CH 223 Chapter Fourteen Concept Guide

1. Identifying Brønsted-Lowry Acids and Bases

Problem

Identify the Brønsted-Lowry acid (a reactant) and its conjugate base (a product) in each of the following reactions:

(a) $HNO_3(l) + H_2O(l) \rightleftharpoons H_3O^+ + NO_3^-$

(b) $H_3O^+ + HS^- \rightleftharpoons H_2S(aq) + H_2O(l)$

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

Solution

The Brønsted-Lowry acids are the species that donates the proton in each reaction. In the above reactions, the Brønsted-Lowry acids are:

(a) HNO_3
(b) H_3O^+
(c) HF

The conjugate base for each acid is the species formed by the removal of a proton from the acid:

(a) NO_3^-
(b) H_2O
(c) F^-

2. Ion Product Constant of Water

Question

What is the concentration of OH^- in a 0.04 M HCl solution?

Approach

Because HCl is a strong acid and is 100% ionized, the H_3O^+ concentration is equivalent to the molarity of the HCl solution, 0.04 M. To solve this problem, use the relationship between the concentrations of H_3O^+ and OH^- and water: $K_w = [H_3O^+]\,[OH^-]$.

Solution

$K_w = [H_3O^+]\,[OH^-]$

Solving this for OH^- and substituting the known values of K_w and $[H_3O^+]$ gives

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{0.04} = 3 \times 10^{-13}\ \mathrm{M}$$

3. pH and pOH

Question

What are the pH and $[H_3O^+]$ of a solution that has $[OH^-] = 2.50 \times 10^{-5}$ M?

Solution

$pOH = -\log [OH^-] = - \log (2.50 \times 10^{-5} \text{ M}) = 4.60$

$pH = 14.00 - pOH = 14.00 - 4.60 = 9.40$

$\log [H_3O^+] = - pH = -9.40$

$[H_3O^+] = 3.98 \times 10^{-10}$

4. K_a-K_b Relationship

Problem

The value of K_a for hydrocyanic acid (HCN) is 6.2×10^{-10}. Calculate the value of K_b for the conjugate base.

Solution

$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+ + CN^-$

In this reaction, the conjugate base is the cyanide ion, CN^-. The value of K_b for the reaction of CN^- as a base with water is:

$CN^- + H_2O(l) \rightleftharpoons HCN(aq) + OH^-$

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$

The value of K_b for the conjugate base, CN^-, is 1.6×10^{-5}.

5. Calculating pH

Question

If the hydronium ion concentration in vinegar is 1.8×10^{-3}, what is its pH?

Solution

$pH = - \log [H_3O^+] = - \log (1.8 \times 10^{-3}) = 2.74$

6. Calculating pH

Problem

Find the pH of a 0.052 M hypobromous acid (HBrO) solution.

$HBrO(aq) + H_2O(l) \rightleftharpoons H_3O^+ + BrO^-$ $K_a = 2.2 \times 10^{-9}$

Approach

Write the corresponding equilibrium expression and identify what is unknown. Make a table to include the chemical equation, initial concentrations, changes in concentration, and equilibrium concentrations. Substitute the equilibrium concentrations from the table into the equilibrium expression and solve for the unknown (x). If an approximation was made, remember to check for validity. Finally, answer the question in the problem using some form of the value of x.

Solution

The unknown is $[H_3O^+]$ at equilibrium. Letting $x = [H_3O^+]$,

	$HBrO(aq)$	**H_3O^+**	**$+ BrO^-$**
Initial	0.052 M	0 M	0 M
Change	- x	+ x	+ x
Equilibrium	0.052 - x	x	x

$$K_a = \frac{[H_3O^+][BrO^-]}{[HBrO]} = \frac{(x)(x)}{(0.052 - x)} = 2.2 \times 10^{-9}$$

$$\text{If } \frac{K_a[\text{initial}]}{1000}, \text{ then } K_a = \frac{x^2}{[\text{initial}] - x} \cong \frac{x^2}{[\text{initial}]}$$

Assuming that (0.052 - x) is approximately equal to 0.052,

$x^2 = (0.052)(2.2 \times 10^{-9}) = 1.1 \times 10^{-10}$ M

$x = 1.1 \times 10^{-5}$ M

$pH = - \log [H_3O^+] = \log (1.1 \times 10^{-5}) = 4.95$

The pH of this solution is 4.95.

7. Predicting the pH of Salt Solutions

Problem

Predict whether each salt listed below has a pH greater then, less than, or equal to 7.

(a) $FeCl_3$

(b) NH_4NO_3

(c) Na_2HPO_4

Solution

(a) Fe^{3+} ion is acidic and Cl^- ion is neutral. Therefore $FeCl_3$ is acidic, and the pH is less than 7.

(b) NH_4^+ is acidic and NO_3^- is neutral. Therefore, NH_4NO_3 is acidic, and the pH is less than 7.

(c) Na^+ is neutral and HPO_4^{2-} is basic. Therefore, Na_2HPO_4 is basic, and the pH is greater than 7.

8. Common Ion Effect

Question

What is the pH of a solution that is 0.10 mol/L in NH_3 and 0.10 mol/L in NH_4NO_3?

$K_b = 1.8 \times 10^{-5}$ for NH_3 at 23 °C.

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

Solution

The ammonia-water equilibrium controls the pH.

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

Let x = OH^-. The ammonium ion concentration at equilibrium is the addition of the amount formed by the above reaction to the amount added as ammonium nitrate. The ammonium nitrate is soluble and a strong electrolyte, thus adding to the total ammonium ion concentration.

	$NH_3(aq) + H_2O(l) \rightleftharpoons$	NH_4^+ +	OH^-
Initial	0.10	0.10	0
Change	- x	+ x	+ x
Equilibrium	0.10 - x	0.10 + x	x

Substituting these values into the equilibrium constant expression:

$$K_b = \frac{(0.10 + x)(x)}{(0.10 - x)} = 1.8 \times 10^{-5}$$

Assuming that x is small relative to the initial NH_3 and NH_4^+ concentrations, this equation becomes

$$K_b = \frac{(0.10)(x)}{(0.10)} = 1.8 \times 10^{-5}$$

$OH^- = x = 1.8 \times 10^{-5}$ mol/L

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The approximation is valid. The pH and pOH of the solution can be calculated by:

$pOH = -\log [OH^-] = - \log (1.8 \times 10^{-5}) = 4.74$

$pH = 14.00 - pOH = 14.00 - 4.74 = 9.26$

The pH of the solution is 9.26, indicating that it is an alkaline solution. For comparison, the pH of a 0.1 mol/L solution of NH_3 is 11.1, thus the alkalinity of the solution has decreased due to the addition of the NH_4^+ ion.

9. Calculate pK_a from K_a

Problem

Calculate pK_a for the following acids:

(a) HSO_4^-, $K_a = 1.2 \times 10^{-2}$

(b) HCN, $K_a = 4.0 \times 10^{-10}$

(c) phenol, C_6H_5OH, $K_a = 1.3 \times 10^{-10}$

Approach

$pK_a = - \log K_a$

Solution

(a) HSO_4^-: $pK_a = - \log (1.2 \times 10^{-2}) = 1.92$

(b) HCN: $pK_a = - \log (4.0 \times 10^{-10}) = 9.40$

(c) phenol, C_6H_5OH: $pK_a = - \log (1.3 \times 10^{-10}) = 9.89$

10. Using the Henderson-Hasselbalch Equation

Question

If 3.00 g of benzoic acid ($C_6H_5CO_2 H$) and 2.00 g of sodium benzoate ($NaC_6H_5CO_2$) are dissolved in enough water to make 1.50 L of solution, what is the pH of this solution? $K_a = 6.3 \times 10^{-5}$ for benzoic acid.

Approach

First, calculate the pK_a of the acid. Then, calculate the concentrations of the benzoic acid and its conjugate base, benzoate ion. Finally, find the pH of the solution using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

Solution

The pK_a of sodium benzoate is:

$pK_a = - \log (6.3 \times 10^{-5}) = 4.20$

The concentrations of benzoic acid and benzoate ion from sodium benzoate are:

$$3.00 \text{ g benzoic acid} \left(\frac{1 \text{ mol}}{122.1 \text{ g}} \right) = 0.0245 \text{ mol benzoic acid}$$

$$2.00 \text{ g sodium benzoate} \left(\frac{1 \text{ mol}}{144.1 \text{ g}} \right) = 0.0139 \text{ mol sodium benzoate}$$

The solution is 1.50 L in volume, therefore the concentration of benzoic acid is:

$$\frac{0.0245\ \text{mol}}{1.50\ \text{L}} = 0.0164\ \text{mol/L}$$

Similarly, the concentration of sodium benzoate is 0.00927 mol/L. Using the Henderson-Hasselbalch equation, the pH is calculated by:

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

$$\text{pH} = 4.20 + \log\frac{0.00927}{0.0164} = 3.95$$

The pH of the solution is 3.95, which is lower than the pK_a because the ratio of sodium benzoate to benzoic acid was less than 1.

11. Common Ion Effect: Preparing Buffers

Question

What ratio of $[CHO_2^{1-}]/[CHO_2H]$ (base/acid) is needed to make a sodium formate-formic acid buffer solution having a pH of 4.80? $K_a = 1.77 \times 10^{-4}$ for formic acid, CHO_2H.

$CHO_2H(aq) + H_2O(l) \rightleftarrows H_3O^+ + CHO_2^-$

Solution

A pH of 4.80 corresponds to $[H_3O^+] = 1.58 \times 10^{-5}$ mol/L. The ratio of acid to common ion in a buffer is given as:

$$[H_3O^+] = \frac{[CHO_2H]}{[CHO_2^-]} \times 1.77 \times 10^{-4} = 1.58 \times 10^{-5}\ \text{mol/L}$$

$$\frac{[CHO_2^-]}{[CHO_2H]} = \frac{1.77 \times 10^{-4}}{1.58 \times 10^{-5}} = 11.2$$

Therefore, the $[CHO_2^-]/[CHO_2H]$ ratio must be 11.2 to 1 to attain a solution having a pH of 4.80 with this buffer system. For example, if 1 mol/L CHO_2 H is used, the solution must be 11.2 mol/L in sodium formate.

12. Titration of a Strong Acid by a Strong Base

Problem

Calculate the pH of a solution in which 10.0 mL of 0.100 mol/L NaOH is added to 20.0 mL of 0.100 mol/L HCl.

Approach

First, write the reaction for NaOH and HCl. Then, calculate the number of moles of each reactant. To find $[H^+]$, calculate the number of moles of excess H^+, and divide by the total volume of solution. Finally, calculate the pH from $[H^+]$.

Solution

These reactants are strong electrolytes, thus this problem is essentially one of stoichiometry. The reaction is:

$H^+ + OH^- \rightarrow H_2O(l)$

Calculate the number of moles of each reactant by multiplying the volume (in liters) of each solution by its molar concentration.

Moles H^+ = 0.0200 L * 0.100 mol/L = 0.00200 mol

Moles OH^- = 0.0100 L * 0.100 mol/L = 0.00100 mol

Since all of the OH^- reacts, the excess H^+ = 0.00200 mol - 0.00100 mol = 0.00100 mol H^+. With this number, we can now calculate the concentration of H^+ by dividing this amount by the total volume of solution:

$$[H^+] = \frac{0.00100 \text{ mol } H^+}{0.0200 \text{ L} + 0.0100 \text{ L solution}} = 0.0333 \text{ mol/L } H^+$$

The pH of the solution is:

$\text{pH} = -\log[H^+] = -\log(0.0333) = 1.48$

13. Titration of Weak Acid by a Strong Base

Problem

Calculate the molar concentration of nicotinate ion at the equivalence point when 20. mL of 0.10 mol/L nicotoinic acid, $HC_6H_4NO_2$, is titrated with 0.10 mol/L sodium hydroxide, NaOH. $K_a = 1.4 \times 10^{-5}$ for nicotinic acid.

$C_6H_4NO_2^- + H_2O(l) \rightleftharpoons HC_6H_4NO_2(aq) + OH^-$

Approach

At the equivalence point, equal molar amounts of nicotinic acid and sodium hydroxide react to give a solution of sodium nicotinate. The molar amount of ion equals the initial amount of acid, therefore we can calculate the moles of nicotinate ion. We can then calculate the concentration of nicotinate ion by dividing the number of moles of nicotinate ion by the total solution volume.

Solution

Assuming the reaction is complete, 20. mL of 0.10 mol/L NaOH is needed to react with 20. mL of 0.10 mol/L nicotinic acid. The molar amount of nicotinate ion formed equals the initial amount of nicotinic acid:

$$\text{Moles of nicotinate ion} = \frac{0.020 \text{ L solution} \times 0.10 \text{ mol } C_6H_4NO_2^-}{1 \text{ L solution}} = 0.0020 \text{ mol } C_6H_4NO_2^-$$

The total volume of the solution is 40. mL assuming there is no loss in volume due to mixing. To find the molar concentration of nicotinate ion, divide the molar amount of nicotinate ion by the total solution volume:

$$\text{Molar concentration of nicotinate ion} = \frac{0.020 \text{ mol } C_6H_4NO_2^-}{0.040 \text{ L solution}} = 0.050 \text{ mol/L}$$

14. Titration of Weak Acid by a Strong Base

Question

Using the information in question 3, calculate the pH of the solution at the equivalence point.

Solution

The K_a for nicotinic acid is 1.4 x 10^{-5}, therefore K_b for nicotinate ion (the conjugate base) is:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-5}} = 7.1 \times 10^{-10}$$

Let x = $[OH^-]$.

	$HC_6H_4NO_2$(aq) + OH^-( )		$C_6H_4NO_2^-$ + H_2O(aq)
Initial	0.050	0	0
Change	- x	+ x	+ x
Equilibrium	0.050 - x	x	x

Substituting into the equilibrium equation, gives

$$K_b = \frac{[HC_6H_4NO_2][OH^-]}{[C_6H_4NO_2^-]} = \frac{x^2}{0.050 - x}$$

$$\text{If } K_a < \frac{[\text{initial}]}{1000}, \text{ then } K_a = \frac{x^2}{[\text{initial}]} \times \cong \frac{x^2}{[\text{initial}]}$$

Assuming that (0.050-x) is approximately equal to 0.050,

$$K_b = \frac{[HC_6H_4NO_2][OH^-]}{[C_6H_4NO_2^-]} = \frac{x^2}{0.050} = 7.1 \times 10^{-10}$$

$[OH^-]$ = x = 6.0 x 10^{-6}

Note that x is very small compared to 0.050, so our assumption is valid. $[OH^-]$ is 6.0 x 10^{-6} mol/L. The pH can now be calculated:

pH = 14.00 - pOH = 14.00 - (- log $[OH^-]$) = 14.00 + log (6.0 x 10^{-6}) = 8.78

The pH of the solution is **8.78**. The solution pH of 8.78 is greater than 7, meaning it is basic. This is expected because the result of a reaction between a weak acid and a strong base is a weak base, and in this case, nicotinate ion.