Chapter XV: Acid-Base Equilibria

Part 1, Sections 89 – 94

Unit 91 – Bronsted-Lowry Acids and Bases

91-1 Write an equation that shows NH_3 acting as a base.

Solution

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq)$$

91-2 Write equations that show $H_2PO_4{}^-$ acting both as an acid and as a base.

Solution

As a base: $H_2PO_4{}^-(aq) + H_2O(l) \rightleftharpoons H_3PO_4(aq) + OH^-(aq)$;
as an acid: $H_2PO_4{}^-(aq) + H_2O(aq) \rightleftharpoons HPO_4{}^{2-}(aq) + H_3O^+(aq)$

91-3 Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) H_3O^+
(b) HCl
(c) CH_3CO_2H
(d) $NH_4{}^+$
(e) $HSO_4{}^-$

Solution

(a) $H_3O^+(aq) \rightleftharpoons H^+(aq) + H_2O(l)$;
(b) $HCl(l) \rightleftharpoons H^+(aq) + Cl^-(aq)$;
(c) $CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2{}^-(aq)$;
(d) $NH_4{}^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$;
(e) $HSO_4{}^-(aq) \rightleftharpoons H^+(aq) + SO_4{}^{2-}(aq)$

91-4 Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) HNO_3
(b) $PH_4{}^+$
(c) H_2S
(d) CH_3CH_2COOH
(e) $H_2PO_4{}^-$
(f) HS^-

Solution

In a Brønsted-Lowry acid, the acid must supply an H^+.

(a) $HNO_3(aq) \rightleftharpoons H^+(aq) + NO_3{}^-(aq)$;

(b) $PH_4^+(aq) \rightleftharpoons H^+(aq) + PH_3(aq)$;
(c) $H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq)$;
(d) $C_2H_5CO_2H(aq) \rightleftharpoons H^+(aq) + C_2H_5CO_2^-(aq)$;
(e) $H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$;
(f) $HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq)$

91-5 Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:
- (a) H_2O
- (b) OH^-
- (c) NH_3
- (d) CN^-
- (e) S^{2-}
- (f) $H_2PO_4^-$

Solution

(a) $H_2O(l) + H^+(aq) \rightleftharpoons H_3O^+(aq)$;
(b) $OH^-(aq) + H^+(aq) \rightleftharpoons H_2O(l)$;
(c) $NH_3(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq)$;
(d) $CN^-(aq) + H^+(aq) \rightleftharpoons HCN(aq)$;
(e) $S^{2-}(aq) + H^+(aq) \rightleftharpoons HS^-(aq)$;
(f) $H_2PO_4^-(aq) + H^+(aq) \rightleftharpoons H_3PO_4(aq)$

91-6 Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:
- (a) HS^-
- (b) PO_4^{3-}
- (c) NH_2^-
- (d) C_2H_5OH
- (e) O^{2-}
- (f) $H_2PO_4^-$

Solution

In a Brønsted-Lowry base, the base must accept an H^+.
(a) $HS^- + H^+ \rightleftharpoons H_2S$;
(b) $PO_4^{3-} + H^+ \rightleftharpoons HPO_4^{2-}$;
(c) $NH_2^- + H^+ \rightleftharpoons NH_3$
(d) $C_2H_5OH + H^+ \rightleftharpoons C_2H_5OH_2^+$;
(e) $O^{2-} + H^+ \rightleftharpoons OH^-$;
(f) $HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^-$

91-7 What is the conjugate acid of each of the following? What is the conjugate base of each?
- (a) OH^-
- (b) H_2O
- (c) HCO_3^-

(d) NH_3
(e) HSO_4^-
(f) H_2O_2
(g) HS^-
(h) $H_5N_2^+$

Solution

(a) H_2O, O^{2-};
(b) H_3O^+, OH^-;
(c) H_2CO_3, CO_3^{2-};
(d) NH_4^+, NH_2^-;
(e) H_2SO_4, SO_4^{2-};
(f) $H_3O_2^+$, HO_2^-;
(g) H_2S; S^{2-};
(h) $H_6N_2^{2+}$, H_4N_2

91-8 What is the conjugate acid of each of the following? What is the conjugate base of each?

(a) H_2S
(b) $H_2PO_4^-$
(c) PH_3
(d) HS^-
(e) HSO_3^-
(f) $H_3O_2^+$
(g) H_4N_2
(h) CH_3OH

Solution

(a) H_3S^+, HS^-;
(b) $H_3PO_4^-$, HPO_4^{2-};
(c) PH_4^+, PH_2^-;
(d) H_2S, S^{2-};
(e) H_2SO_3, SO_3^{2-};
(f) $H_4O_2^{2+}$, H_2O_2;
(g) $H_5N_2^+$, $H_3N_2^-$;
(h) $CH_3OH_2^+$, CH_3O^-

91-9 Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

(a) $HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$
(b) $CN^- + H_2O \longrightarrow HCN + OH^-$
(c) $H_2SO_4 + Cl^- \longrightarrow HCl + HSO_4^-$
(d) $HSO_4^- + OH^- \longrightarrow SO_4^{2-} + H_2O$

(e) $O^{2-} + H_2O \longrightarrow 2OH^-$

(f) $[Cu(H_2O)_3(OH)]^+ + [Al(H_2O)_6]^{3+} \longrightarrow [Cu(H_2O)_4]^{2+} + [Al(H_2O)_5(OH)]^{2+}$

(g) $H_2S + NH_2^- \longrightarrow HS^- + NH_3$

Solution
The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA.
(a) HNO_3(BA), H_2O(BB), H_3O^+(CA),NO_3^-(CB);
(b) CN^-(BB), H_2O(BA), HCN(CA), OH^-(CB);
(c) H_2SO_4(BA), Cl^-(BB), HCl(CA), HSO_4^-(CB);
(d) HSO_4^-(BA), OH^-(BB), SO_4^{2-}(CB), H_2O(CA);
(e) O^{2-}(BB), H_2O(BA) OH^-(CB and CA);
(f) $[Cu(H_2O)_3(OH)]^+$(BB), $[Al(H_2O)_6]^{3+}$(BA), $[Cu(H_2O)_4]^{2+}$(CA), $[Al(H_2O)_5(OH)]^{2+}$(CB); (g) H_2S(BA), NH_2^-(BB), HS^-(CB), NH_3(CA)

91-10 Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

(a) $NO_2^- + H_2O \longrightarrow HNO_2 + OH^-$

(b) $HBr + H_2O \longrightarrow H_3O^+ + Br^-$

(c) $HS^- + H_2O \longrightarrow H_2S + OH^-$

(d) $H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$

(e) $H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-$

(f) $[Fe(H_2O)_5(OH)]^{2+} + [Al(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Al(H_2O)_5(OH)]^{2+}$

(g) $CH_3OH + H^- \longrightarrow CH_3O^- + H_2$

Solution
The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; and its conjugate acid = CA.
(a) NO_2^- (BB), H_2O(BA), HNO_2(CA), OH^-(CB);
(b) HBr(BA), H_2O(BB), H_3O^+ (CA), Br^-(CB);
(c) HS^-(BB), H_2O(BA), H_2S(CA), OH^-(CB)$^-$;
(d) $H_2PO_4^-$ (BA), OH^-(BB), HPO_4^{2-} (CB), H_2O(CA);
(e) $H_2PO_4^-$ (BB), HCl(BA), H_3PO_4(CA), Cl^-(CB);
(f) $[Fe(H_2O)_5(OH)]^{2+}$ (BB), $[Al(H_2O)_6]^{3+}$ (BA), $[Fe(H_2O)_6]^{3+}$ (CA), $[Al(H_2O)_5(OH)]^{2+}$ (CB);
(g) CH_3OH(BA), H^-(BB), CH_3O^- (CB), H_2(CA)

91-11 What are amphiprotic species? Illustrate with suitable equations.
Solution

Amphiprotic species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is H_2O. As an acid: $H_2O(l) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$. As a base: $H_2O(l) + HCl(aq) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

91-12 State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:

(a) H_2O
(b) $H_2PO_4^-$
(c) S^{2-}
(d) CO_3^{2-}
(e) HSO_4^-

Solution

amphiprotic:
(a) $H_2O(l) + HBr(aq) \rightleftharpoons H_3O^+(aq) + Br^-(aq)$,
$H_2O(l) + CN^-(aq) \rightleftharpoons HCN(aq) + OH^-(aq)$;
(b) $H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$,
$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)$;
(e) $HSO_4^-(aq) + HClO_4(aq) \rightleftharpoons H_2SO_4(aq) + ClO_4^-(aq)$,
$HSO_4^-(aq) + OH^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2O(l)$;
not amphiprotic: (c) S^{2-}, (d) CO_3^{2-}

91-13 State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

(a) NH_3
(b) HPO_4^{2-}
(c) Br^-
(d) NH_4^+
(e) ASO_4^{3-}

Solution

(a) $NH_3 + H_3O^+ \rightleftharpoons NH_4OH + H_2O$, $NH_3 + OCH_3^- \rightleftharpoons NH_2^- + CH_3OH$;
(b) $HPO_4^{2-} + OH^- \rightleftharpoons PO_4^{3-} + H_2O$, $HPO_4^{2-} + HClO_4 \rightleftharpoons H_2PO_4^- + ClO_4^-$;
not amphiprotic: (c) Br^-; (d) NH_4^+; (e) AsO_4^{3-}

91-14 Which of the following does not fit the definition of a Brønsted Acid?

(a) H_3PO_4
(b) $H_2PO_4^-$
(c) H_2O
(d) NH_4^+
(e) CO_2

Solution: A Brønsted Acid can donate a proton. All of compounds (a) – (d) have protons that they can donate in aqueous solution. CO_2 does not have any protons, and thus it cannot directly act as a Brønsted

91-15 Which of the following does not fit the definition of a Brønsted Base?

(a) NH_3
(b) H_2O
(c) NH_4^+
(d) HCO_3^-
(e) CO_3^{2-}

Solution: A Brønsted Base can accept a proton. All of the compounds except ammonium ion (NH_4^+) can accept a proton, and so ammonium ion is the only one that cannot act as a Brønsted Base.

91-16 Is the self-ionization of water endothermic or exothermic? The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C and 9.3×10^{-14} at 60 °C.

Solution

Because K_w increases with increasing temperature, the reaction in endothermic. When the temperature of the system is increased, the reaction shifts toward the product side, making K bigger. According to Le Châtelier's principle, the reaction shifts away from the heat term, so the heat term must be on the reactant side of the equation. Therefore, the reaction is endothermic.

Unit 92 – pH and pOH

92-1 Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+] = 1.7 \times 10^{-7}$ *M*. K_w is 2.910×10^{-14} at 40 °C.

Solution

In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C, $[H_3O^+] = [OH^-] = (2.9\ 10^{-14})^{1/2} = 1.7 \times 10^{-7}$.

92-2 The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

Solution

$K_w = [H_3O^+]\,[OH^-] = 2.9 \times 10^{-14}$

$$[H_3O^+] = [OH^-] = \sqrt{2.9 \times 10^{-14}} = 1.70 \times 10^{-7} = 1.7 \times 10^{-7}\ M$$

$pH = pOH = -\log(1.70 \times 10^{-7}) = 6.769 = 6.77$

92-3 The ionization constant for water (K_w) is 9.311×10^{-14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.

Solution
For water, $[H_3O^+]$ = $[OH^-]$ = x.
$K_w = 9.311 \times 10^{-14} = x^2$
$x = 3.051 \times 10^{-7} M = [H_3O^+] = [OH^-]$
pH = –log 3.051×10^{-7} = –(–6.5156) = 6.5156
pOH = pH = 6.5156

92-4 Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.200 *M* HCl
(b) 0.0143 *M* NaOH
(c) 3.0 *M* HNO_3
(d) 0.0031 *M* $Ca(OH)_2$

Solution
pH = –log$[H_3O^+]$, pOH = –log$[OH^-]$;
(a) Hydrochloric acid is a strong acid; therefore, the hydronium ion concentration is the same as the molar concentration of HCl. pH = – log(0.200) = –(–0.699) = 0.699; pOH = 14.00 – pH = 14.00 – 0.699 = 13.30;
(b) NaOH is a strong base that is completely ionized in dilute solution. Therefore, since $[OH^-]$ = 0.0143 *M*, pOH = –log(0.0143) = –(–1.8447) = 1.845; pH = 14.00 – pOH = 14.00 – 1.845 = 12.16;
(c) pH = –log(3.0) = –(0.477) = –0.48; pOH = 14.00 – pH = 14.00 – (–0.477) = 14.477 = 14.48;
(d) $[OH^-]$ = 2(0.0031) = 0.0062 *M*; pOH = –log(0.0062) = –(–2.208) = 2.21; pH = 14.00 – 2.208 = 11.792 = 11.79

92-5 Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.000259 *M* $HClO_4$
(b) 0.21 *M* NaOH
(c) 0.000071 *M* $Ba(OH)_2$
(d) 2.5 *M* KOH

Solution
(a) pH = –log(0.000259) = –(–3.5867) = 3.587; pOH = 14.0000 – 3.5867 = 10.4133 = 10.413;
(b) pOH = –log(0.21) = –(–0.678) = 0.68; pH = 14.000 – 0.678 = 13.322 = 13.32;
(c) since $[OH^-]$ = 2(0.000071) = 0.000142 *M*; pOH = –log(0.000142) = –(–3.848) = 3.85; pH = 14.000 – 3.848 = 10.152 = 10.15;
(d) pOH = –log(2.5) = –(0.398) = –0.40; pH = 14.000 – (–0.398) = 14.398 = 14.4

92-6 What are the pH and pOH of a solution of 2.0 *M* HCl, which ionizes completely?
Solution
HCl is a strong acid that undergoes complete ionization in pure water.
$[H_3O^+]$ = molarity of HCl = 2.0 *M*
pH = –log$[H_3O^+]$ = –log(2.0) = –0.30
pOH = 14.00 – pH = 14.00 – (–0.30) = 14.30

92-7 What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

Solution

$[H_3O^+] = 10^{-6.52} = 3.0 \times 10^{-7}\ M$; pOH = 14.00 – pH; pOH = 14.00 – 6.52 = 7.48; $[\mathrm{OH^-}] = 10^{-7.48} = 3.3 \times 10^{-8}\ M$

92-8 The hydronium ion concentration in a sample of rainwater is found to be $1.7 \times 10^{-6}\ M$ at 25 °C. What is the concentration of hydroxide ions in the rainwater?

Solution

$[H_3O^+]\ [\mathrm{OH^-}] = 1.0 \times 10^{-14}$; $[1.7 \times 10^{-6}][\mathrm{OH^-}] = 1.0 \times 10^{-14}$;

$$[\mathrm{OH^-}] = \frac{1.00 \times 10^{-1}}{1.7 \times 10^{-6}} = 5.9 \times 10^{-9}\ M$$

92-9 The hydroxide ion concentration in household ammonia is $3.2 \times 10^{-3}\ M$ at 25 °C. What is the concentration of hydronium ions in the solution?

Solution

$[H_3O^+]\ [\mathrm{OH^-}] = 1.0 \times 10^{-14}$; $[H_3O^+]\ [3.2 \times 10^{-3}] = 1.0 \times 10^{-14}$; $[\mathrm{OH^-}] = \frac{1.00 \times 10^{-14}}{3.2 \times 10^{-3}} = 3.1 \times 10^{-12}\ M$

Unit 93 – Relative Strengths of Acids and Bases: Ionization Constants

93-1 Determine the $[H^+]$, pH and pOH of the following aqueous solutions at 25 °C.

(a) 0.20 M HCl
(b) 1.00×10^{-3} M HCl.
(c) 0.036 M $HClO_4$
(d) 0.28 M NaOH
(e) 0.20 M $Ca(OH)_2$

Solution:

(a) HCl is a strong acid and will completely dissociate in water to form an 0.20 M solution of H^+. Thus

$$pH = -\log(0.20) = -(-0.70) = 0.70$$
$$pOH = pK_w - pH = 14.00 - 0.70 = 13.30$$

(b) HCl is a strong acid, so the 1.00×10^{-3}M solution will produce a solution with $[H^+] = 1.0 \times 10^{-3}$ M.

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

(c) $HClO_4$ is a strong acid, so the 0.036 M solution will produce a solution with $[H^+] = 0.036$ M.

$$pH = -\log(0.036) = -(-1.44) = 1.44$$
$$pOH = pK_w - pH = 14.00 - 1.44 = 12.56$$

(d) NaOH is a strong base that will completely dissociate in water, so the 0.28M solution will produce a solution that has $[OH^-] = 0.28$ M.

$pOH = -\log[OH^-] = -\log(0.28) = -(-0.55) = 0.55$

$pH = = pK_w - pOH = 14.00 - 0.55 = 13.45$

$pH = -\log[H^+]$, so that $[H^+] = 10^{-pH} = 10^{-13.45} = 3.6 \times 10^{-14}$.

(d) $Ca(OH)_2$ is a strong base that will completely dissociate in water according to the equation

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

Thus, 0.20 M $Ca(OH)_2$ produces a solution that is 2 x 0.20M = 0.40 M in OH^-.

$pOH = -\log[OH^-] = -\log(0.40) = -(-0.40) = 0.40$

$pH = = pK_w - pOH = 14.00 - 0.40 = 13.60$

$pH = -\log[H^+]$, so that $[H^+] = 10^{-pH} = 10^{-13.60} = 2.5 \times 10^{-14}$.

93-2 Show the equilibrium that would be established when the following weak acids are placed into water. What is the pH of the solution at 25 °C? What is the % ionization of each acid? (You will need to look up the ionization constants – the Ka values – in the Appendix.)

(a) 0.156 M HClO

(b) 0.267 M HF

Solution:

(a) HClO is a weak acid that dissociates according to $HClO(aq) \rightleftharpoons H^+(aq) + ClO^-(aq)$

The pKa value is 2.9×10^{-8}. We will need to set up an ICE table in order to solve for the $[H^+]$ at equilibrium:

	$HClO(aq) \rightleftharpoons$	$H^+(aq)$	$ClO^-(aq)$
I	0.156 M	~0	0
C	$-x$	$+x$	$+x$
E	$0.156 - x$	x	x

$$K_a = \frac{[H^+][ClO^-]}{[HClO]}$$

$$2.9 \times 10^{-8} = \frac{(x)(x)}{(0.156 - x)}$$

Since the Ka value is so small, we can assume that x would be negligible compared to 0.156 so that we can assume that we can neglect it. The equation thus becomes:

$$2.9 \times 10^{-8} = \frac{(x)(x)}{(0.156)}$$

$$4.52 \times 10^{-9} = x^2$$

$$\sqrt{4.52 \times 10^{-9}} = \sqrt{x^2}$$

$$x = 6.72 \times 10^{-5}$$

Thus *x* is very small compared to the [ ] of the acid, so our assumption that we could neglect *x* was valid.

Since $x = [H^+] = 6.72 \times 10^{-5}$. The $pH = -\log[H^+] = -\log(6.72 \times 10^{-5}) = -(-4.17) = 4.17$

$pOH = pK_w - pH = 14.00 - 4.17 = 9.83$

(b) HF is a weak acid that dissociates according to $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$
The pKa value is 6.4 x 10^{-4}. We will need to set up an ICE table in order to solve for the $[H^+]$ at equilibrium:

	$HF(aq) \rightleftharpoons$	$H^+(aq)$	$F^-(aq)$
I	0.267 M	~0	0
C	-*x*	+ *x*	+ *x*
E	0.267 - *x*	*x*	*x*

$$K_a = \frac{[\mathrm{H^+}][\mathrm{F^-}]}{[\mathrm{HF}]}$$

$$6.4 \times 10^{-4} = \frac{(\mathrm{x})(\mathrm{x})}{(0.267 - \mathrm{x})}$$

Since the Ka value is so small, we can assume that x would be negligible compared to 0.267 so that we can assume that we can neglect it. The equation thus becomes:

$$6.4 \times 10^{-4} = \frac{(\mathrm{x})(\mathrm{x})}{(0.267)}$$

$$1.71 \times 10^{-4} = x^2$$

$$\sqrt{1.72 \times 10^{-4}} = \sqrt{x^2}$$

$$x = 1.31 \times 10^{-2}$$

Thus *x* is very small compared to the [ ] of the acid, so our assumption that we could neglect *x* was valid. Thus $x = [H^+] = 1.31 \times 10^{-2}$. The pH = $-\log[H^+] = -\log(1.31 \times 10^{-2}) = -(-1.88) = 1.88$

$$\mathrm{pOH} = \mathrm{p}K_w - \mathrm{pH} = 14.000 - 4.172 = 9.828$$

93-3 Show the equilibrium that would be established when the following weak bases are placed into water. What is the pH of the solution at 25 °C

(a) 0.150 M NH_3
(b) 0.067 M CH_3NH_2

Solution:

(a) NH_3 is a weak base that establishes the following equilibrium in aqueous solution:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The pKb value is 1.8 x 10^{-5}. We will need to set up an ICE table in order to solve for the $[H^+]$ at equilibrium:

	$NH_3(aq)$	$\rightleftharpoons NH_4^+(aq)$	$OH^-(aq)$
I	0.150 M	~0	0
C	-*x*	+ *x*	+ *x*
E	0.150 - *x*	*x*	*x*

$$K_b = \frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]}{[\mathrm{NH_3}]}$$

$$1.8\ \times 10^{-5} = \frac{(\mathrm{x})(\mathrm{x})}{(0.150 - \mathrm{x})}$$

Since the Kb value is so small, we can assume that x would be negligible compared to 0.150 so that we can assume that we can neglect it. The equation thus becomes:

$$1.8\ \times 10^{-5} = \frac{(\mathrm{x})(\mathrm{x})}{(0.150)}$$

$$2.7 \times 10^{-6} = x^2$$

$$\sqrt{2.7\ \times 10^{-6}}\ = \sqrt{x^2}$$

$$x = 1.64 \times 10^{-3}$$

Thus *x* is very small compared to the [ ] of the base, so our assumption that we could neglect *x* was valid.

Since x = $[OH^-] = 1.64 \times 10^{-3}$; The pOH = $-\log[OH^-] = -\log(1.64 \times 10^{-3}) = -(-2.78) = 2.78$

$$pH = pK_w - pOH = 14.00 - 2.78 = 11.22$$

(b) CH_3NH_2 is a weak base that establishes the following equilibrium in aqueous solution:

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

The pKb value is 4.4×10^{-4}. We will need to set up an ICE table in order to solve for the $[OH^-]$ at equilibrium:

	$CH_3NH_2(aq)$	$CH_3NH_3^+(aq)$	$OH^-(aq)$
I	0.150 M	~0	0
C	-*x*	+ *x*	+ *x*
E	0.150 - *x*	*x*	*x*

$$K_b = \frac{[CH_3\mathrm{NH}_3^+][\mathrm{OH}^-]}{[CH_3\mathrm{NH}_2]}$$

$$4.4\ \times 10^{-4} = \frac{(\mathrm{x})(\mathrm{x})}{(0.067 - \mathrm{x})}$$

Since the Kb value is so small, we can assume that x would be negligible compared to 0.067 so that we can assume that we can neglect it. The equation thus becomes:

$$4.4\ \times 10^{-4} = \frac{(\mathrm{x})(\mathrm{x})}{(0.067)}$$

$$2.95 \times 10^{-5} = x^2$$

$$\sqrt{2.95\ \times 10^{-5}}\ = \sqrt{x^2}$$

$$x = 5.43 \times 10^{-3}$$

Thus *x* is very small compared to the [ ] of the base, so our assumption that we could neglect *x* was valid.
Since x = $[OH^-] = 5.43 \times 10^{-3}$; The pOH = $-\log[OH^-] = -\log(5.43 \times 10^{-3}) = -(-2.27) = 2.27$

$$pH = pK_w - pOH = 14.00 - 2.27 = 11.73$$

93-4 What is the pH of the following solutions at 25 ºC?

(a) 0.14 M nitric acid, HNO_3.

(b) 0.19 M acetic acid, CH_3COOH

(c) 0.278 M dimethylamine, $(CH_3)_2NH$

(d) 0.245 M nitrous acid, HNO_2

Solution :

(a) HNO_3 is a strong acid so it will completely dissociate in aqueous solution. The [H+] = 0.14 M, so the pH = -log(0.14) = 0.851

(b) Acetic acid is a weak acid, and so only partially dissociates in aqueous solution.

The reaction is:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{H_3}O^+(aq) + \mathrm{CH_3CO_2}^-(aq)$$

The equilibrium expression is:

$$K_a = \frac{[\mathrm{CH_3CO_2}^-][\mathrm{H_3}O^+]}{[\mathrm{CH_3CO_2H}]} = 1.8 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	CH_3CO_2H $\rightleftharpoons$	H_3O^+	$CH_3CO_2^-$
I	0.19 M	~0	0
C	$-x$	$+x$	$+x$
E	$0.19 - x$	x	x

$$K_a = \frac{[\mathrm{CH_3CO_2}^-][\mathrm{H_3}O^+]}{[\mathrm{CH_3CO_2H}]}$$

$$1.8 \times 10^{-5} = \frac{(\mathrm{x})(\mathrm{x})}{(0.19 - \mathrm{x})}$$

Since the Ka value is so small, we can assume that x would be negligible compared to 0.19 so that we can assume that we can neglect it. The equation thus becomes:

$$1.8 \times 10^{-5} = \frac{(\mathrm{x})(\mathrm{x})}{(0.19)}$$

$$3.4 \times 10^{-4} = x^2$$

$$\sqrt{3.4 \times 10^{-4}} = \sqrt{x^2}$$

$$x = 1.8 \times 10^{-4}$$

Thus x is very small compared to the [ ] of the acid, so our assumption that we could neglect x was valid.

Since x = $[H^+] = 1.8 \times 10^{-4}$. The pH = $-\log[H^+] = -\log(1.8 \times 10^{-4}) = -(-1.73) = 1.73$

(c) Diethylamine is a weak base with a Kb of 5.9×10^{-4}, which reacts with water according to

$$(CH_3)_2NH_2(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_3^+(aq) + OH^-(aq)$$

We will need to set up an ICE table in order to solve for the [OH-] at equilibrium:

	$(CH_3)_2NH_2$	$\rightleftharpoons$ $(CH_3)_2NH_3^+$	$OH^-(aq)$
I	0.178 M	~0	0
C	$-x$	$+x$	$+x$
E	$0.278 - x$	x	x

$$K_b = \frac{[(CH_3)_2NH_3^+][OH^-]}{[(CH_3)_2NH_2]}$$

$$5.9 \times 10^{-4} = \frac{(x)(x)}{(0.278 - x)}$$

Since the Kb value is so small, we can assume that x would be negligible compared to 0.278 so that we can assume that we can neglect it. The equation thus becomes:

$$5.9 \times 10^{-4} = \frac{(x)(x)}{(0.278)}$$

$$1.64 \times 10^{-4} = x^2$$

$$\sqrt{1.64 \times 10^{-4}} = \sqrt{x^2}$$

$$x = 1.3 \times 10^{-2}$$

Thus x is <5% of the [ ] of the base, so our assumption that we could neglect x was valid.

Since x = $[OH^-] = 1.3 \times 10^{-2}$; The pOH = $-\log[OH^-] = -\log(1.3 \times 10^{-2}) = -(-1.89) = 1.89$

$$pH = pK_w - pOH = 14.00 - 1.89 = 12.11$$

(d) HNO_2 is a weak acid with a pKa value of 4.5×10^{-4}. It dissociates according to

$$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$$

We will need to set up an ICE table in order to solve for the $[H^+]$ at equilibrium:

	$HNO_2 \rightleftharpoons$	H^+	NO_2^- (aq)
I	0.245 M	~0	0
C	$-x$	$+x$	$+x$
E	$0.245 - x$	x	x

$$K_a = \frac{[\mathrm{H}^+][\mathrm{N}O_2{}^-]}{[\mathrm{HN}O_2]}$$

$$4.5 \times 10^{-4} = \frac{(\mathrm{x})(\mathrm{x})}{(0.245 - \mathrm{x})}$$

Since the Ka value is so small, we can assume that x would be negligible compared to0.245 so that we can assume that we can neglect it. The equation thus becomes:

$$4.5 \times 10^{-4} = \frac{(\mathrm{x})(\mathrm{x})}{(0.245)}$$

$$1.10 \text{ x } 10^{-4} = x^2$$

$$\sqrt{1.10 \times 10^{-4}} = \sqrt{x^2}$$

$$x = 1.05 \text{ x } 10^{-2}$$

Thus x is < 5% of the [ ] of the acid, so our assumption that we could neglect x was valid.

Since x = $[\mathrm{H}^+]$ = 1.05 x 10^{-2}. The pH = -log$[\mathrm{H}^+]$ = -log (1.05 x 10^{-2}) = - (-1.98) = 1.98

93-5 Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected.

(a) 0.0092 *M* HClO, a weak acid
(b) 0.0784 *M* $C_6H_5NH_2$, a weak base
(c) 0.0810 *M* HCN, a weak acid
(d) 0.11 *M* $(CH_3)_3N$, a weak base
(e) 0.120 *M* $\mathrm{Fe}(H_2O)_6{}^{2+}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

Solution

(a) The reaction is: $\mathrm{HClO}(aq) + \mathrm{H}_2O(l) \rightleftharpoons \mathrm{H}_3O^+(aq) + \mathrm{ClO}^-(aq)$

The equilibrium expression is:

$$K_a = \frac{[H_3O^+][\mathrm{ClO}^-]}{[\mathrm{HClO}]} = 2.9 \times 10^{-8}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HClO]	$[H_3O^+]$	$[ClO^-]$
Initial concentration (*M*)	0.0092	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.0092 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that $(0.0092 - x) \approx 0.0092$ gives:

$$\frac{[H_3O^+][\mathrm{ClO}^-]}{[\mathrm{HClO}]} = \frac{(x)(x)}{(0.0092\ -\ x)} \approx \frac{(x)(x)}{0.0092} = 2.9 \times 10^{-8}$$

Solving for x gives $1.63 \times 10^{-5} M$. This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[H_3O^+] = [\mathrm{ClO}^-] = 1.6 \times 10^{-5} M$

$[\mathrm{HClO}^-] = 0.0092 - 1.63 \times 10^{-5} = 0.00918 = 0.0092\ M$

$[\mathrm{OH}^-] = \frac{K_W}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.63 \times 10^{-5}} = 6.1 \times 10^{-10}\ M;$

(b) The reaction is: $C_6H_5\mathrm{NH}_2(aq) + \mathrm{H}_2O(l) \rightleftharpoons \mathrm{C}_6H_5\mathrm{NH}_3{}^+(aq) + \mathrm{OH}^-(aq)$

The equilibrium expression is:

$$K_a = \frac{[C_6H_5\mathrm{NH}_3{}^+][\mathrm{OH}^-]}{[C_6H_5\mathrm{NH}_2]} = 4.3 \times 10^{-10}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[C_6H_5NH_2]$	$[C_5H_5NH_3^+]$	$[OH^-]$
Initial concentration (*M*)	0.0784	0	0
Change (*M*)	−*x*	+*x*	+*x*
Equilibrium (*M*)	0.0784 − *x*	*x*	*x*

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that $(0.0784 - x) \approx 0.0784$ gives:

$$\frac{[C_6H_5\mathrm{NH}_3{}^+][\mathrm{OH}^-]}{[C_6H_5\mathrm{NH}_2]} = \frac{(x)(x)}{(0.0784\ -\ x)} \approx \frac{(x)(x)}{0.0784} = 4.3 \times 10^{-10}$$

Solving for x gives $5.81 \times 10^{-6} M$. This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[C_6H_5\mathrm{NH}_2] = [\mathrm{OH}^-] = 5.8 \times 10^{-6} M$

$[C_6H_5NH_2] = 0.0784 - 5.81 \times 10^{-6} = 0.07839 = 0.0784\ M$

$[H_3O^+] = \frac{K_W}{[\mathrm{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.81 \times 10^{-6}} = 1.7 \times 10^{-9}\ M;$

(c) The reaction is $\mathrm{HCN}(aq)\ +\ \mathrm{H}_2O(l) \rightleftharpoons \mathrm{H}_3O^+(aq) + \mathrm{CN}^-(aq)$.

The equilibrium expression is:

$$K_a = \frac{[H_3O^+][\mathrm{CN}^-]}{[\mathrm{HCN}]} = 4.9 \times 10^{-10}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HClO]	$[H_3O^+]$	$[CN^-]$
Initial concentration (*M*)	0.0810	0	0
Change (*M*)	−*x*	+*x*	+*x*
Equilibrium (*M*)	0.0810 − *x*	*x*	*x*

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that $(0.0810 - x) \approx 0.0810$ gives:

$$\frac{[H_3O^+][\mathrm{CN}^-]}{[\mathrm{HCN}]} = \frac{(x)(x)}{(0.0810 - x)} \approx \frac{(x)(x)}{0.0810} = 4 \times 10^{-10}$$

Solving for x gives 6.30×10^{-6} M. This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[H_3O^+] = [\mathrm{CN}^-] = 6.3 \times 10^{-6}\ M$

$[\mathrm{HCN}] = 0.0810 - 6.30 \times 10^{-6} = 0.08099 = 0.0810\ M$

$[\mathrm{OH}^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{6.30 \times 10^{-6}} = 1.6 \times 10^{-9}\ M;$

(d) The reaction is:

$$(\mathrm{CH_3})_3N(aq) + \mathrm{H_2}O(l) \rightleftharpoons (\mathrm{CH_3})_3\mathrm{NH}^+(aq) + \mathrm{OH}^-(aq)$$

The equilibrium expression is:

$$K_b = \frac{[(\mathrm{CH_3})_3\mathrm{NH}^+][\mathrm{OH}^-]}{[(\mathrm{CH_3})_3N]} = 6.3 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[(\mathrm{CH_3})_3\mathrm{N}]$	$[(\mathrm{CH_3})_3\mathrm{NH}^+]$	$[\mathrm{OH}^-]$
Initial concentration (*M*)	0.11	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.11 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that $(0.11 - x) \approx 0.11$ gives:

$$\frac{[(\mathrm{CH_3})_3\mathrm{NH}^+][\mathrm{OH}^-]}{[(\mathrm{CH_3})_3N]} = \frac{(x)(x)}{(0.11 - x)} \approx \frac{(x)(x)}{0.11} = 6.3 \times 10^{-5}$$

Solving for x gives 2.63×10^{-3} M. This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[(\mathrm{CH_3})_3\mathrm{NH}^+] = [\mathrm{OH}^-] = 2.6 \times 10^{-3}\ M$

$[(\mathrm{CH_3})_3\mathrm{N}] = 0.11 - 2.63 \times 10^{-3} = 0.107 = 0.11\ M$

$[H_3O^+] = \frac{K_w}{[\mathrm{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.63 \times 10^{-3}} = 3.8 \times 10^{-12}\ M;$

(e) The reaction is:

$$\mathrm{Fe}(H_2O)_6{}^{2+}(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{Fe}(H_2O)_5(\mathrm{OH})^+(aq) + \mathrm{H_3}O^+(aq)$$

The equilibrium expression is:

$$K_a = \frac{[\mathrm{Fe}(H_2O)_5(\mathrm{OH})^+][H_3O^+]}{[\mathrm{Fe}(H_2O)_6{}^{2+}]} = 1.6 \times 10^{-7}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[\mathrm{Fe(H_2O)_6}^{2+}]$	$[\mathrm{H_3O}^+]$	$[\mathrm{Fe(H_2O)_5(OH)}^+]$
Initial concentration (*M*)	0.120	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.120 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that $(0.120 - x) \approx 0.120$ gives:

$$\frac{[\mathrm{Fe}(H_2O)_5(\mathrm{OH})^+][H_3O^+]}{[\mathrm{Fe}(H_2O)_6{}^{2+}]} = \frac{(x)(x)}{(0.120\ -\ x)} \approx \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$$

Solving for x gives $1.39 \times 10^{-4} M$. This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[\mathrm{Fe}(H_2O)_5(\mathrm{OH})^+] = [H_3O^+] = 1.4 \times 10^{-4}\ M$

$[\mathrm{Fe}(H_2O)_6{}^{2+}] = 0.120 - 1.39 \times 10^{-4} = 0.1199 = 0.120\ M$

$$[\mathrm{OH}^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.39 \times 10^{-4}} = 7.2 \times 10^{-1}\quad M$$

93-6 Propionic acid, $C_2H_5CO_2H$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the pH of a 0.698 M solution of $C_2H_5CO_2H$?

Solution

The reaction is:

$$C_2H_5\mathrm{CO}_2H(aq)\ +\ \mathrm{H}_2O(l) \rightleftharpoons \mathrm{H}_3O^+(aq)\ +\ \mathrm{C}_2H_5\mathrm{CO}_2{}^-(aq)$$

The equilibrium expression is:

$$K_a\ =\ \frac{[C_2H_5\mathrm{CO}_2{}^-][H_3O^+]}{[C_2H_5\mathrm{CO}_2H]}\ =\ 1.34\ \times\ 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[C_2H_5CO_2H]$	$[H_3O^+]$	$[C_2H_5CO_2^-]$
Initial concentration (M)	0.698	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.698 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that $(0.698 - x) \approx 0.698$ gives:

$$\frac{[C_2H_5\mathrm{CO}_2{}^-][H_3O^+]}{[C_2H_5\mathrm{CO}_2H]}\ =\ \frac{(x)(x)}{(0.698\ -\ x)} \approx \frac{(x)(x)}{0.698}\ =\ 1.34\ \times\ 10^{-5}$$

Solving for x gives $3.058 \times 10^{-3}\ M$. Because this value is 5% of 0.698, our assumption is correct. The equilibrium concentration of hydronium ion is therefore:

$[H_3O^+] = 3.058 \times 10^{-3}\ M$

$\mathrm{pH} = -\log(3.058 \times 10^{-3}) = 2.5146 = 2.515$

93-7 The odor of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1 M aqueous solution of this acid.

Solution

$[H_2O] > [CH_3CO_2H] > [H_3O^+] \approx [CH_3CO_2{}^-] > [OH^-]$

93-8 Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1 *M* aqueous solution of this base.

Solution

$[H_2O] > [NH_3] > [NH_4^+] \approx [OH^-] > [H^+]$

93-9 Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

Solution

$$\underset{\text{BB}}{\mathrm{Mg(OH)_2(s)}} + \underset{\text{BA}}{\mathrm{HCl(aq)}} \rightleftharpoons \underset{\text{CB}}{\mathrm{Mg^{2+}(aq)}} + \underset{\text{CA}}{\mathrm{2Cl^-(aq)}} + \mathrm{2H_2O(l)}$$

93-10 What is the ionization constant at 25 °C for the weak acid $(CH_3)_2NH_2^+$, the conjugate acid of the weak base $(CH_3)_2NH$, $K_b = 5.9 \times 10^{-4}$?

Solution

$K_w = K_a \times K_b$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-1}}{5.9 \times 10^{-4}} = 1.7 \times 10^{-11}$$

93-11 Consult the Table of Kb values to determine if CH_3NH_2 or $(CH_3)_2NH$, is the stronger base. Which conjugate acid, $(CH_3)_2NH_2^+$or $CH_3NH_3^+$, is the stronger acid?

Solution

The strongest base or strongest acid is the one with the larger K_b or K_a, respectively. In these two examples, they are $(CH_3)_2NH$ and $CH_3NH_3^+$.

93-12 Consult the tables of ionization constants to determine which is the stronger acid, NH_4^+ or HBrO?

Solution

Look up (Appendix H) K_a for HBrO. Using the value of K_b for NH_3, calculate its K_a. Then compare the values:

$K_a(\mathrm{HBrO}) = 2.8 \times 10^{-9}$

$K_b(NH_3) = 1.8 \times 10^{-5} = \frac{K_w}{K_a}, K_a(NH_4^+) = 5.6 \times 10^{-10}$

93-13 Consult the tables of ionization constants to determine which is the stronger base, $(CH_3)_3N$ or $H_2BO_3^-$.

Solution

Look up (Appendix I) the value of K_b for $(CH_3)_3N$ and the value of K_a for H_3BO_3. From the latter, calculate the value of K_b for $H_2BO_3^-$. Then compare values:

$K_b(CH_3)_3N = 6.3 \times 10^{-5}$

$K_a(H_3BO_3) = 5.4 \times 10^{-10} = \frac{K_w,}{K_b} K_b = \frac{1.0 \times 10^{-14}}{5.4 \times 10^{-10}} = 1.9 \times 10^{-5}$

A comparison shows that the larger K_b is that of triethylamine.

93-14 Both HF and HCN ionize in water to a limited extent. Consider their Ka values to determine which of the conjugate bases, F^- or CN^-, is the stronger base.

Solution

CN^-; HCN is the weaker acid (smaller Ka value), so CN^- is the stronger base.

93-15 The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($–CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of $C_6H_4OH(CO_2H)$.

Solution

$$[H_2O] > [C_6H_4OH(CO_2H)] > [H^+] > [C_6H_4OH(CO_2)^-] \gg [C_6H_4O(CO_2H)^-] > [\mathrm{OH}^-]$$

93-16 Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

Solution

Inversely proportional. The hydronoim ion and hydroxide ion are related by the K_w equilibrium equation

$$K_w = [H^+][\mathrm{OH}^-]$$

from which we see the inverse relation.

93-17 What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid?

Solution

1. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration. 2. Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+.

93-18 Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water?

(a) addition of NaOH
(b) addition of HCl
(c) addition of NH_4Cl

Solution

The equilibrium is:

$$\mathrm{NH_3}(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{NH_4}^+(aq) + \mathrm{OH}^-(aq)$$

(a) The addition of NaOH adds OH^- to the system and, according to LeChâtelier's principle, the equilibrium will shift to the left. Thus, the percent of converted NH_3 will decrease.
(b) The addition of HCl will add H_3O^+ ions, which will then react with the OH^- ions. Thus, the equilibrium will shift to the right, and the percent will increase.
(c) The addition of NH_4Cl adds $\mathrm{NH_4}^+$ ions, shifting the equilibrium to the left. Thus, the percent will decrease.

93-19 Which of the following will increase the percent of HF that is converted to the fluoride ion in water?

- (a) addition of NaOH
- (b) addition of HCl
- (c) addition of NaF

Solution

The equilibrium is:

$$\mathrm{HF}(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{H_3}O^+(aq) + \mathrm{F}^-(aq)$$

(a) The addition of NaOH adds OH^- to the system, which will then react with the H_3O^+ ions. According to LeChâtelier's principle, the equilibrium will shift to the right. Thus, the percent will increase.

(b) The addition of HCl will add H_3O^+ ions. The equilibrium will shift to the left, and the percent will decrease.

(c) The addition of NaF and F^- ions, shifting the equilibrium to the left. Thus, the percent will decrease.

93-20 What is the effect on the concentrations of $\mathrm{NO_2}^-$, HNO_2, and OH^- when the following are added to a solution of KNO_2 in water:

- (a) HCl
- (b) HNO_2
- (c) NaOH
- (d) NaCl
- (e) KNO_2

Solution

(a) Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2, and decreasing the concentration of $\mathrm{NO_2}^-$ ions.

(b) Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of $\mathrm{NO_2}^-$ ions and decreasing the concentration of OH^- ions.

(c) Adding NaOH adds OH^- ions, which shifts the equilibrium to the left, increasing the concentration of $\mathrm{NO_2}^-$ions and decreasing the concentrations of HNO_2.

(d) Adding NaCl has no effect on the concentrations of the ions.

(e) Adding KNO_2 adds $\mathrm{NO_2}^-$ ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.

93-21 What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?

- (a) HCl
- (b) KF
- (c) NaCl
- (d) KOH
- (e) HF

Solution

(a) Adding HCl will add H_3O^+ ions. The equilibrium will shift to the left, increasing the concentration of HF and decreasing the concentration of F^- ions.

(b) Adding KF increases the concentration of F^- ions, and shifts the equilibrium to the left, increasing the concentration of F^- ions, and shifts the equilibrium to the left, increasing the concentration of HF and decreasing the concentration of H_3O^+ ions.
(c) Adding NaCl has no effect on the concentrations of H_3O^+ ions.
(d) Adding KOH adds OH^- ions, which will react with the H_3O^+ ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of F^- ions and decreasing the concentration of HF.
(e) Adding HF increases the HF concentration, and shifts the equilibrium to the right, increasing the H_3O^+ and F^- ion concentrations.

93-22 Why is the hydronium ion concentration in a solution that is 0.10 *M* in HCl and 0.10 *M* in HCOOH determined by the concentration of HCl?

Solution

The equations of the occurring chemical processes are:

$$\mathrm{HCl}(aq) + \mathrm{H_2}O(l) \longrightarrow \mathrm{H_3}O^+(aq) + \mathrm{Cl}^-(aq)$$
$$\mathrm{CH_3COOH}(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{H_3}O^+(aq) + \mathrm{CH_3COO}^-(aq)$$

This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[H_3O^+]$ produced by the stronger acid.

93-23 From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) CH_3CO_2H: $[H_3O^+] = 1.34 \times 10^{-3}$ *M*;
$[\mathrm{CH_3CO_2}^-] = 1.34 \times 10^{-3}$ *M*;
$[CH_3CO_2H] = 9.866 \times 10^{-2}$ *M*;

(b) ClO^-: $[OH^-] = 4.0 \times 10^{-4}$ *M*;
$[HClO] = 2.38 \times 10^{-4}$ *M*;
$[ClO^-] = 0.273$ *M*;

(c) HCO_2H: $[HCO_2H] = 0.524$ *M*;
$[H_3O^+] = 9.8 \times 10^{-3}$ *M*;
$[\mathrm{HCO_2}^-] = 9.8 \times 10^{-3}$ *M*;

(d) $C_6H_5\mathrm{NH_3}^+$: $[C_6H_5\mathrm{NH_3}^+] = 0.233$ *M*;
$[C_6H_5NH_2] = 2.3 \times 10^{-3}$ *M*;
$[H_3O^+] = 2.3 \times 10^{-3}$ *M*

Solution

(a) The reaction is $\mathrm{CH_3CO_2}H(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{H_3}O^+(aq) + \mathrm{CH_3CO_2}^-(aq)$

$$K_a = \frac{[\mathrm{CH_3CO_2}^-][H_3O^+]}{[\mathrm{CH_3CO_2}H]} = \frac{(1.34 \times 10^{-3})(1.34 \times 10^{-3})}{(9.866 \times 10^{-2})} = 1.82 \times 10^{-5};$$

(b) The reaction is $\mathrm{ClO}^-(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{HClO}(aq) + \mathrm{OH}^-(aq)$

$K_b = \frac{[\mathrm{HClO}][\mathrm{OH}^-]}{[\mathrm{ClO}^-]} = \frac{(2.38 \times 10^{-4})(4.0 \times 10^{-4})}{(0.273)} = 3.5 \times 10^{-7}$;

(c) The reaction is $\mathrm{HCO_2}H(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{H_3}O^+(aq) + \mathrm{HCO_2}^-(aq)$

$K_a = \frac{[\mathrm{HCO_2}^-][H_3O^+]}{[\mathrm{HCO_2}H]} = \frac{(9.8 \times 10^{-3})(9.8 \times 10^{-3})}{(0.524)} = 1.8 \times 10^{-4}$;

(d) The reaction is

$$K_a = \frac{[C_6H_5\mathrm{NH_2}][H_3O^+]}{[C_6H_5\mathrm{NH_3}^+]} = \frac{(2.3 \times 10^{-3})(2.3 \times 10^{-3})}{(0.233)} = 2.3 \times 10^{-5}$$

93-24 From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) NH_3: $[OH^-] = 3.1 \times 10^{-3}$ *M*;
$[NH_4^+] = 3.1 \times 10^{-3}$ *M*;
$[NH_3] = 0.533$ *M*;

(b) HNO_2: $[H_3O^+] = 0.011$ *M*;
$[NO_2^-] = 0.0438$ *M*;
$[HNO_2] = 1.07$ *M*;

(c) $(CH_3)_3N$: $[(CH_3)_3N] = 0.25$ *M*;
$[(CH_3)_3NH^+] = 4.3 \times 10^{-3}$ *M*;
$[OH^-] = 3.7 \times 10^{-3}$ *M*;
(d) NH_4^+: $[NH_4^+] = 0.100$ *M*;
$[NH_3] = 7.5 \times 10^{-6}$*M*;
$[H_3O^+] = 7.5 \times 10^{-6}$*M*

Solution

(a) The reaction is $\mathrm{NH_3}(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{OH}^-(aq) + \mathrm{NH_4}^+(aq)$

$K_b = \frac{[\mathrm{NH_4}^+][\mathrm{OH}^-]}{[\mathrm{NH_3}]} = \frac{(3.1 \times 10^{-3})(3.1 \times 10^{-3})}{(0.533)} = 1.8 \times 10^{-5}$;

(b) The reaction is $\mathrm{HNO_2}(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{H_3}O^+(aq) + \mathrm{NO_2}^-(aq)$

$K_a = \frac{[\mathrm{NO_2}^-][H_3O^+]}{[\mathrm{HNO_2}]} = \frac{(0.0438)(0.011)}{(1.07)} = 4.5 \times 10^{-4}$;

(c) The reaction is $(\mathrm{CH_3})_3N(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{OH}^-(aq) + (\mathrm{CH_3})_3\mathrm{NH}^+(aq)$

$K_b = \frac{[(\mathrm{CH_3})_3\mathrm{NH}^+][\mathrm{OH}^-]}{[(\mathrm{CH_3})_3N]} = \frac{(3.7 \times 10^{-3})(4.3 \times 10^{-3})}{(0.25)} = 6.4 \times 10^{-5}$;

(d) The reaction is $\mathrm{NH_4}^+(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{H_3}O^+(aq) + \mathrm{NH_3}(aq)$

$$K_a = \frac{[\mathrm{NH_3}][H_3O^+]}{[\mathrm{NH_4}^+]} = \frac{(7.5 \times 10^{-6})(7.5 \times 10^{-6})}{(0.100)} = 5.6 \times 10^{-1}$$

93-25 Determine K_b for the nitrite ion, NO_2^-. In a 0.10 *M* solution this base is 0.0015% ionized.

Solution

The reaction is $\mathrm{NO_2}^-(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{HNO_2}(aq) + \mathrm{OH}^-(aq)$.

The concentrations at equilibrium are $[HNO_2^+] = [OH^-] = (1.5 \times 10^{-5})(0.10\ M) = 1.5 \times 10^{-6}\ M$.

$[NH_3] = 0.10\ M - 1.5 \times 10^{-5}\ M = 0.10\ M$

$$K_b = \frac{[\mathrm{HNO_2}][\mathrm{OH}^-]}{[\mathrm{NH_3}]} = \frac{(1.5 \times 10^{-6})(1.5 \times 10^{-6})}{(0.10)} = 2.3 \times 10^{-11}$$

93-26 Determine K_a for hydrogen sulfate ion, HSO_4^-. In a 0.10-*M* solution the acid is 29% ionized.

Solution

The reaction is $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$.

The concentrations at equilibrium are:

$[H_3O^+] = [SO_4^{2-}] = (0.29)(0.10\ M) = 0.029\ M$

$[HSO_4^-] = 0.10\ M - 0.029\ M = 0.071\ M$

$$K_a = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = \frac{(0.029)(0.029)}{(0.071)} = 1.2 \times 10^{-2}$$

93-27 Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

(a) F^-
(b) NH_4^+
(c) AsO_4^{3-}
(d) $(CH_3)_2NH_2^+$
(e) NO_2^-
(f) $HC_2O_4^-$ (as a base)

Solution

(a) The fluoride ion reacts with water as a base in the following way:

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

An expression for the equilibrium is written in the usual way:

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

This expression is related to the ionization of HF:

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.4 \times 10^{-4}$$

Inspection of the expressions for K_b and for K_a indicates an inverse relationship between K_a and K_b with the substitution of $[H_3O^+] = \frac{K_w}{[OH^-]}$ in the expression for $K_aK_b = \frac{[HF][OH^-]}{[F^-]} = \frac{\frac{K_w}{[H_3O^+]} \times [HF]}{[F^-]} = \frac{K_w[HF]}{[F^-][H_3O^+]}$

$$K_b = K_w \times \frac{1}{K_a} = \frac{K_w}{K_a}$$

This final relationship turns out to be the general form for the reaction of an ion from either a weak acid or a weak base.

For the F^- ion:

$K_b = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-4}} = 1.6 \times 10^{-11}$;

(b) This ion is the conjugate acid of the weak base ammonia. Reaction of NH_4^+ gives:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{K_w}{K_b(NH_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$;

(c) $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-1}} = 3.3 \times 10^{-3}$;

(d) $K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-4}} = 1.7 \times 10^{-11}$;

(e) $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = 2.2 \times 10^{-1}$;

(f) $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.0 \times 10^{-2}} = 1.7 \times 10^{-13}$

93-28 Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

(a) HTe^- (as a base)
(b) $(CH_3)_3NH^+$
(c) $HAsO_4{}^{2-}$ (as a base)
(d) $HO_2{}^-$ (as a base)
(e) $C_6H_5NH_3{}^+$
(f) $HSO_3{}^-$ (as a base)

Solution

(a) $K_b = \frac{K_w}{K_a} = \frac{(1.00 \times 10^{-14})}{2.3 \times 10^{-3}} = 4.3 \times 10^{-12}$;

(b) $K_a = \frac{K_w}{K_b} = \frac{(1.00 \times 10^{-1}\ )}{6.3 \times 10^{-5}} = 1.6 \times 10^{-10}$;

(c) $K_b = \frac{K_w}{K_a} = \frac{(1.00 \times 10^{-14})}{1.7 \times 10^{-7}} = 5.9 \times 10^{-8}$;

(d) $K_b = \frac{K_w}{K_a} = \frac{(1.00 \times 10^{-14})}{2.4 \times 10^{-12}} = 4.2 \times 10^{-3}$;

(e) $K_a = \frac{K_w}{K_b} = \frac{(1.00 \times 10^{-14})}{4.3 \times 10^{-10}} = 2.3 \times 10^{-5}$;

(f) $K_b = \frac{K_w}{K_a} = \frac{(1.00 \times 10^{-14})}{1.6 \times 10^{-2}} = 6.3 \times 10^{-13}$

93-29 Using the K_a values in Appendix H, place $Al(H_2O)_6{}^{3+}$ in the correct location in Figure 90-2.

Solution

The reaction is:

$$Al(H_2O)_6{}^{3+}(aq) + H_2O(l) \rightleftharpoons Al(H_2O)_5OH^{2+}(aq) + H_3O^+(aq) \qquad K_a = 1.4 \times 10^{-5}$$

This is a comparatively weak acid. It lies between hydrofluoric acid at $K_a \sim 10^{-4}$ and carbonic acid at $K_a \sim 10^{-6}$.

93-30 White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3, what is the pH?

Solution

First, find the mass of acetic acid. d = 1.007 g/cm^3. Take 1.0 L of solution to have the quantities on a mole basis. Then, since 1000 cm^3 = 1.0 L, 1000 cm^3 × 1.007 g/cm^3 = 1007 g in 1.0 L. Then, 5.00% of this is the mass of acetic acid:

$$\text{Mass (acetic acid)} = 1007\text{ g} \times \frac{5.0\%}{100\%} = 50.35\text{ g}$$

Now calculate the number of moles of acetic acid present. Themolar mass of acetic acid is 60.053 g/mol:

$$\text{mol acetic acid} = \frac{50.35\ \boxed{g}}{60.053\ \boxed{g}\ \text{mol}^{-1}} = 0.838\ \text{mol}$$

From the moles of acetic acid and K_a, calculate $[H_3O^+]$:

$$K_a = 1.8 \times 10^{-5} = \frac{[\mathrm{CH_3CO_2}^-][H_3O^+]}{[\mathrm{CH_3CO_2}H]}$$

	$[CH_3CO_2H]$	$[H_3O^+]$	$[CH_3CO_2^-]$
Initial concentration (*M*)	0.838	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.838 - x$	x	x

Substitution gives:

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.838 - x}$$

Drop x because it is small in comparison with 0.838 *M*.
$x^2 = 0.838(1.8 \times 10^{-5}) = (1.508 \times 10^{-5})^{1/2} = 3.88 \times 10^{-3}\ M$
$\text{pH} = -\log(3.88 \times 10^{-3}) = 2.41$

93-31 The ionization constant of lactic acid, $CH_3CH(OH)CO_2H$, an acid found in the blood after strenuous exercise, is 1.36×10^{-4}. If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

Solution

$$\mathrm{CH_3CHOHCO_2}H(aq) + \mathrm{H_2}O(l) \rightleftharpoons \mathrm{H_3}O^+(aq) + \mathrm{CH_3CHOHCO_2}^-(aq)$$

$$M\ \mathrm{CH_3CHOHCO_2H} = 20.0\ \boxed{g} \times \frac{1\ \text{mol}}{90.0788\ \boxed{g}} = \frac{0.2220\ \text{mol}}{1.00\ \text{L}} = 0.2220\ M\ \mathrm{CH_3CHOHCO_2}H$$

	$[CH_3CHOHCO_2H]$	$[H_3O^+]$	$[CH_3CHOHC_2^-]$
Initial concentration (*M*)	0.2220	~0	~0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.2220 - x$	x	x

At equilibrium:

$$\frac{[H_3O^+][\mathrm{CH_3CHOHCO_2}^-]}{[\mathrm{CH_3CHOHCO_2}H]} = 1.36 \times 10^{-4} = K_a$$

$$\frac{(x)(x)}{(0.2220 - x)} = 4.5 \times 10^{-4}$$

Assume that x is small:

$$\frac{(x)(x)}{(0.2220)} = 1.36 \times 10^{-4}$$

$x^2 = (0.2220) \times 1.36 \times 10^{-4} = 3.02 \times 10^{-5}$
$x = [H_3O^+] = 0.00549$
To check our assumption:

$$\frac{0.00549}{0.2220} = 0.0248\ (2.48\%)$$

Another approximation is not needed.

93-32 Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons ($K_{b1} = 7 \times 10^{-7}$, $K_{b2} = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050-M solution of nicotine?

Solution

$$C_{10}H_{14}N_2(aq) + H_2O(l) \rightleftharpoons C_{10}H_{14}N_2H^+(aq) + OH^-(aq) \qquad (K_{b1} = 7 \times 10^{-7})$$

$$C_{10}H_{14}N_2H^+(aq) + H_2O(l) \rightleftharpoons C_{10}H_{14}N_2{H_2}^{2+}(aq) + OH^-(aq) \qquad (K_{b2} = 1.4 \times 10^{-11})$$

First set up a concentration table:

	$[C_{10}H_{14}N_2]$	$[C_{10}H_{14}N_2H^+]$	$[OH^-]$
Initial concentration (*M*)	0.050	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.050 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium equation and making the assumption that $(0.050 - x) = 0.050$, we get:

$$K_{b1} = \frac{[C_{10}H_{14}N_2H^+][OH^-]}{[C_{10}H_{14}N_2]} = 7 \times 10^{-7}$$

$$= \frac{(x)(x)}{(0.050 - x)} = \frac{x^2}{0.050} = 7 \times 10^{-7}$$

Solving for x gives$1.87 \times 10^{-4} = 2 \times 10^{-4} M = [OH^-]$

Because x is less than 5% of 0.050 and $[OH^-]$ is greater than $4.5 \times 10^{-7} M$, our customary assumptions are justified. We can calculate $[C_{10}H_{14}N_2] = 0.050 - x = 0.050 - 2 \times 10^{-4} = 0.048\ M$; $[OH^-] = [C_{10}H_{14}N_2H^+] = x = 2 \times 10^{-4} M$. Now calculate the concentration of $C_{10}H_2N_2{H_2}^{2+}$in a solution with $[OH^-]$ and $[C_{10}H_2N_2{H_2}^{2+}]$ equal to $2 \times 10^{-4}\ M$. The equilibrium between these species is $C_{10}H_{14}N_2H^+(aq) + H_2O(l) \leftrightarrows C_{10}H_{14}N_2{H_2}^{2+}(aq) + OH^-(aq)$. We know $[C_{10}H_{14}N_2H^+]$ and $[OH^-]$, so we can calculate the concentration of $C_{10}H_2N_2{H_2}^{2+}$ from the equilibrium expression:

$$K_{b2} = \frac{[C_{10}H_{14}N_2{H_2}^{2+}][OH^-]}{[C_{10}H_{14}N_2H^+]} = 1.4 \times 10^{-11}$$

$$= \frac{[C_{10}H_{14}N_2{H_2}^{2+}][2 \times 10^{-4}]}{[2 \times 10^{-4}]}$$

$$[C_{10}H_{14}N_2{H_2}^{2+}] = 1.4 \times 10^{-11}\ M$$

The concentration of OH^- produced in this ionization is equal to the concentration of$C_{10}H_2N_2{H_2}^{2+}$, $1.4 \times 10^{-11} M$, which is much smaller than the $2 \times 10^{-4} M$ produced in the first ionization; therefore, we are justified in neglecting the OH^- formed from $C_{10}H_{14}N_2H^+$.

We can now calculate the concentration of H_3O^+ present from the ionization of water:

$K_a = 1 \times 10^{-14} = [H_3O^+]\ [OH^-]$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{[OH^-]} = \frac{1 \times 10^{-14}}{1.9 \times 10^{-4}} = 5.3 \times 10^{-11}\ M$$

We can now summarize the concentrations of all species in solution as follows:

$[C_{10}H_{14}N_2] = 0.049\ M$
$[C_{10}H_{14}N_2H^+] = 1.9 \times 10^{-4}\ M$
$$[C_{10}H_{14}N_2H_2{}^{2+}] = 1.4 \times 10^{-11}\ M$$
$[OH^-] = 1.9 \times 10^{-4}\ M$
$[H_3O^+] = 5.3 \times 10^{-11}\ M$

93-33 The pH of a 0.23 *M* solution of HF is 1.92. Determine K_a for HF from these data.

Solution

The reaction is:

$$\text{HF}(aq)\ +\ \text{H}_2O(l) \rightleftharpoons \text{H}_3O^+(aq)\ +\ \text{F}^-(aq)$$

The concentrations at equilibrium are:
$[F^-] = [H_3O^+] = 10^{-\text{pH}} = 10^{-1.92} = 0.0120\ M$
$[\text{HF}] = 0.23\ M - 0.0120\ M = 0.218\ M$

$$K_a = \frac{[F^-][H_3O^+]}{[\text{HF}]} = \frac{(0.0120)(0.0120)}{(0.218)} = 6.6\ \times\ 10^{-4}$$

93-34 The pH of a 0.10-*M* solution of caffeine is 11.70. Determine K_b for caffeine from these data:

$$C_8H_{10}N_4O_2(aq) + \text{H}_2O(l)\ \leftleftarrows\ \text{C}_8H_{10}N_4O_2H^+(aq) + \text{OH}^-(aq)$$

Solution

The pOH can be determined from pOH = 14.00 – pH = 14.00 – 11.70 = 2.30. Therefore, the concentrations at equilibrium are:
$[C_8H_{10}N_4O_2H^+] = [OH^-] = 10^{-\text{pOH}} = 10^{-2.30} = 0.00501\ M$
$[C_8H_{10}N_4O_2] = 0.10 - 0.00501 = 0.095\ M$

$$K_b\ =\ \frac{[C_8H_{10}N_4O_2H^+][\text{OH}^-]}{[C_8H_{10}N_4O_2]}\ =\ \frac{(0.00501)(0.00501)}{(0.095)}\ =\ 2.6\ \times\ 10^{-4}$$

93-35 The pH of a solution of household ammonia, a 0.950 *M* solution of NH_3, is 11.612. Determine K_b for NH_3 from these data.

Solution

The reaction is $\text{NH}_3(aq) + \text{H}_2O(l) \rightleftharpoons \text{NH}_4{}^+(aq) + \text{OH}^-(aq)$.
The pOH can be determined from pOH = 14.000 – pH = 14.000 – 11.612 = 2.388. Therefore, the concentrations at equilibrium are $[\text{NH}_4{}^+] = [OH^-] = 10^{-\text{pOH}} = 10^{-2.388} = 0.004093\ M$
$[NH_3] = 0.950 - 0.004093 = 0.9459\ M$

$$K_b = \frac{[\text{NH}_4{}^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.004093)(0.004093)}{(0.9459)} = 1.77 \times 10^{-5}$$

Unit 94 – Relative Strengths of Acids and Bases: Effect of Molecular Structure

94-1 Use this list of important industrial compounds (and Figure 93-2) to answer the following questions regarding: $Ca(OH)_2$, CH_3CO_2H, HCl, H_2CO_3, HF, HNO_2, HNO_3, H_3PO_4, H_2SO_4, NH_3, NaOH, Na_2CO_3.

(a) Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.
(b) Identify the compounds that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.
(c) Identify the compounds that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.

Solution
(a) strong Brønsted-Lowry acids: HCl, HNO_3, H_3PO_4, H_2SO_4; strong Brønsted-Lowry bases: $Ca(OH)_2$, NaOH; (b) CH_3CO_2H, H_2CO_3, HF, HNO_2; (c) NH_3, Na_2CO_3

94-2 Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3.
Solution
The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3.

94-3 Explain why HI is a stronger acid than HF.

Solution
The radius of I is larger than the radius of F. This is why the H-I bond is weaker than the H-F bond, HI is easier to break than HF, and the Ka for HI is greater

94-4 Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

(a) H_2O or HF
(b) $B(OH)_3$ or $Al(OH)_3$
(c) HSO_3^- or HSO_4^-
(d) NH_3 or H_2S
(e) H_2O or H_2Te

Solution
(a) HF; F is more electronegative than O.

(b) $B(OH)_3$; B is more electronegative than Al. Accordingly $Al(OH)_3$ is more basic than $B(OH)_3$.
(c) HSO_4^-; S has a +6 oxidation state in HSO_4^-, but a +4 oxidation state in HSO_3^-. Increasing the oxidation state of the central element in oxyacids increases acidity.
(d) H_2S; NH_3 is a weak base and H_2S is a very weak acid. Therefore, NH_3 as an acid is weaker than H_2S.
(e) H_2Te; Te is below O in group 16. Heavier members in acid-forming groups make stronger acids than lighter members of those groups.

94-5 Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

(a) HSO_4^- or $HSeO_4^-$
(b) NH_3 or H_2O
(c) PH_3 or HI
(d) NH_3 or PH_3
(e) H_2S or HBr

Solution

(a) HSO_4^-; higher electronegativity of the central ion.
(b) H_2O; NH_3 is a base and water is neutral, or decide on the basis of K_a values.
(c) HI; PH_3 is weaker than HCl; HCl is weaker than HI. Thus, PH_3 is weaker than HI.
(d) PH_3; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group.
(e) HBr; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S, so HBr is the stronger acid.

94-6 Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: HCl, HBr, HI
(b) basicity: H_2O, OH^-, H^-, Cl^-
(c) basicity: $Mg(OH)_2$, $Si(OH)_4$, $ClO_3(OH)$ (Hint: Formula could also be written as $HClO_4$.)
(d) acidity: HF, H_2O, NH_3, CH_4

Solution

(a) HCl < HBr < HI; H-X bond energy decreases going down a group. This consideration is more significant than the decrease in electronegativity.
(b) $Cl^- < H_2O < OH^- < H^-$; Cl^- has no tendency to basic action; water forms OH^- in a very low concentration; OH^- is very basic; and H^- is even more willing to donate a pair of electrons.
(c) $ClO_3(OH) < Si(OH)_4 < Mg(OH)_2$; the more nonmetallic the central atom, the more acidic the substance. As a result, base strength increases in the opposite direction.
(d) $CH_4 < NH_3 < H_2O < HF$; this series can be envisioned in terms of increasing electronegativity of the atom attached to hydrogen. The greater the electronegativity, the stronger a binary acid in the same period of the periodic table.

94-7 Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: $NaHSO_3$, $NaHSeO_3$, $NaHSO_4$
(b) basicity: BrO_2^-, ClO_2^-, IO_2^-

(c) acidity: HOCl, HOBr, HOI
(d) acidity: HOCl, HOClO, $HOClO_2$, $HOClO_3$
(e) basicity: NH_2^-, HS^-, HTe^-, PH_2^-
(f) basicity: BrO^-, BrO_2^-, BrO_3^-, BrO_4^-

Solution

(a) $NaHSeO_3 < NaHSO_3 < NaHSO_4$; in polyoxy acids, the more electronegative central element—S, in this case—forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner.
(b) $ClO_2^- < BrO_2^- < IO_2^-$; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three.
(c) HOI < HOBr < HOCl; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three.
(d) $HOCl < HOClO < HOClO_2 < HOClO_3$; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases).
(e) $HTe^- < HS^- << PH_2^- < NH_2^-$; PH_2^- and NH_2^- are anions of weak bases, so they act as strong bases toward H^+. HTe^- and HS^- are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion.
(f) $BrO_4^- < BrO_3^- < BrO_2^- < BrO^-$; with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.