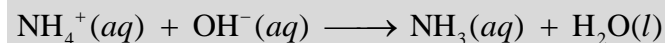


Chemistry 2e
14: Acid-Base Equilibria
14.1: Brønsted-Lowry Acids and Bases

1. Write equations that show NH_3 as both a conjugate acid and a conjugate base.

Solution

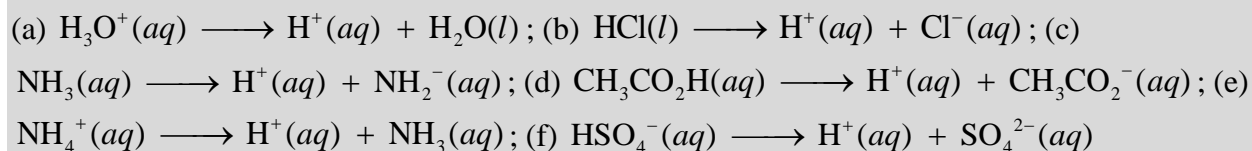
One example for NH_3 as a conjugate acid: $\text{NH}_2^- + \text{H}^+ \longrightarrow \text{NH}_3$; as a conjugate base:



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) NH_3
- (d) $\text{CH}_3\text{CO}_2\text{H}$
- (e) NH_4^+
- (f) HSO_4^-

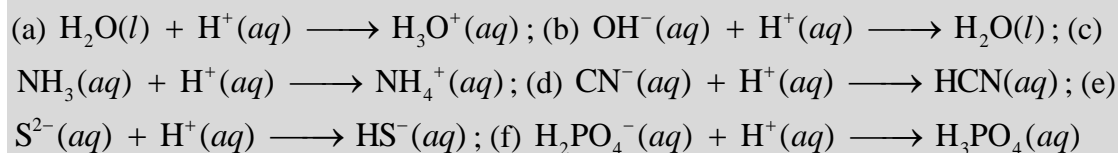
Solution



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



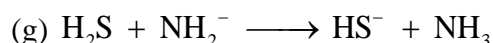
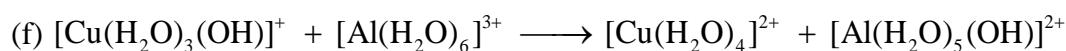
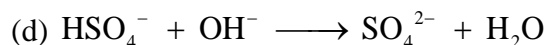
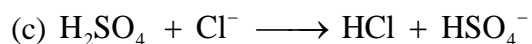
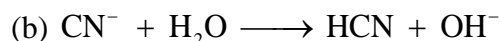
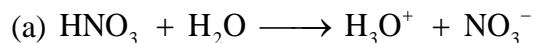
7. What is the conjugate acid of each of the following? What is the conjugate base of each?

- (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) $\text{H}_6\text{N}_2^{2+}$, H_4N_2

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:



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) $[\text{Cu}(\text{H}_2\text{O})_3(\text{OH})]^+$ (BB), $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (BA), $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ (CA), $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ (CB); (g) H_2S (BA), NH_2^- (BB), HS^- (CB), NH_3 (CA)

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: $\text{H}_2\text{O}(aq) + \text{NH}_3(aq) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$.

As a base: $\text{H}_2\text{O}(aq) + \text{HCl}(aq) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)$

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^-

(c) Br^-

(d) NH_4^+

(e) AsO_4^{3-}

Solution

(a) $\text{NH}_3 + \text{H}_3\text{O}^+ \longrightarrow \text{NH}_4\text{OH} + \text{H}_2\text{O}$, $\text{NH}_3 + \text{OCH}_3^- \longrightarrow \text{NH}_2^- + \text{CH}_3\text{OH}$; (b)

$\text{HPO}_4^{2-} + \text{OH}^- \longrightarrow \text{PO}_4^{3-} + \text{H}_2\text{O}$, $\text{HPO}_4^{2-} + \text{HClO}_4 \longrightarrow \text{H}_2\text{PO}_4^- + \text{ClO}_4^-$;

not amphiprotic: (c) Br^- ; (d) NH_4^+ ; (e) AsO_4^{3-}

Chemistry 2e
14: Acid-Base Equilibria
14.2: pH and pOH

15. Explain why a sample of pure water at 40 °C is neutral even though $[\text{H}_3\text{O}^+] = 1.7 \times 10^{-7} \text{ M}$. K_w is 2.910×10^{-14} at 40 °C.

Solution

In a neutral solution $[\text{H}_3\text{O}^+] = [\text{OH}^-]$. At 40 °C,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = (2.910 \times 10^{-14})^{1/2} = 1.7 \times 10^{-7}.$$

17. The ionization constant for water (K_w) is 9.311×10^{-14} at 60 °C. Calculate $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH, and pOH for pure water at 60 °C.

Solution

For water, $[\text{H}_3\text{O}^+] = [\text{OH}^-] = x$.

$$K_w = 9.311 \times 10^{-14} = x^2$$

$$x = 3.051 \times 10^{-7} \text{ M} = [\text{H}_3\text{O}^+] = [\text{OH}^-]$$

$$\text{pH} = -\log 3.051 \times 10^{-7} = -(-6.5156) = 6.5156$$

$$\text{pOH} = 14 - \text{pH} = 6.5156$$

19. 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 $\text{Ba}(\text{OH})_2$

(d) 2.5 M KOH

Solution

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

21. What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

Solution

$$[\text{H}_3\text{O}^+] = 10^{-6.52} = 3.0 \times 10^{-7} \text{ M}; \text{pOH} = 14.00 - \text{pH}; \text{pOH} = 14.00 - 6.52 = 7.48; [\text{OH}^-] = 10^{-7.48} = 3.3 \times 10^{-8} \text{ M}$$

23. Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure 14.2 for useful information.

Solution

From Figure 14.2 the pH of lime juice is equal to 2. The hydronium ion concentration is $\text{pH} = 2 = -\log[\text{H}_3\text{O}^+]$; $[\text{H}_3\text{O}^+] = 1 \times 10^{-2} \text{ M}$; $\text{pH} + \text{pOH} = 14$; $\text{pOH} = 14 - 2 = 12$; $[\text{OH}^-] = 1 \times 10^{-12} \text{ M}$

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

Solution

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}; [\text{H}_3\text{O}^+][3.2 \times 10^{-3}] = 1.0 \times 10^{-14};$$

$$[\text{OH}^-] = \frac{1.00 \times 10^{-14}}{3.2 \times 10^{-3}} = 3.1 \times 10^{-12} \text{ M}$$

Chemistry 2e
14: Acid-Base Equilibria
14.3: Relative Strengths of Acids and Bases

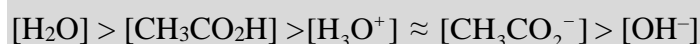
27. Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

Solution

The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms OH^- , which causes the solution to be basic. An example is NaCN. The CN^- reacts with water as follows: $\text{CN}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq)$

29. The odor of vinegar is due to the presence of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, 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



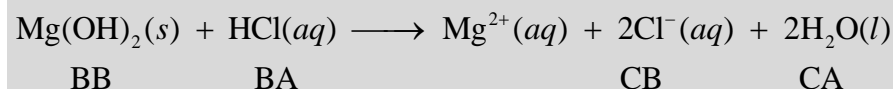
31. Explain why the ionization constant, K_a , for H_2SO_4 is larger than the ionization constant for H_2SO_3 .

Solution

The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3 .

33. Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $\text{Mg}(\text{OH})_2$ 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



35. What is the ionization constant at 25 °C for the weak acid CH_3NH_3^+ , the conjugate acid of the weak base CH_3NH_2 , $K_b = 4.4 \times 10^{-4}$.

Solution

$$K_w = K_a \times K_b$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.3 \times 10^{-11}$$

37. Which base, CH_3NH_2 or $(\text{CH}_3)_2\text{NH}$, is the strongest base? Which conjugate acid, $(\text{CH}_3)_2\text{NH}_2^+$ or CH_3NH_3^+ , is the strongest 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 $(\text{CH}_3)_2\text{NH}$ and CH_3NH_3^+ .

39. Which is the stronger base, $(\text{CH}_3)_3\text{N}$ or H_2BO_3^- ?

Solution

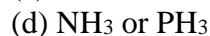
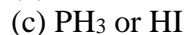
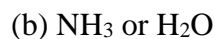
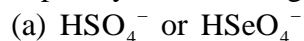
Look up (Appendix I) the value of K_b for $(\text{CH}_3)_3\text{N}$ and the value of K_a for H_3BO_3 . From the latter, calculate the value of K_b for H_2BO_3^- . Then compare values:

$$K_b(\text{CH}_3)_3\text{N} = 6.3 \times 10^{-5}$$

$$K_a(\text{H}_3\text{BO}_3) = 5.4 \times 10^{-10} = \frac{K_w}{K_b}, K_b = \frac{1.0 \times 10^{-14}}{5.4 \times 10^{-10}} = 1.9 \times 10^{-5}$$

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

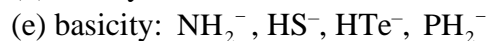
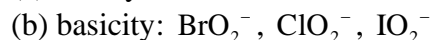
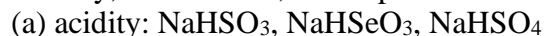
41. Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.



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.

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



Solution

(a) $\text{NaHSeO}_3 < \text{NaHSO}_3 < \text{NaHSO}_4$; 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)

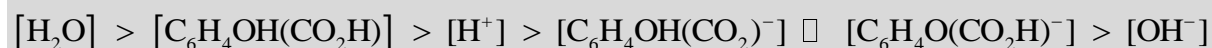
$\text{ClO}_2^- < \text{BrO}_2^- < \text{IO}_2^-$; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (c) $\text{HOI} < \text{HOBr} < \text{HOCl}$; 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) $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$; 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)

$\text{HTe}^- < \text{HS}^- \ll \text{PH}_2^- < \text{NH}_2^-$; 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) $\text{BrO}_4^- < \text{BrO}_3^- < \text{BrO}_2^- < \text{BrO}^-$; 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.

45. 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



47. 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^+ .

48. 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:



(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 NH_4^+ ions, shifting the equilibrium to the left. Thus, the percent will decrease.

50. What is the effect on the concentrations of 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

Solution

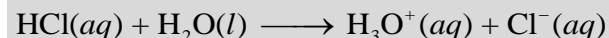
(a) Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2 , and decreasing the concentration of NO_2^- ions. (b) Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of 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 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 NO_2^- ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.

52. 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:



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 $[\text{H}_3\text{O}^+]$ produced by the stronger acid.

54. 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 : $[\text{OH}^-] = 3.1 \times 10^{-3}\text{ M}$;

$[\text{NH}_4^+] = 3.1 \times 10^{-3}\text{ M}$;

$[\text{NH}_3] = 0.533\text{ M}$;

(b) HNO_2 : $[\text{H}_3\text{O}^+] = 0.011\text{ M}$;

$[\text{NO}_2^-] = 0.0438\text{ M}$;

$[\text{HNO}_2] = 1.07\text{ M}$;

(c) $(\text{CH}_3)_3\text{N}$: $[(\text{CH}_3)_3\text{N}] = 0.25\text{ M}$;

$[(\text{CH}_3)_3\text{NH}^+] = 4.3 \times 10^{-3}\text{ M}$;

$[\text{OH}^-] = 3.7 \times 10^{-3}\text{ M}$;

(d) NH_4^+ : $[\text{NH}_4^+] = 0.100\text{ M}$;

$[\text{NH}_3] = 7.5 \times 10^{-6}\text{ M}$;

$[\text{H}_3\text{O}^+] = 7.5 \times 10^{-6}\text{ M}$

Solution

(a) The reaction is $\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{NH}_4^+(aq)$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(3.1 \times 10^{-3})(3.1 \times 10^{-3})}{(0.533)} = 1.8 \times 10^{-5};$$

(b) The reaction is $\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NO}_2^-(aq)$

$$K_a = \frac{[\text{NO}_2^-][\text{H}_3\text{O}^+]}{[\text{HNO}_2]} = \frac{(0.0438)(0.011)}{(1.07)} = 4.5 \times 10^{-4};$$

(c) The reaction is $(\text{CH}_3)_3\text{N}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + (\text{CH}_3)_3\text{NH}^+(aq)$

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

(d) The reaction is $\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NH}_3(aq)$

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{(7.5 \times 10^{-6})(7.5 \times 10^{-6})}{(0.100)} = 5.6 \times 10^{-10}$$

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

Solution

The reaction is $\text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{SO}_4^{2-}(aq)$.

The concentrations at equilibrium are:

$$[\text{H}_3\text{O}^+] = [\text{SO}_4^{2-}] = (0.29)(0.10 \text{ M}) = 0.029 \text{ M}$$

$$[\text{HSO}_4^-] = 0.10 \text{ M} - 0.029 \text{ M} = 0.071 \text{ M}$$

$$K_a = \frac{[\text{SO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_4^-]} = \frac{(0.029)(0.029)}{(0.071)} = 1.2 \times 10^{-2}$$

58. 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) $(\text{CH}_3)_3\text{NH}^+$

(c) HAsO_4^{2-} (as a base)

(d) HO_2^- (as a base)

(e) $\text{C}_6\text{H}_5\text{NH}_3^+$

(f) HSO_3^- (as a base)

Solution

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

$$(b) K_a = \frac{K_w}{K_b} = \frac{(1.00 \times 10^{-14})}{6.3 \times 10^{-5}} = 1.6 \times 10^{-10};$$

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

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

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

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

60. 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 C₆H₅NH₂, a weak base
 (c) 0.0810 M HCN, a weak acid
 (d) 0.11 M (CH₃)₃N, a weak base
 (e) 0.120 M Fe(H₂O)₆²⁺ a weak acid, $K_a = 1.6 \times 10^{-7}$

Solution

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

The equilibrium expression is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} = 2.9 \times 10^{-8}$$

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

	[HClO]	[H ₃ O ⁺]	[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:

$$\frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} = \frac{(x)(x)}{(0.0092 - x)} \approx \frac{(x)(x)}{0.0092} = 2.9 \times 10^{-8}$$

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:

$$[\text{H}_3\text{O}^+] = [\text{ClO}^-] = 1.6 \times 10^{-5}M$$

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

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.63 \times 10^{-5}} = 6.1 \times 10^{-10} M ;$$

(b) The reaction is: $\text{C}_6\text{H}_5\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(aq) + \text{OH}^-(aq)$

The equilibrium expression is:

$$K_a = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = 4.3 \times 10^{-10}$$

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

	$[\text{C}_6\text{H}_5\text{NH}_2]$	$[\text{C}_6\text{H}_5\text{NH}_3^+]$	$[\text{OH}^-]$
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:

$$\frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{(x)(x)}{(0.0784 - x)} \approx \frac{(x)(x)}{0.0784} = 4.3 \times 10^{-10}$$

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:

$$[\text{C}_6\text{H}_5\text{NH}_2] = [\text{OH}^-] = 5.8 \times 10^{-6} M$$

$$[\text{C}_6\text{H}_5\text{NH}_2] = 0.0784 - 5.81 \times 10^{-6} = 0.07839 = 0.0784 M$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.81 \times 10^{-6}} = 1.7 \times 10^{-9} M ;$$

(c) The reaction is $\text{HCN}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq)$.

The equilibrium expression is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = 4.9 \times 10^{-10}$$

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

	$[\text{HCN}]$	$[\text{H}_3\text{O}^+]$	$[\text{CN}^-]$
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:

$$\frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{(x)(x)}{(0.0810 - x)} \approx \frac{(x)(x)}{0.0810} = 4.9 \times 10^{-10}$$

Solving for x gives $6.30 \times 10^{-6} M$. 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:

$$[\text{H}_3\text{O}^+] = [\text{CN}^-] = 6.3 \times 10^{-6} M$$

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

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{6.30 \times 10^{-6}} = 1.6 \times 10^{-9} M ;$$

(d) The reaction is:



The equilibrium expression is:

$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = 6.3 \times 10^{-5}$$

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

	$[(\text{CH}_3)_3\text{N}]$	$[(\text{CH}_3)_3\text{NH}^+]$	$[\text{OH}^-]$
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:

$$\frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = \frac{(x)(x)}{(0.11 - x)} \approx \frac{(x)(x)}{0.11} = 6.3 \times 10^{-5}$$

Solving for x gives $2.63 \times 10^{-3} M$. 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:

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

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

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.63 \times 10^{-3}} = 3.8 \times 10^{-12} M ;$$

(e) The reaction is:



The equilibrium expression is:

$$K_a = \frac{[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^+][\text{H}_3\text{O}^+]}{[\text{Fe}(\text{H}_2\text{O})_6^{2+}]} = 1.6 \times 10^{-7}$$

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

	$[\text{Fe}(\text{H}_2\text{O})_6^{2+}]$	$[\text{H}_3\text{O}^+]$	$[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^+]$
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:

$$\frac{[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^+][\text{H}_3\text{O}^+]}{[\text{Fe}(\text{H}_2\text{O})_6^{2+}]} = \frac{(x)(x)}{(0.120 - x)} \approx \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$$

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:

$$[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^+] = [\text{H}_3\text{O}^+] = 1.4 \times 10^{-4} M$$

$$[\text{Fe}(\text{H}_2\text{O})_6^{2+}] = 0.120 - 1.39 \times 10^{-4} = 0.1199 = 0.120 M$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.39 \times 10^{-4}} = 7.2 \times 10^{-11} \text{ M}$$

62. White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm³, what is the pH?

Solution

First, find the mass of acetic acid. $d = 1.007 \text{ g/cm}^3$. Take 1.0 L of solution to have the quantities on a mole basis. Then, since $1000 \text{ cm}^3 = 1.0 \text{ L}$, $1000 \text{ cm}^3 \times 1.007 \text{ g/cm}^3 = 1007 \text{ g}$ 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. The molar mass of acetic acid is 60.053 g/mol:

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

From the moles of acetic acid and K_a , calculate $[\text{H}_3\text{O}^+]$:

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

	$[\text{CH}_3\text{CO}_2\text{H}]$	$[\text{H}_3\text{O}^+]$	$[\text{CH}_3\text{CO}_2^-]$
Initial concentration (M)	0.838	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.838 - x	x	x

Substitution gives:

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

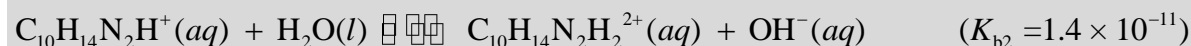
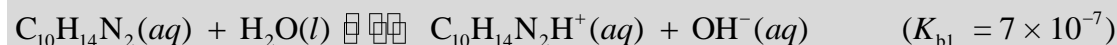
Drop x because it is small in comparison with 0.838 M.

$$x^2 = 0.838(1.8 \times 10^{-5}) = (1.508 \times 10^{-5})^{1/2} = 3.88 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(3.88 \times 10^{-3}) = 2.41$$

64. Nicotine, $\text{C}_{10}\text{H}_{14}\text{N}_2$, 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



First set up a concentration table:

	$[\text{C}_{10}\text{H}_{14}\text{N}_2]$	$[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+]$	$[\text{OH}^-]$
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:

$$K_{b1} = \frac{[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+][\text{OH}^-]}{[\text{C}_{10}\text{H}_{14}\text{N}_2]} = 7 \times 10^{-7}$$

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

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

Because x is less than 5% of 0.050 and $[\text{OH}^-]$ is greater than $4.5 \times 10^{-7} M$, our customary assumptions are justified. We can calculate $[\text{C}_{10}\text{H}_{14}\text{N}_2] = 0.050 - x = 0.050 - 2 \times 10^{-4} = 0.048 M$; $[\text{OH}^-] = [\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+] = x = 2 \times 10^{-4} M$. Now calculate the concentration of $\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}$ in a solution with $[\text{OH}^-]$ and $[\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}]$ equal to $2 \times 10^{-4} M$. The equilibrium between these species is $\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}(aq) + \text{OH}^-(aq)$. We know $[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+]$ and $[\text{OH}^-]$, so we can calculate the concentration of $\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}$ from the equilibrium expression:

$$K_{b2} = \frac{[\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}][\text{OH}^-]}{[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+]} = 1.4 \times 10^{-11}$$

$$= \frac{[\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}][2 \times 10^{-4}]}{[2 \times 10^{-4}]}$$

$$[\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}] = 1.4 \times 10^{-11} M$$

The concentration of OH^- produced in this ionization is equal to the concentration of $\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}$, $1.4 \times 10^{-11} M$, 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 $\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+$.

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

$$K_a = 1 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] = \frac{1 \times 10^{-14}}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{1.9 \times 10^{-4}} = 5.3 \times 10^{-11} M$$

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

$$[\text{C}_{10}\text{H}_{14}\text{N}_2] = 0.049 M$$

$$[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+] = 1.9 \times 10^{-4} M$$

$$[\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}] = 1.4 \times 10^{-11} M$$

$$[\text{OH}^-] = 1.9 \times 10^{-4} M$$

$$[\text{H}_3\text{O}^+] = 5.3 \times 10^{-11} M$$

66. The pH of a 0.15- M solution of HSO_4^- is 1.43. Determine K_a for HSO_4^- from these data.

Solution

The reaction is $\text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{SO}_4^{2-}(aq)$.

The concentrations at equilibrium are $[\text{SO}_4^{2-}] = [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-1.43} = 0.0372 M$

$$[\text{HF}] = 0.15 - 0.0372 M = 0.113 M$$

$$K_a = \frac{[\text{SO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_4^-]} = \frac{(0.0372)(0.0372)}{(0.113)} = 1.2 \times 10^{-2}$$

68. 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 $\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$.

The pOH can be determined from $\text{pOH} = 14.000 - \text{pH} = 14.000 - 11.612 = 2.388$. Therefore, the concentrations at equilibrium are $[\text{NH}_4^+] = [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-2.388} = 0.004093 \text{ M}$

$[\text{NH}_3] = 0.950 - 0.004093 = 0.9459 \text{ M}$

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

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Chemistry 2e
14: Acid-Base Equilibria
14.4: Hydrolysis of Salts

70. Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

- (a) FeCl_3
- (b) K_2CO_3
- (c) NH_4Br
- (d) KClO_4

Solution

(a) FeCl_3 dissociates into Fe^{3+} ions (acidic metal cation) and Cl^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic. (b) K_2CO_3 dissociates into K^+ ions (neutral metal cation) and CO_3^{2-} ions (the conjugate base of a weak acid and therefore basic). The aqueous solution is therefore basic. (c) NH_4Br dissociates into NH_4^+ ions (a weak acid) and Br^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic. (d) KClO_4 dissociates into K^+ ions (neutral metal cation) and ClO_4^- ions (the conjugate base of a strong acid and therefore neutral). The aqueous solution is therefore neutral.

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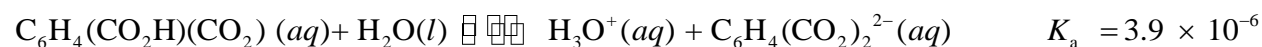
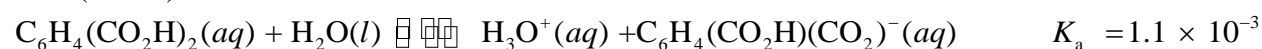
Chemistry 2e
14: Acid-Base Equilibria
14.5: Polyprotic Acids

72. Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-M solution of H_2CO_3 , a diprotic acid: $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, $[\text{H}_2\text{CO}_3]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$? No calculations are needed to answer this question.

Solution

$[\text{H}_3\text{O}^+]$ and $[\text{HCO}_3^-]$ are equal in a 0.134-M solution of H_2CO_3 . K_a of H_2CO_3 is significantly larger than K_a for HCO_3^- . Therefore, very little of HCO_3^- ionizes to give hydronium ions and CO_3^{2-} ions, and the concentrations of H_3O^+ and HCO_3^- are practically equal in an aqueous solution of H_2CO_3 .

74. Calculate the concentration of each species present in a 0.010-M solution of phthalic acid, $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$.



Solution

$[\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2] 7.2 \times 10^{-3}M$, $[\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{CO}_2)^-] = [\text{H}_3\text{O}^+] 2.8 \times 10^{-3}M$, $[\text{C}_6\text{H}_4(\text{CO}_2)_2^{2-}] 3.9 \times 10^{-6}M$, $[\text{OH}^-] 3.6 \times 10^{-12}M$

76. The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

(a) What is K_a for the acid reaction of HTe^- with H_2O ?

(b) What is K_b for the reaction in which HTe^- functions as a base in water?

(c) Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of $[\text{HTe}^-]$ in a 0.10 M solution of H_2Te .

Solution

(a) as an acid,



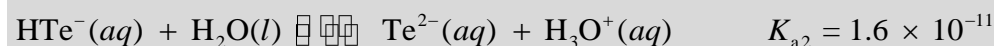
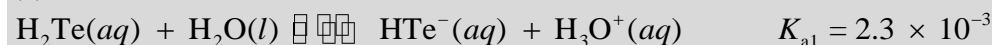
$$K_{a2} = \frac{[\text{Te}^{2-}][\text{H}_3\text{O}^+]}{[\text{HTe}^-]} = 1.6 \times 10^{-11} \quad ;$$

(b) as a base,



$$K_b = \frac{[\text{H}_2\text{Te}][\text{OH}^-]}{[\text{HTe}^-]} = \frac{K_w}{K_{a1}} = \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-3}} = 4.3 \times 10^{-12} ;$$

(c) The reactions and ionization constants are:



As a general rule, if the first ionization constant is larger than the second by a factor of at least 20, then the second ionization can be neglected. Since K_{a1} is 230-times larger than K_{a2} , the

assumption should hold true for HTe^- . To test the assumptions, find $[\text{HTe}^-]$ from the first reaction. The equilibrium expression for this reaction is $K_{a1} = \frac{[\text{HTe}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{Te}]} = 2.3 \times 10^{-3}$.

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

	$[\text{H}_2\text{Te}]$	$[\text{HTe}^-]$	$[\text{H}_3\text{O}^+]$
Initial concentration (M)	0.10	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	$0.10 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.10 - x) \approx 0.10$, gives $\frac{[\text{HTe}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{Te}]} = \frac{(x)(x)}{(0.10 - x)} \approx \frac{(x)(x)}{0.10} = 2.3 \times 10^{-3}$.

Solving for x gives 0.0152 M. Because this value is 15% of 0.10 M, our assumption is incorrect. Therefore, use the quadratic formula. Using the data gives the quadratic equation:

$$x^2 + 2.3 \times 10^{-3}x - 2.3 \times 10^{-4} = 0$$

Using the quadratic formula gives ($a = 1$, $b = 2.3 \times 10^{-3}$, and $c = -2.3 \times 10^{-4}$)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(2.3 \times 10^{-3}) \pm \sqrt{(2.3 \times 10^{-3})^2 - 4(1)(-2.3 \times 10^{-4})}}{2(1)}$$

$$= \frac{-(2.3 \times 10^{-3}) \pm (0.0304)}{2} = 0.0141 \text{ M} \quad (\text{positive root})$$

Thus $[\text{HTe}^-] = 0.014 \text{ M}$. For the second ionization, $K_{a2} = \frac{[\text{Te}^{2-}][\text{H}_3\text{O}^+]}{[\text{HTe}^-]} = 1.6 \times 10^{-11}$.

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

	$[\text{HTe}^-]$	$[\text{Te}^{2-}]$	$[\text{H}_3\text{O}^+]$
Initial concentration (M)	0.0141	0	0.0141
Change (M)	-x	+x	+x
Equilibrium (M)	$0.0141 - x$	x	$0.0141 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.0140 - x) \approx$ and $(0.0141 + x) \approx 0.0141$, gives:

$$\frac{[\text{Te}^{2-}][\text{H}_3\text{O}^+]}{[\text{HTe}^-]} = \frac{(x)(0.0141 + x)}{(0.0141 - x)} \approx \frac{(x)(0.0141)}{0.0141} = 1.6 \times 10^{-11}$$

Solving for x gives $1.6 \times 10^{-11} \text{ M}$. Therefore, compared with 0.014 M, this value is negligible ($1.1 \times 10^{-7} \%$).

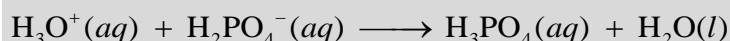
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Chemistry 2e
14: Acid-Base Equilibria
14.6: Buffers

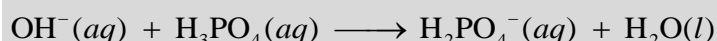
78. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4 .

Solution

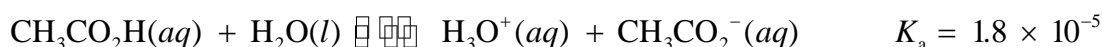
Excess H_3O^+ is removed primarily by the reaction:



Excess base is removed by the reaction:



80. What is $[\text{H}_3\text{O}^+]$ in a solution of 0.25 M $\text{CH}_3\text{CO}_2\text{H}$ and 0.030 M NaCH_3CO_2 ?



Solution

The equilibrium expression is:

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

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

	$[\text{CH}_3\text{CO}_2\text{H}]$	$[\text{H}_3\text{O}^+]$	$[\text{CH}_3\text{CO}_2^-]$
Initial concentration (M)	0.25	0	0.030
Change (M)	-x	+x	+x
Equilibrium (M)	0.25 - x	x	0.030 + x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.25 - x) \approx 0.25$ and $(0.030 + x) \approx 0.030$, gives:

$$\frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(x)(0.030 + x)}{(0.25 - x)} \approx \frac{(x)(0.030)}{0.25} = 1.8 \times 10^{-5}$$

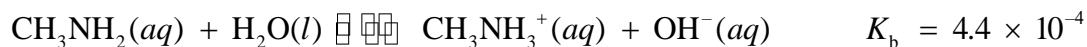
Solving for x gives $1.50 \times 10^{-4} \text{M}$. Because this value is less than 5% of both 0.25 and 0.030, our assumptions are correct. Therefore, $[\text{H}_3\text{O}^+] = 1.5 \times 10^{-4} \text{M}$.

This problem can also be solved using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}; \text{p}K_a = -\log(K_a) = -\log(1.8 \times 10^{-5}) = 4.74; [\text{HA}] \approx [\text{HA}]_0 = [\text{CH}_3\text{CO}_2\text{H}]_0 = 0.25 \text{M}; [\text{A}^-] \approx [\text{NaCH}_3\text{CO}_2] = 0.030 \text{M}. \text{ Using these data:}$$

$$\text{pH} = 4.74 - \log \left(\frac{0.030 \text{ M}}{0.25 \text{ M}} \right) = 3.82; [\text{H}_3\text{O}^+] = 10^{-\text{pH}} \text{M} = 10^{-3.82} \text{M} = 1.5 \times 10^{-4} \text{M}$$

82. What is $[\text{OH}^-]$ in a solution of 0.125 M CH_3NH_2 and 0.130 M $\text{CH}_3\text{NH}_3\text{Cl}$?

**Solution**

The equilibrium expression is:

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = 4.4 \times 10^{-4}$$

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

	$[\text{CH}_3\text{NH}_2]$	$[\text{CH}_3\text{NH}_3^+]$	$[\text{OH}^-]$
Initial concentration (M)	0.125	0.130	0
Change (M)	-x	+x	+x
Equilibrium (M)	$0.125 - x$	$0.130 + x$	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.125 - x) \approx 0.125$ and $(0.130 - x) \approx 0.130$, gives:

$$\frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(0.130 - x)(x)}{(0.125 - x)} \approx \frac{(0.130)(x)}{0.125} = 4.4 \times 10^{-4}$$

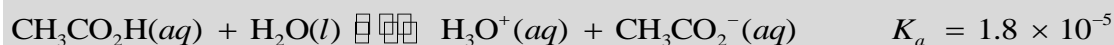
Solving for x gives $4.23 \times 10^{-4} M$. Because this value is less than 5% of both 0.125 and 0.130, our assumptions are correct. Therefore, $[\text{OH}^-] = 4.2 \times 10^{-4} M$.

84. What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

- HCl
- KCH_3CO_2
- NaCl
- KOH
- $\text{CH}_3\text{CO}_2\text{H}$

Solution

The reaction and equilibrium constant are:



- The added HCl will increase the concentration of H_3O^+ slightly, which will react with CH_3CO_2^- and produce $\text{CH}_3\text{CO}_2\text{H}$ in the process. Thus, $[\text{CH}_3\text{CO}_2^-]$ decreases and $[\text{CH}_3\text{CO}_2\text{H}]$ increases.
- The added KCH_3CO_2 will increase the concentration of $[\text{CH}_3\text{CO}_2^-]$ which will react with H_3O^+ and produce $\text{CH}_3\text{CO}_2\text{H}$ in the process. Thus, $[\text{H}_3\text{O}^+]$ decreases slightly and $[\text{CH}_3\text{CO}_2\text{H}]$ increases.
- The added NaCl will have no effect on the concentration of the ions.

(d) The added KOH will produce OH^- ions, which will react with the H_3O^+ , thus reducing $[\text{H}_3\text{O}^+]$. Some additional $\text{CH}_3\text{CO}_2\text{H}$ will dissociate, producing $[\text{CH}_3\text{CO}_2^-]$ ions in the process.

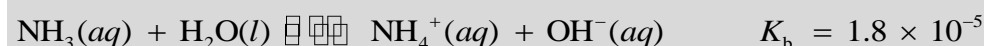
Thus, $[\text{CH}_3\text{CO}_2\text{H}]$ decreases slightly and $[\text{CH}_3\text{CO}_2^-]$ increases.

(e) The added $\text{CH}_3\text{CO}_2\text{H}$ will increase its concentration, causing more of it to dissociate and producing more $[\text{CH}_3\text{CO}_2^-]$ and H_3O^+ in the process. Thus, $[\text{H}_3\text{O}^+]$ increases slightly and $[\text{CH}_3\text{CO}_2^-]$ increases.

86. What will be the pH of a buffer solution prepared from 0.20 mol NH_3 , 0.40 mol NH_4NO_3 , and just enough water to give 1.00 L of solution?

Solution

The reaction and equilibrium constant are:



The equilibrium expression is:

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

The initial concentrations of NH_3 and NH_4^+ are 0.20 M and 0.40 M, respectively. The equilibrium concentrations for this system can be written as follows:

	$[\text{NH}_3]$	$[\text{NH}_4^+]$	$[\text{OH}^-]$
Initial concentration (M)	0.20	0.40	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.20 - x	0.40 + x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.20 - x) \approx 0.20$ and $(0.40 + x) \approx 0.40$, gives:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.40 + x)(x)}{(0.20 - x)} \approx \frac{(0.40)(x)}{0.20} = 1.8 \times 10^{-5}$$

Solving for x gives 9.00×10^{-6} M. Because this value is less than 5% of both 0.20 and 0.40, our assumptions are correct. Therefore, $[\text{OH}^-] = 9.00 \times 10^{-6}$ M. Thus:

$$\text{pOH} = -\log(9.00 \times 10^{-6}) = 5.046$$

$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 5.046 = 8.954 = 8.95$$

88. How much solid $\text{NaCH}_3\text{CO}_2 \cdot 3\text{H}_2\text{O}$ must be added to 0.300 L of a 0.50-M acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

Solution

This problem is most conveniently solved using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

where the base is acetate ion and the acid is acetic acid.

The pK_a for acetic acid is

$$pK_a = -\log K_a = -\log 1.8 \times 10^{-5} = 4.74$$

Substitution of this value and the provided pH into the Henderson-Hasselbalch equation and rearranging to isolate the conjugate acid/base ratio yields

$$[C_2H_3O_2^-] / [HC_2H_3O_2] = 10^{(5.00 - 4.74)} = 10^{0.26} = 1.82$$

The small K_a for acetic acid means very little will undergo acid ionization, and so its concentration will be ~ 0.50 M. The molarity of acetate ion required is therefore

$$[C_2H_3O_2^-] = [HC_2H_3O_2] \times 1.82 = 0.50 \times 1.82 = 0.91 \text{ M}$$

The mass of sodium acetate trihydrate required is then

$$0.91 \text{ mol/L} \times 136.1 \text{ g/mol} \times 0.300 \text{ L} = 37 \text{ g}$$

90. A buffer solution is prepared from equal volumes of 0.200 M acetic acid and 0.600 M sodium acetate. Use 1.80×10^{-5} as K_a for acetic acid.

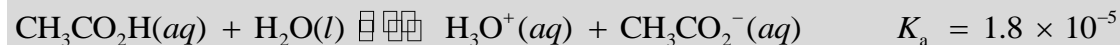
(a) What is the pH of the solution?

(b) Is the solution acidic or basic?

(c) What is the pH of a solution that results when 3.00 mL of 0.034 M HCl is added to 0.200 L of the original buffer?

Solution

(a) The reaction and equilibrium constant are:



The equilibrium expression is:

$$K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$

The molar mass of NH_4Cl is 53.4912 g/mol. The moles of NH_4Cl are:

$$\frac{5.36 \text{ g}}{53.4912 \text{ g mol}^{-1}} = 0.1002 \text{ mol}$$

Assume 0.500 L of each solution is present. The total volume is thus 1.000 L. The initial concentrations of the ions is obtained using $M_1V_1 = M_2V_2$, or:

$$[CH_3CO_2H] = M_1 \times \frac{V_1}{V_2} = (0.200) \times \frac{0.500 \text{ L}}{1.000 \text{ L}} = 0.100 \text{ M}$$

$$[CH_3CO_2^-] = M_1 \times \frac{V_1}{V_2} = (0.600) \times \frac{0.500 \text{ L}}{1.000 \text{ L}} = 0.300 \text{ M}$$

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

	[CH ₃ CO ₂ H]	[H ₃ O ⁺]	[CH ₃ CO ₂ ⁻]
Initial concentration (M)	0.100	0	0.300
Change (M)	-x	+x	+x
Equilibrium (M)	0.100 - x	x	0.300 + x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.100 - x) \approx 0.100$ and $(0.300 + x) \approx 0.300$, gives:

$$\frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(x)(0.300 + x)}{(0.100 - x)} \approx \frac{(x)(0.300)}{0.100} = 1.80 \times 10^{-5}$$

Solving for x gives $6.000 \times 10^{-6} M$. Because this value is less than 5% of both 0.100 and 0.300,

our assumptions are correct. Therefore $[\text{H}_3\text{O}^+] = 6.000 \times 10^{-6} M$:

$$\text{pH} = -\log(6.000 \times 10^{-6}) = 5.2218 = 5.222;$$

(b) The solution is acidic.

(c) Assume that the added H⁺ reacts completely with an equal amount of CH₃CO₂⁻, forming an equal amount of CH₃CO₂H in the process. The moles of H⁺ added equal $0.034 M \times 0.00300 L = 1.02 \times 10^{-4} \text{ mol}$. For the acetic acid, the initial moles present equal $0.2000 M \times 0.200 L = 0.0400 \text{ mol}$, and for acetate ion, $0.600 M \times 0.200 L = 0.120 \text{ mol}$. Thus:

$$\text{mol CH}_3\text{CO}_2\text{H} = 0.0400 + 1.02 \times 10^{-4} = 0.0401 \text{ mol}$$

$$\text{mol CH}_3\text{CO}_2^- = 0.120 - 1.02 \times 10^{-4} = 0.120 \text{ mol}$$

$$\text{Final volume} = 0.200 L + 3.00 \times 10^{-3} L = 0.203 L$$

The initial concentrations are therefore:

$$[\text{CH}_3\text{CO}_2\text{H}] = \frac{0.0401 \text{ mol}}{0.203 L} = 0.198 M$$

$$[\text{CH}_3\text{CO}_2^-] = \frac{0.120 \text{ mol}}{0.203 L} = 0.591 M$$

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

	[CH ₃ CO ₂ H]	[H ₃ O ⁺]	[CH ₃ CO ₂ ⁻]
Initial concentration (M)	0.198	0	0.591
Change (M)	-x	+x	+x
Equilibrium (M)	0.198 - x	x	0.591 + x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.198 - x) \approx 0.198$ and $(0.591 + x) \approx 0.591$, gives:

$$\frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(x)(0.591 + x)}{(0.198 - x)} \approx \frac{(x)(0.591)}{0.198} = 1.80 \times 10^{-5}$$

Solving for x gives $6.03 \times 10^{-6} M$. Because this value is less than 5% of both 0.198 and 0.591,

our assumptions are correct. Therefore, $[\text{H}_3\text{O}^+] = 6.03 \times 10^{-6} M$.

$$\text{pH} = -\log(6.03 \times 10^{-6}) = 5.2197 = 5.220$$

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Chemistry 2e
14: Acid-Base Equilibria
14.7: Acid-Base Titrations

92. Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

Solution

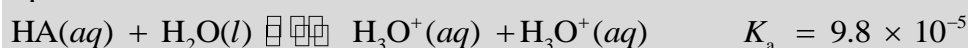
At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example.

94. Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 M barbituric acid ($K_a = 9.8 \times 10^{-5}$) with 0.100 M KOH.

- (a) no KOH added
- (b) 20 mL of KOH solution added
- (c) 39 mL of KOH solution added
- (d) 40 mL of KOH solution added
- (e) 41 mL of KOH solution added

Solution

(a) Let HA represent barbituric acid and A^- represent the conjugate base. The reaction and equilibrium constant are:



$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = 9.8 \times 10^{-5}$$

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

	[HA]	[H ₃ O ⁺]	[A ⁻]
Initial concentration (M)	0.100	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.100 - x	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.100 - x) \approx 0.100$, gives:

$$\frac{[H_3O^+][A^-]}{[HA]} = \frac{(x)(x)}{(0.100 - x)} \approx \frac{(x)(x)}{0.100} = 9.8 \times 10^{-5}$$

Solving for x gives $3.13 \times 10^{-3} M$. Because this value is less than 5% of 0.100, our assumption is correct. Therefore, $[H_3O^+] = 3.13 \times 10^{-3} M$:

$$pH = -\log(3.13 \times 10^{-3}) = 2.504 = 2.50;$$

(b) The moles of OH^- added are given by:

$$\text{mol } OH^- = M \times V = (0.100 M) \times (0.020 L) = 0.00200 \text{ mol}$$

The initial moles of barbituric acid are given by:

$$\text{mol HA} = M \times V = (0.100 M) \times (0.040 L) = 0.00400 \text{ mol}$$

Assume that the added hydroxide ion reacts completely with an equal number of moles of HA, forming an equal number of moles of A^- in the process. Thus, the moles of the ions are given by:

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14.7: Acid-Base Titrations

$$\text{mol HA} = 0.00400 - 0.00200 = 0.00200 \text{ mol}$$

$$\text{mol A}^- = 0.00200 \text{ mol}$$

The total volume is:

$$40.0 \text{ mL} + 20.0 \text{ mL} = 60.0 \text{ mL} = 0.0600 \text{ L}$$

The initial concentrations of the ions are given by:

$$[\text{HA}] = \frac{0.00200 \text{ mol}}{0.0600 \text{ L}} = 0.0333 \text{ M}$$

$$[\text{A}^-] = \frac{0.00200 \text{ mol}}{0.0600 \text{ L}} = 0.0333 \text{ M}$$

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

	[HA]	[H ₃ O ⁺]	[A ⁻]
Initial concentration (M)	0.0333	0	0.0333
Change (M)	-x	+x	+x
Equilibrium (M)	0.0333 - x	x	0.0333 + x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.0333 - x) \approx 0.0333$ and $(0.0333 + x) \approx 0.0333$, gives:

$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(0.0333 + x)}{(0.0333 - x)} \approx \frac{(x)(0.0333)}{0.0333} = 9.8 \times 10^{-5}$$

Solving for x gives $9.8 \times 10^{-5} \text{ M}$. Because this value is less than 5% of 0.0333, our assumptions are correct. Therefore, $[\text{H}_3\text{O}^+] = 9.8 \times 10^{-5} \text{ M}$:

$$\text{pH} = -\log(9.8 \times 10^{-5}) = 4.009 = 4.01;$$

(c) The moles of OH⁻ added are given by:

$$\text{mol OH}^- = M \times V = (0.100 \text{ M}) \times (0.039 \text{ L}) = 0.00390 \text{ mol}$$

The initial moles of barbituric acid are given by:

$$\text{mol HA} = M \times V = (0.100 \text{ M}) \times (0.040 \text{ L}) = 0.00400 \text{ mol}$$

Assume that the added hydroxide ion reacts completely with an equal number of moles of HA, forming an equal number of moles of A⁻ in the process. Thus, the moles of the ions are given by:

$$\text{mol HA} = 0.00400 - 0.00390 = 0.00010 \text{ mol}$$

$$\text{mol A}^- = 0.00930 \text{ mol}$$

The total volume is:

$$40.0 \text{ mL} + 39.0 \text{ mL} = 79.0 \text{ mL} = 0.0790 \text{ L}$$

The initial concentrations of the ions are given by:

$$[\text{HA}] = \frac{0.00010 \text{ mol}}{0.0790 \text{ L}} = 0.00127 \text{ M}$$

$$[\text{A}^-] = \frac{0.00390 \text{ mol}}{0.0790 \text{ L}} = 0.0494 \text{ M}$$

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

	[HA]	[H ₃ O ⁺]	[A ⁻]
Initial concentration (M)	0.00127	0	0.0494
Change (M)	-x	+x	+x
Equilibrium (M)	0.00127 - x	x	0.0494 + x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.00127 - x) \approx 0.00127$ and $(0.0494 + x) \approx 0.0494$, gives:

$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(0.0494 + x)}{(0.00127 - x)} \approx \frac{(x)(0.0494)}{0.00127} = 9.8 \times 10^{-5}$$

Solving for x gives $2.52 \times 10^{-6} M$. Because this value is less than 5% of 0.00127 and 0.0494, our assumptions are correct. Therefore, $[\text{H}_3\text{O}^+] = 2.52 \times 10^{-6} M$:

$$\text{pH} = -\log(2.52 \times 10^{-6}) = 5.599 = 5.60;$$

(d) The moles of OH⁻ added are given by:

$$\text{mol OH}^- = M \times V = (0.100 M) \times (0.040 L) = 0.00400 \text{ mol}$$

The initial moles of barbituric acid are given by:

$$\text{mol HA} = M \times V = (0.100 M) \times (0.040 L) = 0.00400 \text{ mol}$$

This is the equivalence point, where the moles of base added equal the moles of acid present initially. At the equivalence point:

$$\text{mol A}^- = 0.00400 \text{ mol}$$

The total volume is:

$$40.0 \text{ mL} + 40.0 \text{ mL} = 80.0 \text{ mL} = 0.0800 L$$

The initial concentration of the conjugate base is:

$$[\text{A}^-] = \frac{0.00400 \text{ mol}}{0.0800 L} = 0.0500 M$$

The reaction and equilibrium constant are:



$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{9.8 \times 10^{-4}} = 1.02 \times 10^{-10}$$

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

	[A ⁻]	[HA]	[OH ⁻]
Initial concentration (M)	0.0500	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.0500 - x	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.0500 - x) \approx 0.0500$, gives:

$$\frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{(x)(x)}{(0.0500 - x)} \approx \frac{(x)(x)}{0.0500} = 1.02 \times 10^{-10}$$

Solving for x gives $2.26 \times 10^{-6} M$. Because this value is less than 5% of 0.0500, our assumption is correct. Therefore, $[\text{OH}^-] = 2.26 \times 10^{-6} M$:

$$\text{pOH} = -\log(2.26 \times 10^{-6}) = 5.646$$

$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 5.646 = 8.354 = 8.35;$$

(e) The moles of OH^- added are given by:

$$\text{mol OH}^- = M \times V = (0.100 M) \times (0.041 L) = 0.00410 \text{ mol}$$

The initial moles of barbituric acid are given by:

$$\text{mol HA} = M \times V = (0.100 M) \times (0.040 L) = 0.00400 \text{ mol}$$

This is past the equivalence point, where the moles of base added exceed the moles of acid present initially. The excess moles of hydroxide ion are given by:

$$\text{mol OH}^- = 0.00410 - 0.00400 = 0.00010 \text{ mol}$$

The total volume is:

$$40.0 \text{ mL} + 41.0 \text{ mL} = 81.0 \text{ mL} = 0.0810 \text{ L}$$

The concentration of OH^- is:

$$[\text{OH}^-] = \frac{0.00010 \text{ mol}}{0.0810 \text{ L}} = 0.0012 M$$

$$\text{pOH} = -\log(0.0012) = 2.921$$

$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 2.921 = 11.079 = 11.08$$

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