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These are homework exercises to accompany the Textmap created for "Chemistry: The Central Science" by Brown et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here. In addition to these publicly available questions, access to private problems bank for use in exams and homework is available to faculty only on an individual basis; please contact Delmar Larsen for an account with access permission.
16.1: Acids and Bases: A Brief Review

16.2: Brønsted–Lowry Acids and Bases

Conceptual Problems

1. Identify the conjugate acid–base pairs in each equilibrium.
   a. \(\text{HSO}^\cdot_{4}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{SO}^{2\cdot}_{4}(aq) + \text{H}_3\text{O}^+{(aq)}\)
   b. \(\text{C}_3\text{H}_7\text{NO}_2(aq) + \text{H}_3\text{O}^+{(aq)} \rightleftharpoons \text{C}_3\text{H}_8\text{NO}^+_{2}(aq) + \text{H}_2\text{O}(l)\)
   c. \(\text{CH}_3\text{O}_2\text{H}(aq) + \text{NH}_3(aq) \rightleftharpoons \text{CH}_3\text{CO}^\cdot_{2}(aq) + \text{NH}^+_{4}(aq)\)
   d. \(\text{SbF}_5(aq) + 2\text{HF}(aq) \rightleftharpoons \text{H}_2\text{F}^+(aq) + \text{SbF}^{\cdot}_{6}(aq)\)

2. Identify the conjugate acid–base pairs in each equilibrium.
   a. \(\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+{(aq)} + \text{F}^-(aq)\)
   b. \(\text{CH}_3\text{CH}_2\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{CH}_2\text{NH}^+_{3}(aq) + \text{OH}^-(aq)\)
   c. \(\text{C}_3\text{H}_7\text{NO}_2(aq) + \text{OH}^-(aq) \rightleftharpoons \text{C}_3\text{H}_6\text{NO}^\cdot_{2}(aq) + \text{H}_2\text{O}(l)\)
   d. \(\text{CH}_3\text{CO}_2\text{H}(aq) + 2\text{HF}(aq) \rightleftharpoons \text{CH}_3\text{C(OH)}^\cdot_{2}(aq) + \text{HF}^{\cdot}_{2}(aq)\)

3. Salts such as NaH contain the hydride ion \(\text{H}^\cdot\). When sodium hydride is added to water, it produces hydrogen gas in a highly vigorous reaction. Write a balanced chemical equation for this reaction and identify the conjugate acid–base pairs.

4. Write the expression for \(K_a\) for each reaction.
   a. \(\text{HCO}^\cdot_{3}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CO}^{2\cdot}_{3}(aq) + \text{H}_3\text{O}^+{(aq)}\)
   b. \(\text{formic acid}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{formate}(aq) + \text{H}_3\text{O}^+(aq)\)
   c. \(\text{H}_3\text{PO}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{PO}^\cdot_{4}(aq) + \text{H}_3\text{O}^+(aq)\)

5. Write an expression for the ionization constant \(K_b\) for each reaction.
   a. \(\text{OCH}^\cdot_{3}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HOCH}_{3}(aq) + \text{OH}^-(aq)\)
   b. \(\text{NH}^\cdot_{2}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_{3}(aq) + \text{OH}^-(aq)\)
   c. \(\text{S}^\cdot_{2}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HS}^\cdot(\text{aq}) + \text{OH}^-(\text{aq})\)

6. Predict whether each equilibrium lies primarily to the left or to the right.
   a. \(\text{HBr}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+{(aq)} + \text{Br}^-(aq)\)
   b. \(\text{NaH}(s) + \text{NH}_3(aq) \rightleftharpoons \text{H}_2(g) + \text{NaNH}_2(s)\)
   c. \(\text{OCH}^\cdot_{3}(aq) + \text{NH}_3(aq) \rightleftharpoons \text{CH}_3\text{OH}(aq) + \text{NH}^\cdot_{2}(aq)\)
   d. \(\text{NH}_3(aq) + \text{HCl}(aq) \rightleftharpoons \text{NH}^\cdot_{4}(aq) + \text{Cl}^-(aq)\)

7. Species that are strong bases in water, such as \(\text{CH}_3^\cdot\), \(\text{NH}_2^\cdot\), and \(\text{S}^\cdot_{2}\), are leveled to the strength of \(\text{OH}^\cdot\), the conjugate base of \(\text{H}_2\text{O}\). Because their relative base strengths are indistinguishable in water, suggest a method for identifying which is the strongest base. How would you distinguish between the strength of the acids \(\text{HO}^\cdot(\text{OH}_3)\), \(\text{H}_2\text{SO}_4(\text{aq})\), and \(\text{HClO}_4(\text{aq})\)?

8. Is it accurate to say that a 2.0 M solution of \(\text{H}_2\text{SO}_4\), which contains two acidic protons per molecule, is 4.0 M in \(\text{H}^+(aq)\)? Explain your answer.
9. The alkalinity of soil is defined by the following equation: alkalinity = \([HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]\). The source of both \([HCO_3^-]\) and \([CO_3^{2-}\) is \([H_2CO_3]\). Explain why the basicity of soil is defined in this way.

10. Why are aqueous solutions of salts such as \([CaCl_2]\) neutral? Why is an aqueous solution of \([NaNH_2]\) basic?

11. Predict whether the aqueous solutions of the following are acidic, basic, or neutral.
   a. \([Li_3N]\)
   b. \([NaH]\)
   c. \([KBr]\)
   d. \([C_2H_5NH_3Cl]\)

12. When each compound is added to water, would you expect the \((pH)\) of the solution to increase, decrease, or remain the same?
   a. \([LiCH_3]\)
   b. \([MgCl_2]\)
   c. \([K_2O]\)
   d. \([C_3H_3\_2NH\_2^+Br\_\_^-]\)

13. Which complex ion would you expect to be more acidic: \([Pb(H_2O)_4^{2+}]\) or \([Sn(H_2O)_4^{2+}]\)? Why?

14. Would you expect \([Sn(H_2O)_4^{2+}]\) or \([Sn(H_2O)_6^{4+}]\) to be more acidic in aqueous solutions? Why?

15. Is it possible to arrange the hydrides \([LiH]\), \([RbH]\), \([KH]\), \([CsH]\), and \([NaH]\) in order of increasing base strength in aqueous solution? Why or why not?

---

**Conceptual Answer**

1. a. \([\text{acid}]\) \(HSO^−_{4}(aq) + \text{base} \rightarrow \text{conjugate base} \cdot SO^{2−}_{4}(aq) + \text{conjugate acid} \cdot H_3O^+(aq)\)

   b. \([\text{base}]\) \(C_3H_7NO_{2}(aq) + \text{acid} \rightarrow \text{conjugate acid} \cdot C_3H_8NO^+_{2}(aq) + \text{conjugate base} \cdot H_2O(l)\)

   c. \([\text{acid}]\) \(HOAc\cdot(aq) + \text{base} \rightarrow \text{conjugate base} \cdot CH_3CO^−_{2}(aq) + \text{conjugate acid} \cdot NH^+_{4}(aq)\)

   d. \([\text{acid}]\) \(SbF_{5}(aq) + \text{base} \rightarrow \text{conjugate acid} \cdot H_2F^+(aq) + \text{conjugate base} \cdot SbF_6^−(aq)\)

2. a. \([\text{acid}]\) \(HF\cdot(aq) + \text{base} \rightarrow \text{conjugate acid} \cdot H_3O^+(aq) + \text{conjugate base} \cdot F^−(aq)\)

   b. \([\text{base}]\) \(CH_{3}CH_{2}NH_{2}\cdot(aq) + \text{acid} \rightarrow \text{conjugate acid} \cdot CH_{3}CH_{2}NH_{3}^{+}(aq) + \text{conjugate base} \cdot OH^−(aq)\)
3. \[
\underset{\text{base}}{NaH\,(s)} + \underset{\text{acid}}{H_{2}O\,(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_{2}\,(g)} + \underset{\text{conjugate base}}{NaOH\,(aq)}
\]

4. 

a. \[
K_a=\frac{[CO_{3}^{2-}][H_{3}O^{+}]}{[HCO_{3}^{-}]}
\]

b. \[
K_a=\frac{[formate][H_{3}O^{+}]}{[formic\,acid]}
\]

c. \[
K_a=\frac{[H_{2}PO_{4}^{-}][H_{3}O^{+}]}{[H_{3}PO_{4}]}
\]

5. 

a. \[
K_b=\frac{[CO_{3}^{2-}][H_{3}O^{+}]}{[HCO_{3}^{-}]}
\]

b. \[
K_b=\frac{[NH_{3}][OH^{-}]}{[NH_{2}^{-}]}
\]

c. \[
K_b=\frac{[HS^{-}][OH^{-}]}{[S^{2-}]}
\]

6. Strong acids have the smaller \(pK_a\).

a. Equilibrium lies primarily to the right because \(HBr\) \((pK_a=-8.7)\) is a stronger acid than \(H_{2}O\) \((pK_a=14)\) and \(Br^-\) \((pK_a=-8.7)\) is a stronger base than \(HBr\) \((pK_a=-8.7)\).  

b. Equilibrium lies primarily to the left because \(H_{2}O\) \((pK_a=14)\) is a stronger acid than \(NH_{3}\) \((pK_a=38)\) and \(NH_{2}^-\) \((pK_a=38)\) is a stronger base than \(NH_{3}\) \((pK_a=38)\).  

c. Equilibrium lies primarily to the left because \(CH_{3}OH\) \((pK_a=17)\) is a stronger acid than \(H_{2}SO_{4}\) \((pK_a=38)\) and \(H_{2}SO_{4}\) \((pK_a=38)\) is a stronger base than \(CH_{3}OH\) \((pK_a=17)\).  

d. Equilibrium lies to the right because \(HCl\) \((pK_a=-7)\) is a stronger acid than \(NH_{4}^{+}\) \((pK_a=9.3)\) and \(Cl^-\) \((pK_a=-7)\) is a stronger base than \(NH_{4}^{+}\) \((pK_a=9.3)\).  

7. To identify the strongest base we can determine their weakest conjugate acid. The conjugate acids of \(CH_{3}^{+}\), \(NH_{2}^{+}\), and \(S^{2-}\) are \(CH_{4}\), \(NH_{3}\), and \(HS^{-}\), respectively. Next, we consider that acidity increases with positive charge on the molecule, thus ruling out that \(S^{2-}\) is the weakest base. Finally, we consider that acidity increases with electronegativity, therefore \(NH_{3}\) is the second most basic and \(CH_{4}\) is the most basic. To distinguish between the strength of the acids \(HIO_{3}\), \(H_{2}SO_{4}\), and \(HClO_{4}\) we can consider that the higher electronegativity and oxidation state of the central nonmetal is the more acidic, therefore the order of acidity is: \(HIO_{3}\) \((S^{2-})\) \(<\(H_{2}SO_{4}\) \((Cl^{2-})\) \(<\(HClO_{4}\) because electronegativity and oxidation state increases as follows: \((S^{2-})\) \(<\(Cl^{2-}\).
8. It is not accurate to say that a 2.0 M solution of $H_2SO_4$, which contains two acidic protons per molecule, is 4.0 M in $H^+\text{)}$ because a 2.0 M solution of $H_2SO_4$ is equivalent to 4.0 N in $H^+\text{)}$.

\[
\left(\text{frac}(2.0,\text{mol}\cdot H_2SO_4)\right)\cdot\left(\text{frac}(2,\text{eq}\cdot H^+)\right)=\text{frac}4,\text{eq}\cdot H^+)\text{(L)}=4\text{N},H^+\text{)}
\]

9. Alkalinity is a measure of acid neutralizing capability. The basicity of the soil is defined this way because bases such as $HCO_3^-$ and $CO_3^{2-}$ can neutralize acids in soil. Because most soil has a pH between 6 and 8, alkalinity can be estimated by its carbonate species alone. At a near neutral pH, most carbonate species are bicarbonate.

10. Aqueous solutions of salts such as $(CaCl_2)$ are neutral because it is created from hydrochloric acid (a strong acid) and calcium hydroxide (a strong base). An aqueous solution of $(NaNH_2)$ is basic because it can deprotonate alkenes, alcohols, and a host of other functional groups with acidic protons such as esters and ketones.

11.

a. $(Li_3N)$ is a base because the lone pair on the nitrogen can accept a proton.

b. $(NaH)$ is a base because the hydrogen has a negative charge.

c. $(KBr)$ is neutral because it is formed from $(KOH)$ (a strong acid) and $(KOH)$ (a strong base).

d. $(C_2H_5NH_3Cl)$ is acidic because it can donate a proton.

12.

a. The pH is expected to increase. $(\text{under}\text{text}{acid})\text{LtCH}_3\text{(aq)}+\text{under}{base}\text{H}_2\text{O}(l)\text{rightleflharpoo}{conjugate base}\text{OH}(aq)+\text{under}{conjugate acid}\text{CH}_4(aq)$

b. The pH is expected to increase. $(\text{under}{acid})\text{MgCl}_2(aq)+\text{under}{base}\text{H}_2\text{O}(l)\text{rightleflharpoo}{conjugate acid}\text{HCl}(aq)+\text{under}{conjugate base}\text{MgO}(aq)$

c. The pH is expected to remain the same. $(K_2O(aq)+H_2O(l)\text{rightleflharpoo}2\text{KOH}(aq))$

d. The pH is expected to increase. $(\text{under}{acid})\text{(CH}_3\text{)_2NH}_2\text{Br}(aq)+\text{under}{base}\text{H}_2\text{O}(l)\text{rightleflharpoo}{conjugate acid}\text{H}_3\text{O}^+(aq)+\text{under}{conjugate base}\text{(CH}_3\text{)_2NH}(aq))$

13. $(Sn(H_2O)_4^{2+})$ is expected to be more acidic than $(Pb(H_2O)_4^{2+})$ because $(Sn)$ is more electronegative than $(Pb)$.

14. $(Sn(H_2O)_6^{4+})$ is expected to be more acidic than $(Sn(H_2O)_4^{2+})$ because the charge on $(Sn)$ is greater ($(4^{+}>2^{+})$).

15. Yes, it is possible the order of increasing base strength is: $(LiH<NaH<RbH<CsH)$ because increasing base strength is dependent on decreasing electronegativity.
Numerical Problems

1. Arrange these acids in order of increasing strength.
   - acid A: $pK_a = 1.52$
   - acid B: $pK_a = 6.93$
   - acid C: $pK_a = 3.86$

   Given solutions with the same initial concentration of each acid, which would have the highest percent ionization?

2. Arrange these bases in order of increasing strength:
   - base A: $pK_b = 13.10$
   - base B: $pK_b = 8.74$
   - base C: $pK_b = 11.87$

   Given solutions with the same initial concentration of each base, which would have the highest percent ionization?

3. Calculate the $K_a$ and the $pK_a$ of the conjugate acid of a base with each $pK_b$ value.
   a. 3.80
   b. 7.90
   c. 13.70
   d. 1.40
   e. -2.50

4. Benzoic acid is a food preservative with a $pK_a$ of 4.20. Determine the $K_b$ and the $pK_b$ for the benzoate ion.

5. Determine $K_a$ and $pK_a$ of boric acid $[B(OH)_3]$, solutions of which are occasionally used as an eyewash; the $pK_b$ of its conjugate base is 4.80.

Numerical Answers

1. Acids in order of increasing strength: (acid B < acid C < acid A). Given the same initial concentration of each acid, the highest percent of ionization is acid A because it is the strongest acid.

2. Bases in order of increasing strength: (base A < base C < base B). Given the solutions with the same initial concentration of each base, the higher percent of ionization is base A because it is the weakest base.

3. 
   a. 
   $(pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 3.80 = 10.2)$
   
   
   $(K_a = 10^{10.2} = 6.31 \times 10^{-11})$
b. \( pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 7.90 = 6.10 \)
\( K_a = 10^{-pK_a} = 10^{-6.10} = 7.94 \times 10^{-7} \)

c. \( pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 7.90 = 3.000 \times 10^{-1} \)
\( K_a = 10^{-pK_a} = 10^{-3.000 \times 10^{-1}} = -5.012 \times 10^{-1} \)

d. \( pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 1.40 = 12.6 \)
\( K_a = 10^{-pK_a} = 10^{-12.6} = 2.51 \times 10^{-13} \)

e. \( pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 7.90 = 16.5 \)
\( K_a = 10^{-pK_a} = 10^{-16.5} = 3.16 \times 10^{-17} \)

4. \( pK_a + pK_b = 14 \rightarrow pK_b = 14 - pK_a = 14 - 4.20 = 9.80 \)
\( K_b = 10^{-pK_b} = 10^{-9.80} = 1.58 \times 10^{-10} \)

5. \( pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 4.80 = 9.20 \)
\( K_a = 10^{-pK_a} = 10^{-9.20} = 6.31 \times 10^{-10} \)

16.3: The Autoionization of Water

Conceptual Problems

1. What is the relationship between the value of the equilibrium constant for the autoionization of liquid water and the tabulated value of the ion-product constant of liquid water \( (K_w) \)?

2. The density of liquid water decreases as the temperature increases from 25°C to 50°C. Will this effect cause \( (K_w) \) to increase or decrease? Why?

3. Show that water is amphiprotic by writing balanced chemical equations for the reactions of water with \( (HNO_3) \) and \( (NH_3) \). In which reaction does water act as the acid? In which does it act as the base?

4. Write a chemical equation for each of the following.
   a. Nitric acid is added to water.
b. Potassium hydroxide is added to water.
c. Calcium hydroxide is added to water.
d. Sulfuric acid is added to water.

5. Show that \(K\) for the sum of the following reactions is equal to \(K_w\).

\[
\begin{align*}
\text{HMnO}_4\text{(aq)} & \rightleftharpoons H^+(\text{aq}) + \text{MnO}^{4-}\text{(aq)} \\
\text{MnO}^{4-}\text{(aq)} + \text{H}_2\text{O}\text{(l)} & \rightarrow \text{HMnO}_4\text{(aq)} + \text{OH}^-\text{(aq)}
\end{align*}
\]

Conceptual Answers

1. \[
[K_{\text{auto}} = \dfrac{[H_3O^+][OH^-]}{[H_2O]^2}]
\]
\[
[K_w = [H_3O^+][OH^-] = K_{\text{auto}}[H_2O]^2]
\]

2. This will affect \(K_w\) as it is dependent on temperature. As the temperature increases, an endothermic process occurs (energy must be absorbed to break the bonds). Consequently, according to Le Chatelier, an increase in temperature favors the forward reaction thus the position of equilibrium shifts toward the right-hand side and \(K_w\) becomes larger.

3. Water acts as the base: \[
\text{H}_2\text{O}\text{(l)} + \text{HNO}_3\text{(g)} \rightarrow H_3\text{O}^+\text{(aq)} + \text{NO}^{3-}\text{(aq)}
\]
Water acts as the acid: \[
\text{H}_2\text{O}\text{(l)} + \text{NH}_3\text{(g)} \rightarrow \text{OH}^-\text{(aq)} + \text{NH}^{4+}\text{(aq)}
\]

4. 

a. \[
\text{HNO}_3\text{(aq)} + \text{H}_2\text{O}\text{(l)} \rightleftharpoons H_3\text{O}^+\text{(aq)} + \text{HNO}_3\text{^{-}(aq)}
\]

b. \[
\text{KOH}\text{(s)} + \text{H}_2\text{O}\text{(l)} \rightleftharpoons K^-\text{(aq)} + \text{OH}^-\text{(aq)}
\]

c. \[
\text{Ca(OH)}_2\text{(s)} + \text{H}_2\text{O}\text{(l)} \rightleftharpoons \text{Ca}^{2+}\text{(aq)} + 2\text{OH}^-\text{(aq)}
\]

d. \[
\text{H}_2\text{SO}_4\text{(aq)} + \text{H}_2\text{O}\text{(l)} \rightleftharpoons \text{HSO}_4^-\text{(aq)} + \text{H}^+\text{(aq)}
\]

5. \[
\text{H}_2\text{O}\text{(l)} \rightleftharpoons H^+\text{(aq)} + \text{OH}^-\text{(aq)}
\]
\[
K_w = [H^+][OH^-]
\]

Numerical Problems

1. The autoionization of sulfuric acid can be described by the following chemical equation:
\[
\text{H}_2\text{SO}_4\text{(l)} + \text{H}_2\text{SO}_4\text{(aq)} \rightleftharpoons \text{H}_3\text{SO}_4^-\text{(aq)} + \text{HSO}_4^-\text{(aq)}
\]
At 25°C, \(K = 3 \times 10^{-4}\). Write an equilibrium constant expression for \(K_{\text{H}_2\text{SO}_4}\) that is analogous to \(K_w\). The density of \(\text{H}_2\text{SO}_4\text{(aq)}\) is \(1.8\text{frac(gcm^3)}\) at 25°C. What is the concentration of \(\text{H}_3\text{SO}_4^-\text{(aq)}\)? What fraction of \(\text{H}_2\text{SO}_4\text{(aq)}\) is ionized?
2. An aqueous solution of a substance is found to have \([H_3O]^+ = 2.48 \times 10^{-8}; M\). Is the solution acidic, neutral, or basic?

3. The pH of a solution is 5.63. What is its pOH? What is the \([OH^-]\)? Is the solution acidic or basic?

4. State whether each solution is acidic, neutral, or basic.
   a. \(\{[H_3O]^+ = 8.6 \times 10^{-3}; M\}\)
   b. \(\{[H_3O]^+ = 3.7 \times 10^{-9}; M\}\)
   c. \(\{[H_3O]^+ = 2.1 \times 10^{-7}; M\}\)
   d. \(\{[H_3O]^+ = 1.4 \times 10^{-6}; M\}\)

5. Calculate the pH and the pOH of each solution.
   a. 0.15 \(\{M, HBr\}\)
   b. 0.03 \(\{M, KOH\}\)
   c. \(\{2.3 \times 10^{-3}; M, HNO_3\}\)
   d. \(\{9.78 \times 10^{-2}; M, NaOH\}\)
   e. 0.00017 \(\{M, HCl\}\)
   f. 5.78 \(\{M, HI\}\)

6. Calculate the pH and the pOH of each solution.
   a. 25.0 mL of \(2.3 \times 10^{-2}; M, HCl\), diluted to 100 mL
   b. 5.0 mL of \(1.87, M, NaOH\), diluted to 125 mL
   c. 5.0 mL of \(5.98, M, HCl\) added to 100 mL of water
   d. 25.0 mL of \(3.7, M, HNO_3\) added to 250 mL of water
   e. 35.0 mL of \(0.046, M, HI\) added to 500 mL of water
   f. 15.0 mL of \(0.0087, M, KOH\) added to 250 mL of water.

7. The pH of stomach acid is approximately 1.5. What is the \([H^+]\)?

8. Given the pH values in parentheses, what is the \([H^+]\) of each solution?
   a. household bleach (11.4)
   b. milk (6.5)
   c. orange juice (3.5)
   d. seawater (8.5)
   e. tomato juice (4.2)

9. A reaction requires the addition of 250.0 mL of a solution with a pH of 3.50. What mass of HCl (in milligrams) must be dissolved in 250 mL of water to produce a solution with this pH?

10. If you require 333 mL of a pH 12.50 solution, how would you prepare it using a 0.500 M sodium hydroxide stock solution?

---

**Numerical Answers**

1. 

\[ [K\_\{H\_2SO\_4\}]=[H\_3SO\_4\_4^+][HSO\_4^-]=K[H\_2SO\_4\_2^+] \]
\([H_3SO_4^{+}] = 0.3\) M

So the fraction ionized is 0.02.

2. The solution is basic because the \(pH = -\log([H_3O^+] + ) = -\log(2.48 \times 10^{-8}) = 7.61 > 7\).

3. \(pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 5.63 = 8.37\)

\([OH^-] = 10^{-pOH} = 10^{-4.27} \times 10^{-9}\)

The \(pH = 5.63 < 7\), therefore the solution is acidic.

4.

a. The solution is acidic. \(pH = -\log([H_3O^+] + ) = -\log(8.6 \times 10^{-3}) = 2.1 < 7\)

b. The solution is basic. \(pH = -\log([H_3O^+] + ) = -\log(3.7 \times 10^{-9}) = 8.4 > 7\)

c. The solution is acidic. \(pH = -\log([H_3O^+] + ) = -\log(2.1 \times 10^{-7}) = 6.7 < 7\)

d. The solution is acidic. \(pH = -\log([H_3O^+] + ) = -\log(1.4 \times 10^{-6}) = 5.9 < 7\)

5.

a.

\(pH = -\log([H_3O^+] + ) = -\log(0.15) = 0.82\)

\(pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 0.82 = 13\)

b.

\(pOH = -\log([OH^-] + ) = -\log(0.03) = 2\)

\(pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 2 = 12\)

c.

\(pH = -\log([H_3O^+] + ) = -\log(2.3 \times 10^{-3}) = 2.6\)

\(pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 2.6 = 11\)

d.

\(pOH = -\log([OH^-] + ) = -\log(9.78 \times 10^{-2}) = 1.01\)

\(pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 1.01 = 13\)
e. \[ \begin{align*} 
\text{pH} &= -\log([\text{H}_3\text{O}^+]) = -\log(0.00017) = 3.8 \\
\text{pH} + \text{pOH} &= 14 \Rightarrow \text{pOH} = 14 - \text{pH} = 14 - 3.8 = 10 
\end{align*} \]

f. \[ \begin{align*} 
\text{pH} &= -\log([\text{H}_3\text{O}^+]) = -\log(5.78) = -0.762 \\
\text{pH} + \text{pOH} &= 14 \Rightarrow \text{pOH} = 14 - \text{pH} = 14 - (-0.762) = 14.8 
\end{align*} \]

6. a. \[ \begin{align*} 
25.0 \text{ mL} & \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{2.3 \times 10^{-2} \text{ mol}}{1 \text{ L}} \times \frac{1}{100 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 0.060 \text{ M HCl} \\
\text{pH} &= -\log([\text{H}_3\text{O}^+]) = -\log(0.060) = 1.22 \\
\text{pH} + \text{pOH} &= 14 \Rightarrow \text{pOH} = 14 - \text{pH} = 14 - 1.22 = 12.78 
\end{align*} \]

b. \[ \begin{align*} 
5.0 \text{ mL} & \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.87 \text{ mol}}{1 \text{ L}} \times \frac{1}{125 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 7.5 \times 10^{-2} \text{ M NaOH} \\
\text{pOH} &= -\log([\text{OH}^-]) = -\log(7.5 \times 10^{-2}) = 1.1 \\
\text{pH} + \text{pOH} &= 14 \Rightarrow \text{pH} = 14 - \text{pOH} = 14 - 1.1 = 12.9 
\end{align*} \]

c. \[ \begin{align*} 
5.0 \text{ mL} & \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{5.98 \text{ mol}}{1 \text{ L}} \times \frac{1}{100 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 0.20 \text{ M HCl} \\
\text{pH} &= -\log([\text{H}_3\text{O}^+]) = -\log(0.20) = 0.70 \\
\text{pH} + \text{pOH} &= 14 \Rightarrow \text{pOH} = 14 - \text{pH} = 14 - 0.70 = 13.3 
\end{align*} \]

d. \[ \begin{align*} 
25.0 \text{ mL} & \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{3.7 \text{ mol}}{1 \text{ L}} \times \frac{1}{250 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 0.370 \text{ M HNO}_3 \\
\text{pH} &= -\log([\text{H}_3\text{O}^+]) = -\log(0.370) = 0.432 \\
\text{pH} + \text{pOH} &= 14 \Rightarrow \text{pOH} = 14 - \text{pH} = 14 - 0.432 = 13.568 
\end{align*} \]

e. \[ \begin{align*} 
35.0 \text{ mL} & \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.046 \text{ mol}}{1 \text{ L}} \times \frac{1}{500 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 3 \times 10^{-3} \text{ M HI} \\
\text{pH} &= -\log([\text{H}_3\text{O}^+]) = -\log(3 \times 10^{-3}) = 2.52 \\
\text{pH} + \text{pOH} &= 14 \Rightarrow \text{pOH} = 14 - \text{pH} = 14 - 2.52 = 11.48 
\end{align*} \]
f. \( (15.0 \text{ mL}) \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.0087 \text{ mol}}{1 \text{ L}} \times \frac{1}{125 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 5.20 \times 10^{-4} \text{ M KOH} \)

\( \text{pOH} = -\log([OH^-]) = -\log(5.20 \times 10^{-4}) = 3.28 \)

\( \text{pH} + \text{pOH} = 14 \rightarrow \text{pH} = 14 - 3.28 = 10.72 \)

7. \( [H^+] = 10^\text{pH} = 10^{-1.5} = 3.2 \times 10^{-2} \text{ M} \)

8.

a. \( [H^+] = 10^{-11.4} = 3.98 \times 10^{-12} \text{ M} \)

b. \( [H^+] = 10^{-6.5} = 3.2 \times 10^{-7} \text{ M} \)

c. \( [H^+] = 10^{-3.5} = 3.2 \times 10^{-4} \text{ M} \)

d. \( [H^+] = 10^{-8.5} = 3.2 \times 10^{-9} \text{ M} \)

e. \( [H^+] = 10^{-4.2} = 6.3 \times 10^{-5} \text{ M} \)

9. 2.9 mg \( [HCl] \)

\( [H^+] = 10^{\text{pH}} = 10^{-3.50} = 3.1622 \times 10^{-4} \text{ M} \)

\( \text{mg} \text{ HCl} \times \frac{1 \text{ g HCl}}{1000 \text{ mg HCl}} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} \times \frac{1}{250 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 3.1622 \times 10^{-4} \text{ M HCl} \)

\( \rightarrow \frac{\text{mol HCl}}{9115 \text{ L HCl}} = 3.1622 \times 10^{-4} \text{ M HCl} \rightarrow x = 2.9 \text{ mol HCl} \rightarrow x = 2.9 \)

10. To prepare the stock solution, \( (2.11 \times 10^{-2} \text{ L}) \) of \( (0.500 \text{ M}, \text{NaOH}) \) solution is required.

\( \text{mg} \text{ NaOH} \times \frac{1 \text{ g NaOH}}{1000 \text{ mg NaOH}} \times \frac{1 \text{ mol NaOH}}{0.333 \text{ g} \times 2.11 \times \frac{1 \text{ L}}{10^\text{pH}} = 10^{-1.5} = 0.03162 \text{ M} \)

\( \text{pH} + \text{pOH} = 14 \rightarrow \text{pOH} = 14 - 12.50 = 1.5 \)
Concentual Problems

1. Several factors affect the relative strengths of acids and bases. For each pair, identify the most important factor in determining which is the stronger acid or base in aqueous solution.
   a. \(\text{CH}_3\text{CCl}_2\text{CH}_2\text{CO}_2\text{H}\) versus \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\)
   b. \(\text{CH}_3\text{CO}_2\text{H}\) versus \(\text{CH}_3\text{CH}_2\text{OH}\)
   c. \(\text{HClO}\) versus \(\text{HBrO}\)
   d. \(\text{ice(\text{CH}_3\text{C}(=\text{O})\text{NH}_2)}\) versus \(\text{CH}_3\text{CH}_2\text{NH}_2\)
   e. \(\text{H}_3\text{AsO}_4\) versus \(\text{H}_3\text{AsO}_3\)

2. The stability of the conjugate base is an important factor in determining the strength of an acid. Which would you expect to be the stronger acid in aqueous solution—\((\text{C}_6\text{H}_5\text{NH}_3^{\text{+}})\) or \((\text{NH}_4^{\text{+}})\)? Justify your reasoning.

3. Explain why \(\text{H}_2\text{Se}\) is a weaker acid than \(\text{HBr}\).

4. Arrange the following in order of decreasing acid strength in aqueous solution: \(\text{H}_3\text{PO}_4\), \(\text{CH}_3\text{PO}_3\text{H}_2\), and \(\text{HClO}_3\).

5. Arrange the following in order of increasing base strength in aqueous solution: \(\text{ice(\text{CH}_3\text{S}^-)}\), \(\text{OH}^-\), and \(\text{CF}_3\text{S}^-\).

6. Arrange the following in order of increasing acid strength in aqueous solution: \(\text{HClO}_2\), \(\text{HNO}_2\), and \(\text{HNO}_3\).

7. Do you expect \(\text{H}_2\text{SO}_3\) or \(\text{H}_2\text{SeO}_3\) to be the stronger acid? Why?

8. Give a plausible explanation for why \(\text{H}_3\text{O}\text{H}_3\) is a stronger acid than \(\text{H}_3\text{O}\text{H}_1\) in aqueous solution. Do you
expect \(\text{CHCl}_2\text{CH}_2\text{OH}\) to be a stronger or a weaker acid than \(\text{CH}_3\text{OH}\)? Why?

9. Do you expect \(\text{Cl}_2\text{NH}\) or \(\text{NH}_3\) to be the stronger base in aqueous solution? Why?

---

**Conceptual Answers**

1. 
   
a. The most important factor in determining the stronger acid is considering the inductive effect. Chlorine is an electron-withdrawing group. It pulls electron density away from the compound by means of the inductive effect through the sigma bond. In considering the conjugate base of \(\text{CH}_3\text{CCl}_2\text{CH}_2\text{CO}_2\text{H}\), Chlorine absorbs some of the electron density or excess negative charge on the oxygen atom. This causes the C bonded to the attached Chlorine atoms to be partially positive. The conjugate base of \(\text{CH}_3\text{CCl}_2\text{CH}_2\text{CO}_2\text{H}\) is more stable, thus more acidic than the conjugate base of \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\).

   b. The most important factor in determining the stronger acid is knowing the \(pK_a\) values for functional groups. The \(pK_a\) of alcohol is about 16 while the \(pK_a\) of a carboxylic acid is about 5. Therefore, \(\text{CH}_3\text{CO}_2\text{H}\) is more acidic than \(\text{CH}_3\text{CH}_2\text{OH}\).

   c. The most important factor in determining the stronger acid is electronegativity. The chlorine atom is more electronegative than the bromine atom, therefore \(\text{HClO}\) is more acidic than \(\text{HBrO}\).

   d. The most important factor in determining the stronger acid is considering resonance. The \(\text{CH}_3\text{C}(=\text{O})\text{NH}_2\) has a resonance which increases the stability of the conjugate base (therefore increasing acidity) because the negative charge can be delocalized. Thus, \(\text{CH}_3\text{C}(=\text{O})\text{NH}_2\) is more acidic than \(\text{CH}_3\text{CH}_2\text{NH}_2\).

   e. The most important factor in determining the stronger acid is considering oxidation states on the central nonmetal. \(\text{H}_3\text{AsO}_4\) has an oxidation state of +5 which is larger and thus more acidic than \(\text{H}_3\text{AsO}_3\) which has an oxidation state of +3.

2. \(\text{CF}_3\text{S}^- < \text{CH}_3\text{S}^- < \text{OH}^-\) (strongest base)

3. \(\text{H}_2\text{Se}\) is a weaker acid than \(\text{HBr}\) because \(\text{Br}^-\) is more electronegative than \(\text{Se}^-\) thus more stable.

4. \(\text{HClO}_3 > \text{CH}_3\text{PO}_3\text{H}_2 > \text{H}_3\text{PO}_4\)

   This is because \(\text{H}_3\text{PO}_4\) is a polyprotic acid which contains more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus, acid strength decreases with the loss of subsequent protons, and, correspondingly, the \(pK_a\) increases which indicate it is the most basic. The conjugate base of \(\text{ClO}^-(3^-)\) has a much smaller charge to volume ratio, thus most stable and acidic.
5. \(\text{CF}_3\text{S}^-<\text{OH}^-<\text{CH}_3\text{S}^-\)

\(\text{CF}_3\text{S}^-\) is the most acidic because of the three electronegative Fluorines. \(\text{OH}^-\) is the strongest base in water. Thus, \(\text{CH}_3\text{S}^-\) is in between these aqueous solutions.

6. \(\text{HNO}_2<\text{HClO}_2<\text{HNO}_3\)

\(\text{HNO}_3\) has resonance stabilization, therefore it is the most acidic. Between \(\text{HClO}_2\) and \(\text{HNO}_2\), \(\text{Cl}\) is the most electronegative therefore \(\text{HClO}_2\) is more acidic than \(\text{HNO}_2\).

7. I expect \(\text{H}_2\text{SO}_3\) to be the stronger acid because it is more electronegative or has greater attraction which means it'll be less inclined to share their electrons with a proton.

8. \(\text{CF}_3\text{OH}\) is a stronger acid than \(\text{CH}_3\text{OH}\) in aqueous solution because \(\text{F}\) is more electronegative than \(\text{H}\).

9. It would be expected that \(\text{NH}_3\) be a stronger base than \(\text{Cl}_2\text{NH}\) because it is electronegative due to the two \(\text{Cl}\) atoms.

16.11: Lewis Acids and Bases

Problems

1. Identify the nature of each of the following as either a Lewis Acid or a Lewis Base:
   a. \(\text{NH}_3\)
   b. \(\text{Ag}^+\)
   c. \(\text{Ni}^{2+}\)
   d. \(\text{Pt}^{4+}\)
   e. \(\text{H}_2\text{O}\)
   f. \(\text{SO}_2\)

2. Explain why \(\text{SiF}_4\) can act as a Lewis Acid.

3. Identify the nature of each of the following as either a Lewis Acid or a Lewis Base:
   a. \([\text{Fe(CN)}_6]^{3-}\)
   b. \([\text{Ni(NH}_3)_6]^{2+}\)
   c. \([\text{CdBr}_4]^{2-}\)

4. What is the product of the reaction of \(\text{CO}_2 + \text{OH}^- \rightarrow \) ?

5. In the reactions below, which is the Lewis Acid and/or which is the Lewis Base?
   a. \(\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+\)
   b. \(\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{O}^+\)
6. In the complex ion, \([PtCl_6]^{2-}\) which is the Lewis Acid and which is the Lewis base?

7. The reaction of \((AgCl) + (NH_3)\) produces what complex ion?

---

**Solutions**

1. 
   a. \((NH_3)\) is a Lewis base because nitrogen has a lone pair of electrons to "donate."
   b. \((Ag^+)(+)\) is a Lewis acid because it has an unfilled octet and thus is able to accept a pair of electrons.
   c. \((Ni^{+}(+)\) is a Lewis acid because it has an unfilled octet and thus is able to accept a pair of electrons.
   d. \((Pt^{4+}(+)\) is a Lewis acid because it has an unfilled octet and thus is able to accept a pair of electrons.
   e. \((H_2O)\) is a Lewis base because oxygen has two lone pairs of electrons to "donate."
   f. \((SO_2)\) is a Lewis acid because sulfur has an unfilled octet and thus is able to accept a pair of electrons.

2. \((SiF_4)\) has a central Silicon Atom which can **expand its octet** to 12 (compared to the typical 8) so that it forms \([SiF_6]^{2-}\).

3. 
   a. Lewis Acid: \((Fe^{3+})\), Lewis Base: \((CN^-)\)
   b. Lewis Acid: \((Ni^{2+})\), Lewis Base: \((NH_3)\)
   c. Lewis Acid: \((Cd^{2+})\), Lewis Base: \((Br^-)\)

4. This reaction forms a bicarbonate ion. \((CO_2 + OH^- \rightarrow O--COH=O)\).

5. 
   a. Lewis Acid: \((H^+)\), Lewis Base: \((NH_3)\)
   b. Lewis Acid: \((H^+)\), Lewis Base: \((H_2O)\)

6. \((Pt^{4+})\) is the Lewis acid and \((Cl^-)\) is the Lewis base.

7. \((AgCl + 2\,(NH_3) \rightarrow [Ag(NH_3)_2]^+ + Cl^-)\)

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**Conceptual Problems**

1. Construct a table comparing how \(OH^-\), \(NH_3\), \(H_2O\), and \(BCl_3\) are classified according to the Arrhenius, the Brønsted–Lowry, and the Lewis definitions of acids and bases

2. Describe how the proton \((H^+)\) can simultaneously behave as an Arrhenius acid, a Brønsted–Lowry acid, and
a Lewis acid.

3. Would you expect aluminum to form compounds with covalent bonds or coordinate covalent bonds? Explain your answer.

4. Classify each compound as a Lewis acid or a Lewis base and justify your choice.
   
a. \(\text{AlCl}_3\)
   
b. \(\text{CH}_3\text{N}\)
   
c. \(\text{IO}_3^-\)

5. Explain how a carboxylate ion \((\text{RCO}_2^-)\) can act as both a Brønsted–Lowry base and a Lewis base.

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**Conceptual Answers**

1. | Arrhenius Acid | Arrhenius Base | Brønsted–Lowry Acid | Brønsted–Lowry Base | Lewis Acid | Lewis Base |
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</thead>
<tbody>
<tr>
<td>(\text{OH}^-)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>(\text{NH}_3)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
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<tr>
<td>(\text{H}_2\text{O})</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>(\text{BCl}_3)</td>
<td>X</td>
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</tbody>
</table>

An Arrhenius acid is a molecule that when dissolved in water it will donate an \(\text{H}^+\) in solution.

An Arrhenius base is a molecule that when dissolved in water it will donate an \(\text{OH}^-\) in solution.

A Brønsted–Lowry acid is a molecule that when dissolved in a solution it will donate an \(\text{H}^+\) in solution.

A Brønsted–Lowry base is a molecule that when dissolved in a solution it will donate an atom or ion capable of accepting or bonding to a free proton in solution.

A Lewis acid is an atom or molecule that accepts an electron pair.
A Lewis base is an atom or molecule that donates an electron pair.

2. The proton $(H^+)$ can simultaneously behave as an Arrhenius acid because when it is dissolved in water it will donate itself. $(H^+ + H_2O \rightleftharpoons H_3O^+)$

The proton $(H^+)$ can simultaneously behave as a Brønsted–Lowry acid because when it is dissolved in solution it will donate itself.

$(H^+ + B^- \rightleftharpoons HB)$

The proton $(H^+)$ can simultaneously behave as a Lewis acid as it can accept an electron pair.

$(H^+ + B^- \rightleftharpoons HB)$

3. It is expected that Aluminum forms a coordinate covalent bond as it can participate in a Lewis acid and a Lewis base interaction. For example $(Al^{3+} + H_2O \rightleftharpoons [Al(OH_2)_{6}]^{3+})$

4. 
   a. $(AlCl_3)$ is a Lewis as $(Al)$ can accept an electron pair.
   b. $(CH_3N)$ is a Lewis base as $(N)$ can donate an electron pair.
   c. $(IO_3^-)$ is a Lewis base as $(I)$ can donate an electron pair.

5. The carboxylate ion $(RCO_2^-)$ can act as Brønsted–Lowry base because when dissolved in a solution the electron rich $(O)$ is capable of accepting a proton. The carboxylate ion $(RCO_2^-)$ can act as a Lewis base because the electron rich $(O)$ can donate an electron pair.

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**Numerical Problems**

1. In each reaction, identify the Lewis acid and the Lewis base and complete the reaction by writing the products(s).

   a. $(CH_3)_2O + AlCl_3$
   b. $SnCl_4 + 2 Cl^-$

2. Use Lewis dot symbols to depict the reaction of BCl$_3$ with dimethyl ether $[(CH_3)_2O]$. How is this reaction similar to that in which a proton is added to ammonia?

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**Answer**

1. 
   a. The Lewis acid is $(AlCl_3)$ and the Lewis base is $(CH_3)_{2}O)$. 

\((\text{CH}_3)_2\text{O} + \text{AlCl}_3 \rightleftharpoons \text{AlCl}_3 \cdot \text{O(\text{CH}_3)}_2\)\\
b. The Lewis acid is \((\text{SnCl}_4)\) and the Lewis base is \((\text{Cl}^-)\).
\((\text{SnCl}_4 + 2\text{Cl}^- \rightleftharpoons \text{SnCl}_6^{2-})\)

2.
\((\text{BCl}_3 + (\text{CH}_3)_2\text{O} \rightleftharpoons \text{BCl}_3 \cdot \text{O(\text{CH}_3)}_2)\)

This reaction is similar to that in which a proton is added to ammonia as it also involves a Lewis acid and a Lewis base interaction.