\text{OH}^+(\text{aq})$

10.61 (a) $K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$

Concentration



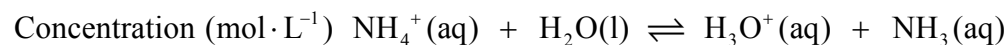
initial	0.63	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.63 - x$	—	x	x

$$K_b = \frac{[\text{HCH}_3\text{CO}_2][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]} = 5.6 \times 10^{-10} = \frac{x^2}{0.63 - x} \approx \frac{x^2}{0.63}$$

$$x = 1.9 \times 10^{-5} = [\text{OH}^-], \text{pOH} = -\log(1.9 \times 10^{-5}) = 4.72$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.72 = 9.28$$

(b) $K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-15}} = 5.6 \times 10^{-10}$



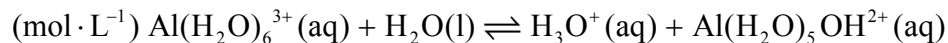
initial	0.19	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.19 - x$	—	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4\text{Cl}]} = 5.6 \times 10^{-10} = \frac{x^2}{0.19 - x} \approx \frac{x^2}{0.19}$$

$$x = 1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(1.0 \times 10^{-5}) = 5.00$$

(c) Concentration



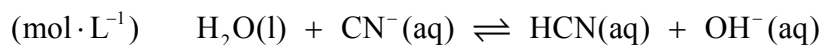
initial	0.055	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.055 - x$	—	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Al}(\text{H}_2\text{O})_5\text{OH}^{2+}]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]} = 1.4 \times 10^{-5} = \frac{x^2}{0.055 - x} \approx \frac{x^2}{0.055}$$

$$x = 8.8 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(8.8 \times 10^{-4}) = 3.06$$

(d) Concentration



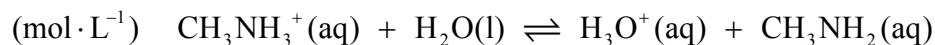
initial	—	0.065	0	0
change	—	$-x$	$+x$	$+x$
equilibrium	—	$0.065 - x$	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{x^2}{0.065 - x} \approx \frac{x^2}{0.065}$$

$$x = [\text{OH}^-] = 1.1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log(1.1 \times 10^{-3}) = 2.96, \text{pH} = 11.04$$

10.63 Concentration



initial	0.510	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.510 - x$	—	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]} = 2.8 \times 10^{-11} = \frac{x^2}{0.510 - x} \approx \frac{x^2}{0.510}$$

$$x = 3.8 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(3.8 \times 10^{-6}) = 5.4$$

10.65 (a) 250 mL of solution contains 5.34 g $\text{KC}_2\text{H}_3\text{O}_2$, molar

$$\text{mass} = 98.14 \text{ g} \cdot \text{mol}^{-1}$$

$$(5.34 \text{ g } \text{KC}_2\text{H}_3\text{O}_2) \left(\frac{1 \text{ mol } \text{KC}_2\text{H}_3\text{O}_2}{98.14 \text{ g } \text{KC}_2\text{H}_3\text{O}_2} \right) \left(\frac{1}{0.250 \text{ L}} \right) = 0.218 \text{ M } \text{KC}_2\text{H}_3\text{O}_2$$

Concentration

(mol · L ⁻¹)	$\text{H}_2\text{O(l)}$	$+ \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$	$\rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2(\text{aq})$	$+ \text{OH}^-(\text{aq})$
initial	—	0.218	0	0
change	—	-x	+x	+x
equilibrium	—	0.218 - x	x	x

$$\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.218 - x} \approx \frac{x^2}{0.218}$$

$$[\text{OH}^-] = 1.1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{H}_3\text{O}^+] = 9.1 \times 10^{-10} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(9.1 \times 10^{-10}) = 9.04$$

(b) 100 mL of solution contains 5.75 g NH_4Br , molar mass =

$$97.95 \text{ g} \cdot \text{mol}^{-1}$$

$$(5.75 \text{ g } \text{NH}_4\text{Br}) \left(\frac{1 \text{ mol } \text{NH}_4\text{Br}}{97.95 \text{ g } \text{NH}_4\text{Br}} \right) \left(\frac{1}{0.100 \text{ L}} \right) = 0.587 \text{ M } \text{NH}_4\text{Br}$$

Concentration

(mol · L ⁻¹)	$\text{NH}_4^+(\text{aq})$	$+ \text{H}_2\text{O(l)}$	$\rightleftharpoons \text{NH}_3(\text{aq})$	$+ \text{H}_3\text{O}^+(\text{aq})$
initial	0.587	—	0	0
change	-x	—	+x	+x

equilibrium $0.587 - x$ — x x

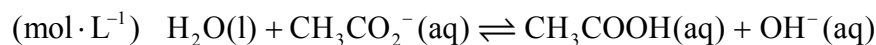
$$\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.587 - x} \approx \frac{x^2}{0.587}$$

$$[\text{H}_3\text{O}^+] = 1.8 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

10.67 (a) $\frac{0.020 \text{ mol} \cdot \text{L}^{-1} \text{ NaCH}_3\text{CO}_2 \times 0.150 \text{ L}}{0.500 \text{ L}} = 0.0400 \text{ mol} \cdot \text{L}^{-1}$

Concentration



initial	—	0.0400	0	0
change	—	$-x$	$+x$	$+x$
equilibrium	—	$0.0400 - x$	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]}$$

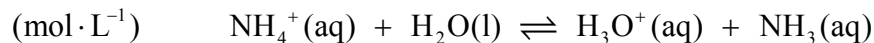
$$5.6 \times 10^{-10} = \frac{x^2}{0.0400 - x} \approx \frac{x^2}{0.0400}$$

$$x = 4.7 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} = [\text{CH}_3\text{COOH}]$$

(b) $\left(\frac{2.16 \text{ g NH}_4\text{Br}}{400 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol NH}_4\text{Br}}{97.95 \text{ g NH}_4\text{Br}} \right)$

$$= 0.0551 (\text{mol NH}_4\text{Br}) \cdot \text{L}^{-1}$$

Concentration

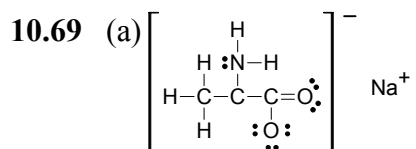


initial	0.0551	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.0551 - x$	—	x	x

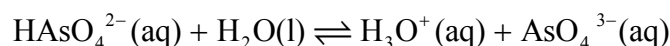
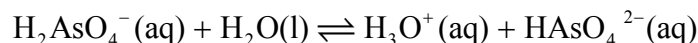
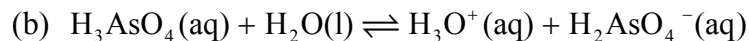
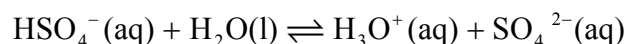
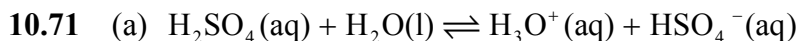
$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.0551 - x} \approx \frac{x^2}{0.0551}$$

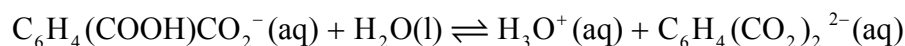
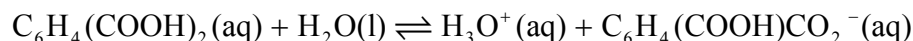
$$x = 5.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} = [\text{H}_3\text{O}^+] \text{ and } \text{pH} = -\log(5.5 \times 10^{-6}) = 5.26$$



$$(b) \text{pH} = \frac{1}{2}(\text{p}K_{a_1} + \text{p}K_{a_2}) = \frac{1}{2}(2.34 + 9.89) = 6.1$$



(c)



10.73 The initial concentrations of HSO_4^- and H_3O^+ are both $0.15 \text{ mol} \cdot \text{L}^{-1}$ as a result of the complete ionization of H_2SO_4 in the first step. The second ionization is incomplete.

Concentration

(mol · L ⁻¹)	HSO_4^-	+	H_2O	\rightleftharpoons	H_3O^+	+	SO_4^{2-}
initial	0.15		—		0.15		0
change	-x		—		+x		+x
equilibrium	0.15 - x		—		0.15 + x		x

$$K_{a2} = 1.2 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(0.15 + x)(x)}{0.15 - x}$$

$$x^2 + 0.162x - 1.8 \times 10^{-3} = 0$$

$$x = \frac{-0.162 + \sqrt{(0.162)^2 + (4)(1.8 \times 10^{-3})}}{2} = 0.0104 \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{H}_3\text{O}^+] = 0.15 + x = (0.15 + 0.0104) \text{ mol} \cdot \text{L}^{-1} = 0.16 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(0.16) = 0.80$$

10.75 (a) Because $K_{a2} \ll K_{a1}$, the second ionization can be ignored.

Concentration

(mol · L ⁻¹)	H_2CO_3	+	H_2O	\rightleftharpoons	H_3O^+	+	HCO_3^-
initial	0.010		—		0		0
change	-x		—		+x		+x
equilibrium	0.010 - x		—		x		x

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{0.010 - x} \approx \frac{x^2}{0.010} = 4.3 \times 10^{-7}$$

$$x = [\text{H}_3\text{O}^+] = 6.6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(6.6 \times 10^{-5}) = 4.18$$

(b) Because $K_{a2} \ll K_{a1}$, the second ionization can be ignored.

Concentration

(mol · L ⁻¹)	$(\text{COOH})_2$	+	H_2O	\rightleftharpoons	H_3O^+	+	$(\text{COOH})\text{CO}_2^-$
initial	0.10		—		0		0
change	-x		—		+x		+x
equilibrium	0.10 - x		—		x		x

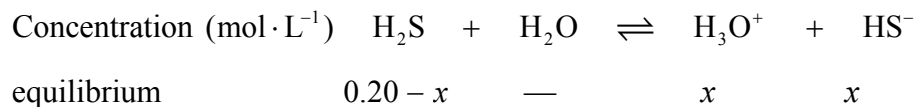
$$K_{a1} = 5.9 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][(\text{COOH})\text{CO}_2^-]}{[(\text{COOH})_2]} = \frac{x^2}{0.10 - x}$$

$$x^2 + 5.9 \times 10^{-2}x - 5.9 \times 10^{-3} = 0$$

$$x = \frac{-5.9 \times 10^{-2} + \sqrt{(5.9 \times 10^{-2})^2 + (4)(5.9 \times 10^{-3})}}{2} = 0.053 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(0.053) = 1.28$$

(c) Because $K_{a2} \ll K_{a1}$, the second ionization can be ignored.



$$K_{a1} = 1.3 \times 10^{-7} = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}$$

$$x = [\text{H}_3\text{O}^+] = 1.6 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(1.6 \times 10^{-4}) = 3.80$$

10.77 (a) The pH is given by $\text{pH} = \frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2})$. From Table 10.9, we find

$$K_{a1} = 1.5 \times 10^{-2} \quad \text{p}K_{a1} = 1.82$$

$$K_{a2} = 1.2 \times 10^{-7} \quad \text{p}K_{a2} = 6.92$$

$$\text{pH} = \frac{1}{2}(1.82 + 6.92) = 4.37$$

(b) The pH of a salt solution of a polyprotic acid is independent of the concentration of the salt, therefore $\text{pH} = 4.37$.

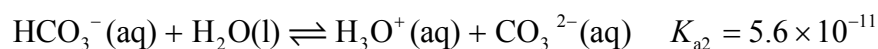
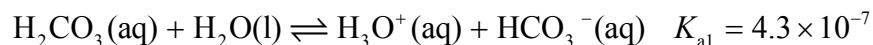
10.79 (a) The pH is given by $\text{pH} = \frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2})$. For the monosodium salt, the pertinent values are $\text{p}K_{a1}$ and $\text{p}K_{a2}$:

$$\text{pH} = \frac{1}{2}(3.14 + 5.95) = 4.55$$

(b) For the disodium salt, the pertinent values are $\text{p}K_{a2}$ and $\text{p}K_{a3}$:

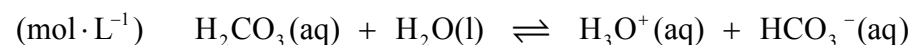
$$\text{pH} = \frac{1}{2}(5.95 + 6.39) = 6.17$$

10.81 The equilibrium reactions of interest are



Because the second ionization constant is much smaller than the first, we can assume that the first step dominates:

Concentration



initial	0.0456	—	0	0
change	$-x$	—	$+x$	$+x$
final	$0.0456 - x$	—	$+x$	$+x$

$$K_{\text{a1}} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$4.3 \times 10^{-7} = \frac{(x)(x)}{0.0456 - x} = \frac{x^2}{0.0456 - x}$$

Assume that $x \ll 0.0456$

$$\text{Then } x^2 = (4.3 \times 10^{-7})(0.0456)$$

$$x = 1.4 \times 10^{-4}$$

Because $x < 1\%$ of 0.0456, the assumption was valid.

$$x = [\text{H}_3\text{O}^+] = [\text{HCO}_3^-] = 1.4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

This means that the concentration of H_2CO_3 is $0.0456 \text{ mol} \cdot \text{L}^{-1} -$

$0.00014 \text{ mol} \cdot \text{L}^{-1} = 0.0455 \text{ mol} \cdot \text{L}^{-1}$. We can then use the other equilibria

to determine the remaining concentrations:

$$K_{\text{a2}} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$5.6 \times 10^{-11} = \frac{(1.4 \times 10^{-4})[\text{CO}_3^{2-}]}{(1.4 \times 10^{-4})}$$

$$[\text{CO}_3^{2-}] = 5.6 \times 10^{-11} \text{ mol} \cdot \text{L}^{-1}$$

Because $5.6 \times 10^{-11} \ll 1.4 \times 10^{-4}$, the initial assumption that the first ionization would dominate is valid.

To calculate $[\text{OH}^-]$, we use the K_{w} relationship:

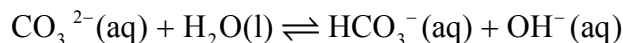
$$K_{\text{w}} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$[\text{OH}^-] = \frac{K_{\text{w}}}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14}}{1.4 \times 10^{-4}} = 7.1 \times 10^{-11} \text{ mol} \cdot \text{L}^{-1}$$

$$\begin{aligned} \text{In summary, } [\text{H}_2\text{CO}_3] &= 0.0455 \text{ mol} \cdot \text{L}^{-1}, [\text{H}_3\text{O}^+] = [\text{HCO}_3^-] \\ &= 1.4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}, \end{aligned}$$

$$[\text{CO}_3^{2-}] = 5.6 \times 10^{-11} \text{ mol} \cdot \text{L}^{-1}, [\text{OH}^-] = 7.1 \times 10^{-11} \text{ mol} \cdot \text{L}^{-1}.$$

10.83 The equilibrium reactions of interest are now the base forms of the carbonic acid equilibria, so K_b values should be calculated for the following changes:



$$K_{b1} = \frac{K_w}{K_{a2}} = \frac{1.00 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.8 \times 10^{-4}$$



$$K_{b2} = \frac{K_w}{K_{a1}} = \frac{1.00 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$$

Because the second hydrolysis constant is much smaller than the first, we can assume that the first step dominates:

Concentration

(mol · L ⁻¹)	CO ₃ ²⁻ (aq)	+	H ₂ O(l)	⇌	HCO ₃ ⁻ (aq)	+	OH ⁻ (aq)
initial	0.0456	—			0		0
change	-x	—			+x		+x
final	0.0456 - x	—			+x		+x

$$K_{b1} = \frac{[\text{HCO}_3^{-}][\text{OH}^{-}]}{[\text{CO}_3^{2-}]}$$

$$1.8 \times 10^{-4} = \frac{(x)(x)}{0.0456 - x} = \frac{x^2}{[0.0456 - x]}$$

Assume that $x \ll 0.0456$

$$\text{Then } x^2 = (1.8 \times 10^{-4})(0.0456)$$

$$x = 2.9 \times 10^{-3}$$

Because $x > 5\%$ of 0.0456, the assumption was not valid and the full expression should be solved using the quadratic equation:

$$x^2 + 1.8 \times 10^{-4}x - (1.8 \times 10^{-4})(0.0456) = 0$$

Solving using the quadratic equation gives $x = 0.0028 \text{ mol} \cdot \text{L}^{-1}$.

$$x = [\text{HCO}_3^{-}] = [\text{OH}^{-}] = 0.0028 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{Therefore, } [\text{CO}_3^{2-}] = 0.0456 \text{ mol} \cdot \text{L}^{-1} - 0.0028 \text{ mol} \cdot \text{L}^{-1} = 0.0428 \text{ mol} \cdot \text{L}^{-1}$$

We can then use the other equilibria to determine the remaining concentrations:

$$K_{b2} = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]}$$

$$2.3 \times 10^{-8} = \frac{[\text{H}_2\text{CO}_3](0.0028)}{(0.0028)}$$

$$[\text{H}_2\text{CO}_3] = 2.3 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$$

Because $2.3 \times 10^{-8} \ll 0.0028$, the initial assumption that the first hydrolysis would dominate is valid. To calculate $[\text{H}_3\text{O}^+]$, we use the K_w relationship:

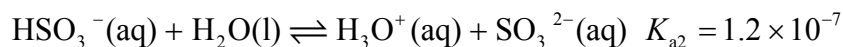
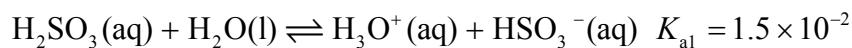
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.0028} = 3.6 \times 10^{-12} \text{ mol} \cdot \text{L}^{-1}$$

In summary, $[\text{H}_2\text{CO}_3] = 2.3 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$, $[\text{OH}^-] = [\text{HCO}_3^-] = 0.0028 \text{ mol} \cdot \text{L}^{-1}$, $[\text{CO}_3^{2-}] = 0.0428 \text{ mol} \cdot \text{L}^{-1}$, $[\text{H}_3\text{O}^+] = 3.6 \times 10^{-12} \text{ mol} \cdot \text{L}^{-1}$

- 10.85** (a) phosphorous acid: The two $\text{p}K_a$ values are 2.00 and 6.59. Because $\text{pH} = 6.30$ lies between $\text{p}K_{a1}$ and $\text{p}K_{a2}$, the dominant form will be the singly deprotonated HA^- ion.
- (b) oxalic acid: The two $\text{p}K_a$ values are 1.23 and 4.19. Because $\text{pH} = 6.30$ lies above $\text{p}K_{a2}$, the species present in largest concentration will be the doubly deprotonated A^{2-} ion.
- (c) hydrosulfuric acid: The two $\text{p}K_a$ values are 6.89 and 14.15. Because $\text{pH} = 6.30$ lies below both $\text{p}K_a$ values, the species present in highest concentrations will be the fully protonated H_2A form.

10.87 The equilibria present in solution are



The calculation of the desired concentrations follows exactly after the method derived in Eq. 25, substituting H_2SO_3 for

H_2CO_3 , HSO_3^- for HCO_3^- , and SO_3^{2-} for CO_3^{2-} . First, calculate the quantity f (at $\text{pH} = 5.50$ $[\text{H}_3\text{O}^+] = 10^{-5.5} = 3.2 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$):

$$\begin{aligned} f &= [\text{H}_3\text{O}^+]^2 + [\text{H}_3\text{O}^+] K_{\text{a1}} + K_{\text{a1}} K_{\text{a2}} \\ &= (3.2 \times 10^{-6})^2 + (3.2 \times 10^{-6})(1.5 \times 10^{-2}) + (1.5 \times 10^{-2})(1.2 \times 10^{-7}) \\ &= 5.0 \times 10^{-8} \end{aligned}$$

The fractions of the species present are then given by

$$\alpha(\text{H}_2\text{SO}_3) = \frac{[\text{H}_3\text{O}^+]^2}{f} = \frac{(3.2 \times 10^{-6})^2}{5.0 \times 10^{-8}} = 2.1 \times 10^{-4}$$

$$\alpha(\text{HSO}_3^-) = \frac{[\text{H}_3\text{O}^+] K_{\text{a1}}}{f} = \frac{(3.2 \times 10^{-6})(1.5 \times 10^{-2})}{5.0 \times 10^{-8}} = 0.96$$

$$\alpha(\text{SO}_3^{2-}) = \frac{K_{\text{a1}} K_{\text{a2}}}{f} = \frac{(1.5 \times 10^{-2})(1.2 \times 10^{-7})}{5.0 \times 10^{-8}} = 0.036$$

Thus, in a $0.150 \text{ mol} \cdot \text{L}^{-1}$ solution at $\text{pH} 5.50$, the dominant species will be HSO_3^- with a concentration of $(0.150 \text{ mol} \cdot \text{L}^{-1})(0.96) = 0.14 \text{ mol} \cdot \text{L}^{-1}$.

The concentration of

H_2SO_3 will be $(2.1 \times 10^{-4})(0.150 \text{ mol} \cdot \text{L}^{-1}) = 3.2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ and the

concentration of SO_3^{2-} will be

$$(0.036)(0.150 \text{ mol} \cdot \text{L}^{-1}) = 0.0054 \text{ mol} \cdot \text{L}^{-1}.$$

10.89 (a) Concentration

(mol · L ⁻¹)	B(OH) ₃	+	2 H ₂ O	⇌	H ₃ O ⁺	+	B(OH) ₄ ⁻
initial	1.0 × 10 ⁻⁴	—	—		0		0
change	-x	—	—		+x		+x
equilibrium	1.0 × 10 ⁻⁴ - x	—	—		x		x

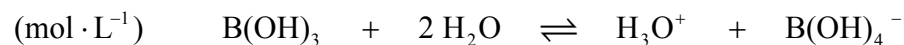
$$K_a = 7.2 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{B}(\text{OH})_4^-]}{[\text{B}(\text{OH})_3]} = \frac{x^2}{1.0 \times 10^{-4} - x} \approx \frac{x^2}{1.0 \times 10^{-4}}$$

$$x = [\text{H}_3\text{O}^+] = 2.7 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$$

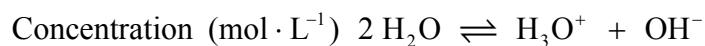
$$\text{pH} = -\log(2.7 \times 10^{-7}) = 6.57$$

Note: this value of $[\text{H}_3\text{O}^+]$ is not much different from the value for pure water, $1.0 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$; therefore, it is at the lower limit of safely ignoring the contribution to $[\text{H}_3\text{O}^+]$ from the autoprotolysis of water. The exercise should be solved by simultaneously considering both equilibria.

Concentration



$$\text{equilibrium} \quad 1.0 \times 10^{-4} - x \quad \quad \quad x \quad \quad y$$



$$\text{equilibrium} \quad \quad \quad \quad \quad x \quad \quad z$$

Because there are now two contributions to $[\text{H}_3\text{O}^+]$, $[\text{H}_3\text{O}^+]$ is no longer equal to $[\text{B}(\text{OH})_4^-]$, nor is it equal to $[\text{OH}^-]$, as in pure water. To avoid a cubic equation, x will again be ignored relative to $1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$.

This approximation is justified by the approximate calculation above, and because K_a is very small relative to 1.0×10^{-4} . Let a = initial

concentration of $\text{B}(\text{OH})_3$, then

$$K_a = 7.2 \times 10^{-10} = \frac{xy}{a - x} \approx \frac{xy}{a} \text{ or } y = \frac{aK_a}{x}$$

$$K_w = 1.0 \times 10^{-14} = xz$$

Electroneutrality requires

$$x = y + z \text{ or } z = x - y; \text{ hence, } K_w = xz = x(x - y).$$

Substituting for y from above:

$$x \times \left(x - \frac{aK_a}{x} \right) = K_w$$

$$x^2 - aK_a = K_w$$

$$x^2 = K_w + aK_a$$

$$x = \sqrt{K_w + aK_a} = \sqrt{1.0 \times 10^{-14} + 1.0 \times 10^{-4} \times 7.2 \times 10^{-10}}$$

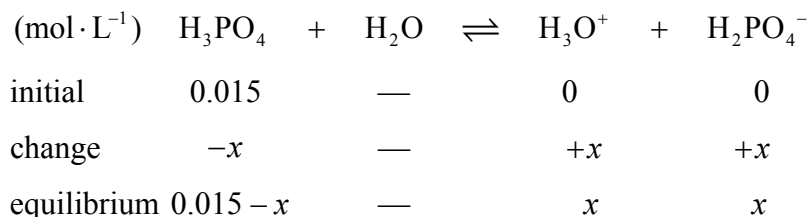
$$x = 2.9 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(2.9 \times 10^{-7}) = 6.54$$

This value is slightly, but measurably, different from the value 6.57 obtained by ignoring the contribution to $[\text{H}_3\text{O}^+]$ from water.

(b) In this case, the second ionization can safely be ignored; $K_{a2} \ll K_{a1}$.

Concentration



$$K_{a1} = 7.6 \times 10^{-3} = \frac{x^2}{0.015 - x}$$

$$x^2 + 7.6 \times 10^{-3}x - 1.14 \times 10^{-4} = 0$$

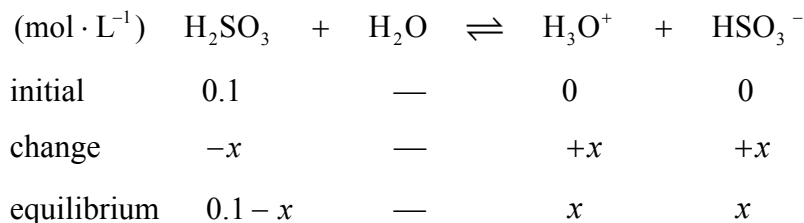
$$x = [\text{H}_3\text{O}^+] = \frac{-7.6 \times 10^{-3} + \sqrt{(7.6 \times 10^{-3})^2 + 4.56 \times 10^{-4}}}{2}$$

$$= 7.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(7.5 \times 10^{-3}) = 2.12$$

(c) In this case, the second ionization can safely be ignored; $K_{a2} \ll K_{a1}$.

Concentration



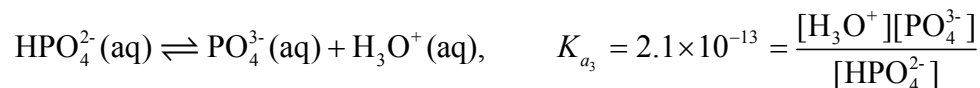
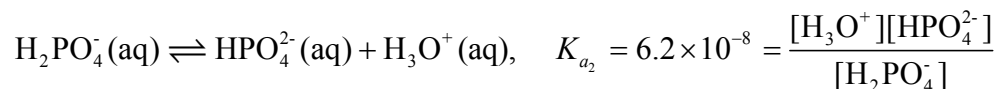
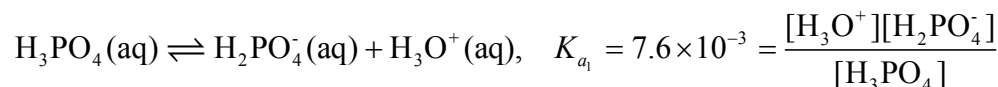
$$K_{a1} = 1.5 \times 10^{-2} = \frac{x^2}{0.10 - x}$$

$$x^2 + 1.5 \times 10^{-2}x - 1.5 \times 10^{-3} = 0$$

$$x = [\text{H}_3\text{O}^+] = \frac{-1.5 \times 10^{-2} + \sqrt{(1.5 \times 10^{-2})^2 + 6.0 \times 10^{-3}}}{2} = 0.032 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(0.032) = 1.49$$

10.91 The three equilibria involved are:



We also know that the combined concentration of all the phosphate species is:

$$[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] = 1.5 \times 10^{-2}$$

and the hydronium ion concentration is:

$$[\text{H}] = 10^{-\text{pH}} = 10^{-2.25} = 5.62 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

At this point it is a matter of solving this set of simultaneous equations to obtain the concentrations of the phosphate containing species. We start by dividing both sides of the equilibrium constant expressions above by the given hydronium ion concentration to obtain three ratios:

$$1.35 = \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}, \quad 1.10 \times 10^{-5} = \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}, \quad \text{and} \quad 3.74 \times 10^{-11} = \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$

Through rearrangement and substitution of these three ratios, we can obtain the following expressions:

$$[\text{H}_2\text{PO}_4^-] = 1.35 \cdot [\text{H}_3\text{PO}_4],$$

$$\begin{aligned} [\text{HPO}_4^{2-}] &= 1.10 \times 10^{-5} \cdot [\text{H}_2\text{PO}_4^-] = 1.10 \times 10^{-5} \cdot 1.35 \cdot [\text{H}_3\text{PO}_4] \\ &= 1.48 \times 10^{-5} \cdot [\text{H}_3\text{PO}_4], \text{ and} \end{aligned}$$

$$\begin{aligned} [\text{PO}_4^{3-}] &= 3.74 \times 10^{-11} \cdot [\text{HPO}_4^{2-}] = 3.74 \times 10^{-11} \cdot 1.48 \times 10^{-5} \cdot [\text{H}_3\text{PO}_4] \\ &= 5.54 \times 10^{-16} \cdot [\text{H}_3\text{PO}_4]. \end{aligned}$$

Substituting these expressions back into the sum:

$$\begin{aligned} & [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] = \\ & = [\text{H}_3\text{PO}_4] + (1.35 \cdot [\text{H}_3\text{PO}_4]) + (1.48 \times 10^{-5} \cdot [\text{H}_3\text{PO}_4]) + (5.54 \times 10^{-16} \cdot [\text{H}_3\text{PO}_4]) \\ & = 1.5 \times 10^{-2} \end{aligned}$$

we find:

$$\begin{aligned} [\text{H}_3\text{PO}_4] &= 6.4 \times 10^{-3}, \\ [\text{H}_2\text{PO}_4^-] &= 1.35 \cdot [\text{H}_3\text{PO}_4] = 8.6 \times 10^{-3}, \\ [\text{HPO}_4^{2-}] &= 1.48 \times 10^{-5} \cdot [\text{H}_3\text{PO}_4] = 9.4 \times 10^{-8}, \text{ and} \\ [\text{PO}_4^{3-}] &= 5.54 \times 10^{-16} \cdot [\text{H}_3\text{PO}_4] = 3.5 \times 10^{-18}. \end{aligned}$$

10.93 We can use the relationship derived in the text:

$$[\text{H}_3\text{O}^+]^2 - [\text{HA}]_{\text{initial}}[\text{H}_3\text{O}^+] - K_w = 0, \text{ in which HA is any strong acid.}$$

$$[\text{H}_3\text{O}^+]^2 - (6.55 \times 10^{-7})[\text{H}_3\text{O}^+] - (1.00 \times 10^{-14}) = 0$$

Solving using the quadratic equation gives

$$[\text{H}_3\text{O}^+] = 6.70 \times 10^{-7}, \text{ pH} = 6.174.$$

This value is slightly lower than the value calculated, based on the acid concentration alone ($\text{pH} = -\log(6.55 \times 10^{-7}) = 6.184$).

10.95 We can use the relationship derived in the text:

$$[\text{H}_3\text{O}^+]^2 + [\text{B}]_{\text{initial}}[\text{H}_3\text{O}^+] - K_w = 0, \text{ in which B is any strong base.}$$

$$[\text{H}_3\text{O}^+]^2 + (9.78 \times 10^{-8})[\text{H}_3\text{O}^+] - (1.00 \times 10^{-14}) = 0$$

Solving using the quadratic equation gives

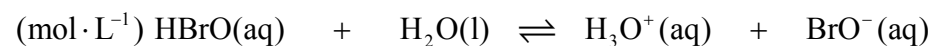
$$[\text{H}_3\text{O}^+] = 6.24 \times 10^{-8}, \text{ pH} = 7.205.$$

This value is higher than the value calculated, based on the base concentration alone ($\text{pOH} = -\log(9.78 \times 10^{-8}) = 7.009$).

10.97 (a) In the absence of a significant effect due to the autoprotolysis of water, the pH values of the 1.00×10^{-4} M and 1.00×10^{-6} M HBrO solutions can be calculated as described earlier.

For $1.00 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$:

Concentration



initial	1.00×10^{-4}	—	0	0
change	$-x$	—	$+x$	$+x$
final	$1.00 \times 10^{-4} - x$	—	$+x$	$+x$

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

$$2.0 \times 10^{-9} = \frac{(x)(x)}{1.00 \times 10^{-4} - x} = \frac{x^2}{[1.00 \times 10^{-4} - x]}$$

Assume $x \ll 1.00 \times 10^{-4}$

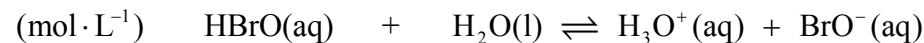
$$x^2 = (2.0 \times 10^{-9})(1.00 \times 10^{-4})$$

$$x = 4.5 \times 10^{-7}$$

Because $x < 1\%$ of 1.00×10^{-4} , the assumption was valid. Given this value, the pH is then calculated to be $-\log(4.5 \times 10^{-7}) = 6.35$.

For $1.00 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$:

Concentration



initial	1.00×10^{-6}	—	0	0
change	$-x$	—	$+x$	$+x$
final	$1.00 \times 10^{-6} - x$	—	$+x$	$+x$

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

$$2.0 \times 10^{-9} = \frac{(x)(x)}{1.00 \times 10^{-6} - x} = \frac{x^2}{[1.00 \times 10^{-6} - x]}$$

Assume $x \ll 1.00 \times 10^{-6}$

$$x^2 = (2.0 \times 10^{-9})(1.00 \times 10^{-6})$$

$$x = 4.5 \times 10^{-8}$$

x is 4.5% of 1.00×10^{-6} , so the assumption is less acceptable. The pH is calculated to be $-\log(4.5 \times 10^{-8}) = 7.35$. Because this predicts a basic solution, it is not reasonable.

(b) To calculate the value taking into account the autoprotolysis of water, we can use equation (22):

$$x^3 + K_a x^2 - (K_w + K_a \cdot [\text{HA}]_{\text{initial}})x - K_w \cdot K_a = 0, \text{ where } x = [\text{H}_3\text{O}^+].$$

To solve the expression, you substitute the values of $K_w = 1.00 \times 10^{-14}$, the initial concentration of acid, and $K_a = 2.0 \times 10^{-9}$ into this equation and then solve the expression either by trial and error or, preferably, using a graphing calculator such as the one found on the CD accompanying this text.

Alternatively, you can use a computer program designed to solve simultaneous equations. Because the unknowns include

$[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, $[\text{HBrO}]$, and $[\text{BrO}^-]$, you will need four equations. As seen in the text, pertinent equations are

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

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

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

$$[\text{HBrO}]_{\text{initial}} = [\text{HBrO}] + [\text{BrO}^-]$$

Both methods should produce the same result.

The values obtained are

$$[\text{H}_3\text{O}^+] = 4.6 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}, \text{ pH} = 6.34 \text{ (compare to 6.35 obtained in (a))}$$

$$[\text{BrO}^-] = 4.4 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{HBrO}] \cong 1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{OH}^-] = 2.2 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$$

Similarly, for $[\text{HBrO}]_{\text{initial}} = 1.00 \times 10^{-6}$:

$$[\text{H}_3\text{O}^+] = 1.1 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}, \text{pH} = 6.96 \text{ (compare to 7.32 obtained in (a))}$$

$$[\text{BrO}^-] = 1.8 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{HBrO}] \cong 9.8 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{OH}^-] = 9.1 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$$

Note that for the more concentrated solution, the effect of the autoprotolysis of water is very small. Notice also that the less concentrated solution is more acidic, due to the autoprotolysis of water, than would be predicted if this effect were not operating.

- 10.99** (a) In the absence of a significant effect due to the autoprotolysis of water, the pH values of the $8.50 \times 10^{-5} \text{ M}$ and $7.37 \times 10^{-6} \text{ M}$ HCN solutions can be calculated as described earlier.

For $8.50 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$:

Concentration

(mol · L ⁻¹)	HCN(aq)	+	H ₂ O(l)	⇌	H ₃ O ⁺ (aq)	+	CN ⁻ (aq)
initial	8.50×10^{-5}		—		0		0
change	$-x$		—		$+x$		$+x$
final	$8.50 \times 10^{-5} - x$		—		$+x$		$+x$

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

$$4.9 \times 10^{-10} = \frac{(x)(x)}{8.5 \times 10^{-5} - x} = \frac{x^2}{[8.5 \times 10^{-5} - x]}$$

Assume $x \ll 8.5 \times 10^{-5}$

$$x^2 = (4.9 \times 10^{-10})(8.5 \times 10^{-5})$$

$$x = 2.0 \times 10^{-7}$$

Because $x < 1\%$ of 8.50×10^{-5} , the assumption was valid. Given this value, the pH is then calculated to be $-\log(2.0 \times 10^{-7}) = 6.69$.

For $7.37 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$:

Concentration

(mol · L ⁻¹)	HCN(aq)	+	H ₂ O(l)	⇌	H ₃ O ⁺ (aq)	+	CN ⁻ (aq)
initial	7.37 × 10 ⁻⁶		—		0		0
change	-x		—		+x		+x
final	7.37 × 10 ⁻⁶ - x		—		+x		+x

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

$$4.9 \times 10^{-10} = \frac{(x)(x)}{7.37 \times 10^{-6} - x} = \frac{x^2}{[7.37 \times 10^{-6} - x]}$$

Assume $x \ll 7.37 \times 10^{-6}$

$$x^2 = (4.9 \times 10^{-10})(7.37 \times 10^{-6})$$

$$x = 6.0 \times 10^{-8}$$

x is < 1% of 7.37×10^{-6} , so the assumption is still reasonable. The pH is then calculated to be $-\log(6.0 \times 10^{-8}) = 7.22$. This answer is not reasonable because we know HCN is an acid.

(b) To calculate the value, taking into account the autoprotolysis of water, we can use equation (21):

$$x^3 + K_a x^2 - (K_w + K_a \cdot [\text{HA}]_{\text{initial}})x - K_w \cdot K_a = 0, \text{ where } x = [\text{H}_3\text{O}^+].$$

To solve the expression, you substitute the values of $K_w = 1.00 \times 10^{-14}$, the initial concentration of acid, and $K_a = 4.9 \times 10^{-10}$ into this equation and then solve the expression either by trial and error or, preferably, using a graphing calculator such as the one found on the CD accompanying this text.

Alternatively, you can use a computer program designed to solve simultaneous equations. Because the unknowns include $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, $[\text{HBrO}]$, and $[\text{BrO}^-]$, you will need four equations. As seen in the text, the pertinent equations are

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

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

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

$$[\text{HCN}]_{\text{initial}} = [\text{HCN}] + [\text{CN}^-]$$

Both methods should produce the same result.

For $[\text{HCN}] = 8.5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, the values obtained are

$$[\text{H}_3\text{O}^+] = 2.3 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}, \text{ pH} = 6.64 \text{ (compare to 6.69 obtained in (a))}$$

$$[\text{CN}^-] = 1.8 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{HCN}] \cong 8.5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{OH}^-] = 4.4 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$$

Similarly, for $[\text{HCN}]_{\text{initial}} = 7.37 \times 10^{-6}$:

$$[\text{H}_3\text{O}^+] = 1.2 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}, \text{ pH} = 6.92 \text{ (compare to 7.22 obtained in (a))}$$

$$[\text{CN}^-] = 3.1 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{HCN}] \cong 7.3 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{OH}^-] = 8.6 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$$

Note that for the more concentrated solution, the effect of the autoprotolysis of water is smaller. Notice also that the less concentrated solution is more acidic, due to the autoprotolysis of water, than would be predicted if this effect were not operating.

10.101 (a) Assuming all sulfur is converted to SO_2 , the amount of SO_2 produced is:

$$\frac{(1.00 \times 10^3 \text{ kg})(0.025)(1000 \text{ g} \cdot \text{kg}^{-1})}{32.07 \text{ g} \cdot \text{mol}^{-1}} = 780 \text{ mol of S}$$

Therefore, $(780 \text{ mol})(64.07 \text{ g} \cdot \text{mol}^{-1}) = 50,000 \text{ g}$ or 50 kg of SO_2 is produced

(b) To determine the pH we first must calculate the volume of water in which this 50 kg of SO_2 is dissolved:

$$V = (2 \text{ cm})(2.6 \text{ Km}) \left(\frac{1000 \text{ m}}{1 \text{ Km}} \right)^2 \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^2 \left(\frac{1 \text{ L}}{1000 \text{ cm}^3} \right) = 5.2 \times 10^7 \text{ L}$$

The concentration of $\text{SO}_2(\text{aq})$ is then:

$$(780 \text{ mol}) / (5.2 \times 10^7 \text{ L}) = 1.5 \times 10^{-5} \text{ M} . \text{ We can assume that upon}$$

solution the $\text{SO}_2(\text{aq})$ is converted to sulfurous acid and the pH is calculated as described earlier:

Concentration

(mol · L ⁻¹)	$\text{H}_2\text{SO}_3(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{H}_3\text{O}^+(\text{aq})$	+	$\text{HSO}_3^-(\text{aq})$
initial	1.50×10^{-5}		—		0		0
change	$-x$		—		$+x$		$+x$
final	$1.50 \times 10^{-5} - x$		—		$+x$		$+x$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]}$$

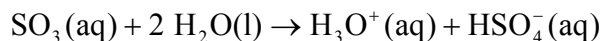
$$1.55 \times 10^{-2} = \frac{(x)(x)}{1.5 \times 10^{-5} - x}$$

Employing the quadratic formula we find

$$x = [\text{H}_3\text{O}^+] = 1.5 \times 10^{-5}, \text{ giving a pH of}$$

$$\text{pH} = \log(1.5 \times 10^{-5}) = 4.8$$

(c) When dissolved in water, SO_3 will form sulfuric acid:



The first deprotonation of sulfuric acid is complete, the concentration of hydronium ion due to the second deprotonation of sulfuric acid may be found as described earlier:

Concentration

(mol · L ⁻¹)	$\text{HSO}_4^-(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{H}_3\text{O}^+(\text{aq})$	+	$\text{SO}_4^{2-}(\text{aq})$
initial	1.50×10^{-5}		—		1.50×10^{-5}		0
change	$-x$		—		$+x$		$+x$
final	$1.50 \times 10^{-5} - x$		—		$1.50 \times 10^{-5} - x$		$+x$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

$$1.2 \times 10^{-2} = \frac{(1.5 \times 10^{-5} + x)(x)}{1.5 \times 10^{-5} - x}$$

Employing the quadratic formula we find

$$x = [\text{H}_3\text{O}^+] = 1.495 \times 10^{-5},$$

and the total hydronium ion concentration to be

$$1.495 \times 10^{-5} + 1.5 \times 10^{-5} = 3.0 \times 10^{-5}.$$

$$\text{Therefore, } \text{pH} = -\log(3.0 \times 10^{-5}) = 4.5$$

10.103 (a) $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = x^2 = 3.8 \times 10^{-7}$

$$[\text{H}_3\text{O}^+] = x = 1.9 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 6.72$$

(b) There are three data points available:

$$25^\circ\text{C} (K_w = 1.0 \times 10^{-14}), 40^\circ\text{C} (K_w = 3.8 \times 10^{-14}), \text{ and } 37^\circ\text{C} (K_w = 2.1 \times 10^{-14})$$

T	$1/T \text{ (K}^{-1}\text{)}$	$\ln K_w$
25°C	0.003356	-32.2362
37°C	0.003226	-31.4943
40°C	0.003195	-31.1376

The slope is equal to $-\Delta H^\circ/R$ and the intercept equals $\Delta S^\circ/R$.

$$\Delta H^\circ = -(-6502 \text{ K})(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 54 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S^\circ = -(-10.43)(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 87 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

(c) The equation determined from the graph is for $\ln K_w$. In order to write an equation for the pH dependence of pure water, we must rearrange the equation.

First we note the relationship between K_w and the pH of pure water.

$$[\text{H}_3\text{O}^+] = K_w^{1/2}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\frac{1}{2} \log K_w$$

$$\ln K_w = -\frac{6501}{T} - 10.43$$

$$2.303 \log K_w = -\frac{6501}{T} - 10.43$$

$$\log K_w = -\frac{2823}{T} - 4.529$$

$$\text{pH} = -\frac{1}{2} \log K_w$$

$$\text{pH} = \frac{1411}{T} + 2.264$$

10.105 (a) We begin by finding the empirical formula of the compound:

$$\text{C: } \frac{0.942 \text{ g CO}_2}{44.011 \text{ g} \cdot \text{mol}^{-1}} = 0.0214 \text{ mol CO}_2 \therefore 0.214 \text{ mol C}$$

$$(0.214 \text{ mol C})(12.011 \text{ g} \cdot \text{mol}^{-1}) = 0.257 \text{ g C}$$

$$\text{H: } \frac{0.0964 \text{ g H}_2\text{O}}{18.0158 \text{ g} \cdot \text{mol}^{-1}} = 0.00535 \text{ mol H}_2\text{O} \therefore 0.0107 \text{ mol H}$$

$$(0.0107 \text{ mol H})(1.008 \text{ g} \cdot \text{mol}^{-1}) = 0.0108 \text{ g H}$$

$$\text{Na: } \frac{0.246 \text{ g H}_2\text{O}}{22.99 \text{ g} \cdot \text{mol}^{-1}} = 0.0107 \text{ mol Na}$$

$$(0.0107 \text{ mol Na})(22.99 \text{ g} \cdot \text{mol}^{-1}) = 0.0246 \text{ g Na}$$

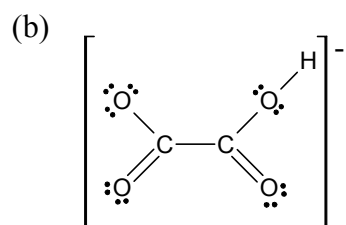
$$\text{O: mass of O} = 1.200 \text{ g} - 0.257 \text{ g} - 0.0108 \text{ g} - 0.0246 \text{ g} = 0.686 \text{ g of O}$$

$$\frac{0.686 \text{ g O}}{16.00 \text{ g} \cdot \text{mol}^{-1}} = 0.0429 \text{ mol O}$$

Dividing through by 0.0107 moles, we find the empirical formula to be:

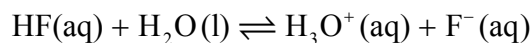


A molar mass of $112.02 \text{ g} \cdot \text{mol}^{-1}$ indicates that this is also the molecular formula.

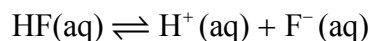


(c) The dissolved substance is sodium oxalate, it is capable of gaining or loosing a proton and, therefore, amphiprotic. $\text{pH} = \frac{1}{2}(\text{p}K_{a_1} + \text{p}K_{a_2}) = 2.7$

10.107 We wish to calculate K_a for the reaction



This equation is equivalent to



This latter writing of the expression is simpler for the purpose of the thermodynamic calculations.

The ΔG° value for this reaction is easily calculated from the free energies given in the appendix:

$$= (-278.79 \text{ kJ} \cdot \text{mol}^{-1}) - (-296.82 \text{ kJ} \cdot \text{mol}^{-1}) = 18.03 \text{ kJ} \cdot \text{mol}^{-1} - RT \ln K$$

$$K = e^{-\Delta G^\circ / RT}$$

$$K = e^{-(18030 \text{ J} \cdot \text{mol}^{-1}) / [8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}](298 \text{ K})} = 6.9 \times 10^{-4}$$

10.109 (a) $\text{D}_2\text{O} + \text{D}_2\text{O} \rightleftharpoons \text{D}_3\text{O}^+ + \text{OD}^-$

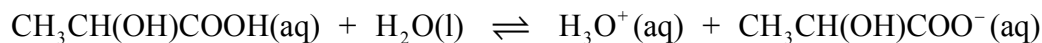
(b) $K_{\text{D}_2\text{O}} = [\text{D}_3\text{O}^+][\text{OD}^-] = 1.35 \times 10^{-15}$, $\text{p}K_{\text{D}_2\text{O}} = -\log K_{\text{D}_2\text{O}} = 14.870$

(c) $[\text{D}_3\text{O}^+] = [\text{OD}^-] = \sqrt{1.35 \times 10^{-15}} = 3.67 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$

(d) $\text{pD} = -\log(3.67 \times 10^{-8}) = 7.435 = \text{pOD}$

(e) $\text{pD} + \text{pOD} = \text{p}K_{\text{D}_2\text{O}}(\text{D}_2\text{O}) = 14.870$

10.111



Concentration ($\text{mol} \cdot \text{L}^{-1}$)

initial	1.00	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$1.00 - x$	—	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]} = \frac{x^2}{1.00-x} = 8.4 \times 10^{-4}$$

$$x = 0.029$$

$$\text{Percent deprotonation} = \frac{0.029}{1.00}(100\%) = 2.9\% \text{ deprotonated}$$

To calculate T_f for this solution we need the concentration in moles of solute per kilogram of solvent. Assuming a density of $1 \text{ g}\cdot\text{cm}^{-3}$, 1.00 L of solution will weigh 1000 g. One liter of solution will contain 1 mole (90.08 g) of lactic acid. Therefore, one liter of solution will contain $1000 \text{ g} - 90.08 \text{ g} = 910 \text{ g}$ or 0.910 kg of solvent.

$$\text{The molarity of the solution is: } \frac{1.029 \text{ mol solute}}{0.910 \text{ kg solvent}} = 1.13 \text{ m}.$$

$$\Delta T_f = (1.86 \text{ K}\cdot\text{Kg}\cdot\text{mol}^{-1})(1.13 \text{ mol}\cdot\text{Kg}^{-1}) = 2.1 \text{ K}$$

The temperature at which the solution will freeze is 271 K

$$\mathbf{10.113} \quad T' = 30^\circ\text{C} = 303 \text{ K}, T = 20^\circ\text{C} = 293 \text{ K}$$

$$\ln\left(\frac{K'_a}{K_a}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T} - \frac{1}{T'}\right) = \frac{\Delta H^\circ}{R}\left(\frac{T' - T}{TT'}\right)$$

This is the van't Hoff equation.

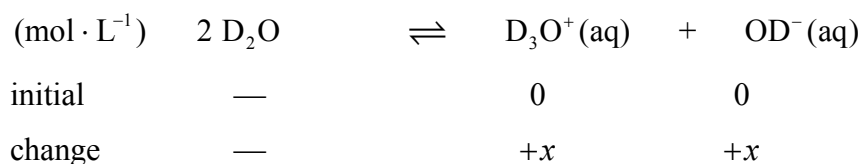
$$\ln\left(\frac{1.768 \times 10^{-4}}{1.765 \times 10^{-4}}\right) = \frac{\Delta H^\circ}{8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}\left(\frac{303 \text{ K} - 293 \text{ K}}{293 \text{ K} \times 303 \text{ K}}\right) = 0.0017$$

10.115 (a) The equilibrium constant for the autoprotolysis of pure deuterium oxide is given by:

$$K = e^{-\Delta G^\circ/RT} = e^{-84800 \text{ J}\cdot\text{mol}^{-1}/(8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298 \text{ K})} = 1.37 \times 10^{-15}$$

The concentration of $\text{D}_3\text{O}^+(\text{aq})$ at equilibrium is found in the familiar way:

Concentration



equilibrium $\rightleftharpoons +x \rightleftharpoons +x$

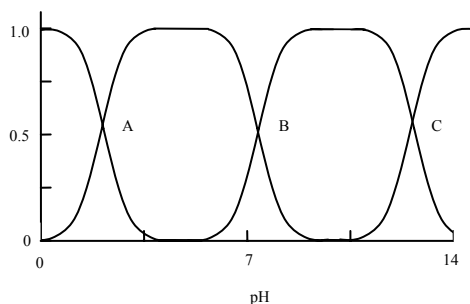
$$K = [\text{D}_3\text{O}^+][\text{OD}^-] = 1.37 \times 10^{-15}$$

$$[\text{D}_3\text{O}^+] = 3.7 \times 10^{-8}$$

$$\text{pD} = -\log(3.7 \times 10^{-8}) = 7.4$$

(b) Given the expression for K in part (b) above, it is apparent that as T increases K will increase resulting in an increase in $[\text{D}_3\text{O}^+(\text{aq})]$ and a decrease in pD.

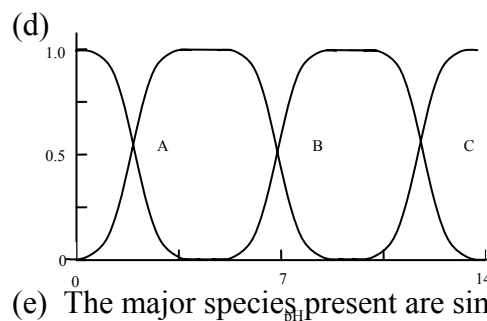
10.117 (a) and (b) Buffer regions are marked A, B, and C.



(c) Region A: H_3PO_4 and H_2PO_4^-

Region B: H_2PO_4^- and HPO_4^{2-}

Region C: HPO_4^{2-} and PO_4^{3-}

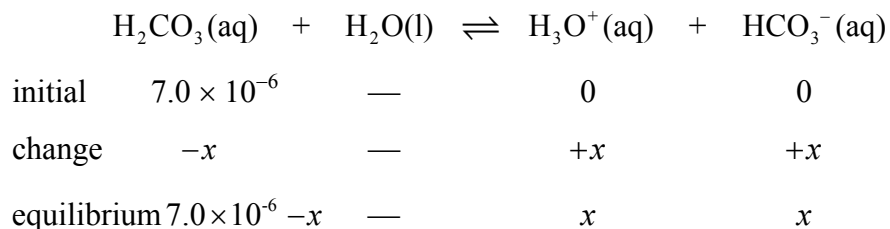


(e) The major species present are similar for both H_3PO_4 and

H_3AsO_4 : H_2EO_4^- and HEO_4^{2-} where $\text{E} = \text{P}$ or As . For As , there is more HAsO_4^{2-} than H_2AsO_4^- , with a ratio of approximately 0.63 to 0.37, or 1.7 : 1. For P , the situation is reversed, with more H_2PO_4^- than HPO_4^{2-} in a ratio of about 0.61 to 0.39, or 2.2 : 1.

10.119 Given that CO_2 will react with water to form carbonic acid, H_2CO_3 , it only remains to determine the concentration of H_3O^+ due to the deprotonation of H_2CO_3 .

$$[\text{CO}_2] = (2.3 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1})(3.04 \times 10^{-4} \text{ atm}) = 7.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$



$$K_a = 10^{-pK_a} = 10^{-6.37} = 4.27 \times 10^{-7} = \left(\frac{x^2}{7.0 \times 10^{-6}} \right)$$

$$x = [\text{H}_3\text{O}^+] = 1.73 \times 10^{-6}$$

$$\text{pH} = -\log(1.73 \times 10^{-6}) = 5.75$$