Acid-Base Equilibrium

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Introduction to Aqueous Acids

- Acids: taste sour and cause certain dyes to change color.

Introduction to Aqueous Acids

Introduction to Aqueous Bases

- Bases: taste bitter, feel soapy and cause certain dyes to turn color.

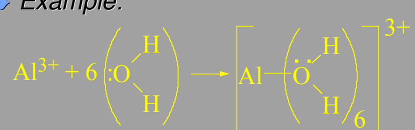
Introduction to Aqueous Bases

Models of Acids and Bases

- Arrhenius: Acids produce H^+ & bases produce OH^- ion in aqueous solutions .
- Brønsted-Lowry: Acids are H^+ donors & bases are proton acceptors.
  - $HCl + H_2O \rightarrow Cl^- + H_3O^+$
    acid base

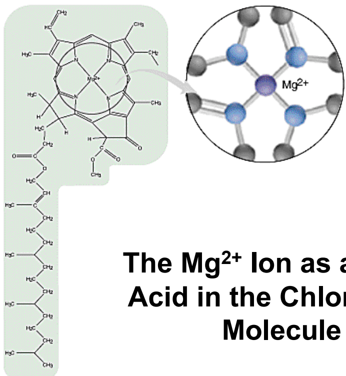
Lewis Acids and Bases

- Lewis Acid: electron pair acceptor
- Lewis Base: electron pair donor
- Example:



Lewis Acids and Bases

Lewis Acid-Base Theory



The Mg^{2+} Ion as a Lewis Acid in the Chlorophyll Molecule

Conjugate Acid/Base Pairs

- $HA(aq) + H_2O(l) \rightarrow H_3O^+(aq) + A^-(aq)$

acid 1	base 2	conj acid 2	conj base 1

- conjugate acid: formed when the proton is transferred to the base.
- conjugate base: everything that remains of the acid molecule after a proton is lost.

Click to reveal the conjugate acid and the conjugate base of each species.

Conjugate acid		Conjugate base
	NH_3	
	H_2O	
	$H_2PO_4^-$	
	OH^-	

Strong & Weak Acids: Dissociation Constant (K_a)

- $HA(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + A^-(aq)$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{[HA]}$$

- $HA(aq) \leftrightarrows H^+(aq) + A^-(aq)$

Acid Strength

Strong Acid:

- *Equilibrium position lies far to the right. (HNO_3); Ka >> 1*
- *Produces a conjugate base. (NO_3^-) and a conjugate acid which are weaker than the starting acid and base (H_2O).*

Acid Strength

Strong Acids:

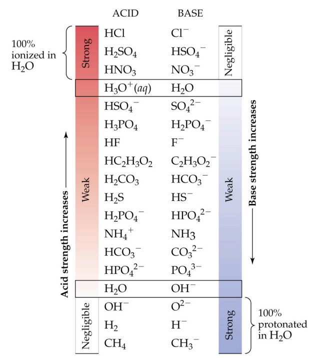
Strong Acid	Formula
Hydrochloric	HCl
Hydrobromic	HBr
Hydroiodic	HI
Nitric	HNO_3
Chloric	$HClO_3$
Perchloric	$HClO_4$
Sulfuric *	H_2SO_4

Acid Strength

(continued)

Weak Acid:

- *Equilibrium lies far to the left. (CH_3COOH); Ka < 1*
- *Yields a stronger (relatively strong) conjugate base than water. (CH_3COO^-)*



Weak Acids

- *Weak acids are only partially ionized in solution.*

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad or \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

- *K_a is the acid dissociation constant.*

Percent Ionization

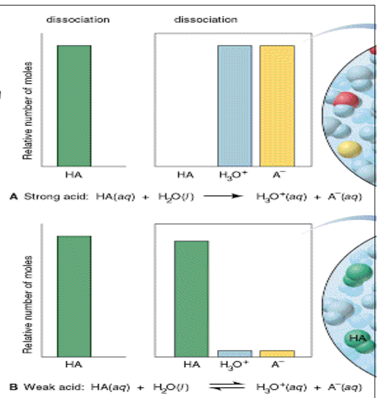
- *Percent ionization is a way to assess relative acid strengths.*
- *For the reaction*

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$\%\ \text{ionization} = \frac{[H^+]_{eqm}}{[HA]_0} \times 100$$

- *Percent ionization relates the $H_3O^+(aq)$ equilibrium concentration, $[H^+]_{eqm}$, to the initial $HA(aq)$ concentration, $[HA]_0$.*

The Extent of Dissociation for Strong and Weak Acids

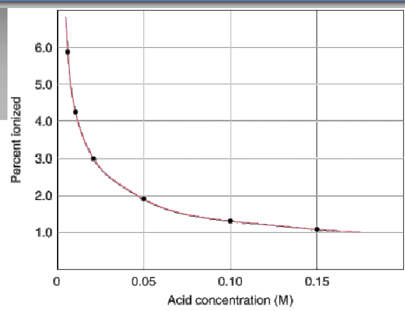


Weak Acids

- *The higher percent ionization, the stronger the acid.*
- *Percent ionization of a weak acid decreases as the molarity of the solution increases.*
- *For acetic acid, 0.05* M *solution is 2.0 % ionized whereas a 0.15* M *solution is 1.0 % ionized.*

Weak Acids

Percent Ionization



QUESTION

Nitric acid, HNO_3, is considered to be a strong acid whereas nitrous acid, HNO_2, is considered to be a weak acid. Which of the statements here is fully correct?

1. Nitric acid has an aqueous equilibrium that lies far to the right and NO_3^- is considered a weak conjugate base.
2. Nitric acid has a stronger conjugate base than nitrous acid.
3. The dissociation of nitrous acid compared to an equal concentration of nitric acid produces more H^+.
4. The equilibrium of nitrous acid lies far to the left and the conjugate base is weaker than the conjugate base of nitric acid.

Bases

- *"Strong" and "weak" are used in the same sense for bases as for acids.*
- *Strong = complete dissociation, K_b >> 1 (concentration of hydroxide ion in solution)*

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

- $NaOH(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq)$

Bases

(continued)

- *Weak bases have very little dissociation, K_b < 1 (little ionization with water)*
- $CH_3NH_2(aq) + H_2O(l) \leftrightarrows CH_3NH_3^+(aq) + OH^-(aq)$
- *How conductive is NaOH(aq) vs morphine, $C_{17}H_{19}NO_3$ (aq)?*

QUESTION

Aniline, $C_6H_5NH_2$, was isolated in the 1800s and began immediate use in the dye industry. What is the formula of the conjugate acid of this base?

1. $C_6H_5NH_2^+$
2. $C_6H_5NH_3^+$
3. $C_6H_5NH^-$
4. $C_6H_5NH^+$

Acid-Base Strengths

Strong Acid:

$$HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$$

Strong Base:

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

Acid-Base Strengths

Weak Acid:

$$HC_2H_3O_2\,(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

Weak Base:

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

Water as an Acid and a Base
Self-ionization

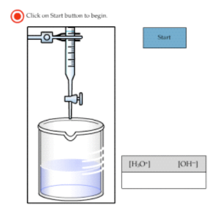
Water as an Acid and a Base

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

- *Water is amphoteric (it can behave either as an acid or a base).*
  - $H_2O + H_2O \rightarrow H_3O^+ + OH^-$

    acid 1   base 2   conj acid 2   conj base 1
  - $K_w = 1 \times 10^{-14}$ *at 25°C*

Water as an Acid and a Base
Self-ionization



The pH Scale

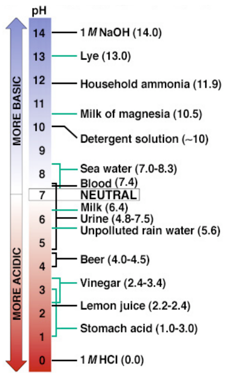
- $pH \approx -\log[H^+] \approx -\log[H_3O^+]$
- *pH in water ranges from 0 to 14.*

  $K_w = 1.00 \times 10^{-14} = [H^+]\,[OH^-]$

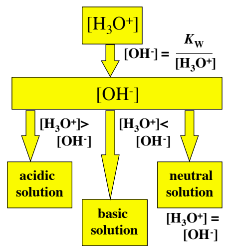
  $pK_w = 14.00 = pH + pOH$
- *As pH rises, pOH falls (sum = 14.00).*
- *There are no theoretical limits on the values of pH or pOH. (e.g. pH of 2.0 M HCl is -0.301)*

The Relations Among $[H_3O^+]$, pH, $[OH^-]$, and pOH

		$[H_3O^+]$	pH	$[OH^-]$	pOH
MORE BASIC ↑		1.0×10^{-15}	15.00	1.0×10^{1}	−1.00
		1.0×10^{-14}	14.00	1.0×10^{0}	0.00
		1.0×10^{-13}	13.00	1.0×10^{-1}	1.00
	BASIC	1.0×10^{-12}	12.00	1.0×10^{-2}	2.00
		1.0×10^{-11}	11.00	1.0×10^{-3}	3.00
		1.0×10^{-10}	10.00	1.0×10^{-4}	4.00
		1.0×10^{-9}	9.00	1.0×10^{-5}	5.00
		1.0×10^{-8}	8.00	1.0×10^{-6}	6.00
	NEUTRAL	1.0×10^{-7}	7.00	1.0×10^{-7}	7.00
MORE ACIDIC ↓		1.0×10^{-6}	6.00	1.0×10^{-8}	8.00
		1.0×10^{-5}	5.00	1.0×10^{-9}	9.00
		1.0×10^{-4}	4.00	1.0×10^{-10}	10.00
	ACIDIC	1.0×10^{-3}	3.00	1.0×10^{-11}	11.00
		1.0×10^{-2}	2.00	1.0×10^{-12}	12.00
		1.0×10^{-1}	1.00	1.0×10^{-13}	13.00
		1.0×10^{0}	0.00	1.0×10^{-14}	14.00
		1.0×10^{1}	−1.00	1.0×10^{-15}	15.00



The pH Values of Some Familiar Aqueous Solutions



QUESTION

In a solution of water at a particular temperature the $[H^+]$ may be 1.2×10^{-6} M. What is the $[OH^-]$ in the same solution? Is the solution acidic, basic, or neutral?

1. 1.2×10^{-20} *M*; acidic
2. 1.2×10^{-20} *M*; basic
3. 8.3×10^{-9} *M*; basic
4. 8.3×10^{-9} *M*; acidic

The pH Scale

$[H^+]$	$[OH^-]$	pH	pOH	acidic or basic?
7.5×10^{-3} *M*	*1.3x10⁻¹²*	*2.12*	*11.88*	
2.8x10⁻⁵	3.6×10^{-10} *M*	*4.6*		
5.62x10⁻⁹		8.25		
			5.70	

QUESTION

An environmental chemist obtains a sample of rainwater near a large industrial city. The $[H^+]$ was determined to be 3.5×10^{-6} *M*. What is the pH, pOH, and $[OH^-]$ of the solution?

1. pH = 5.46 ; pOH = 8.54; $[OH^-] = 7.0 \times 10^{-6}$ *M*
2. pH = 5.46 ; pOH = 8.54; $[OH^-] = 2.9 \times 10^{-9}$ *M*
3. pH = 12.56 ; pOH =1.44 ; $[OH^-] = 3.6 \times 10^{-2}$ *M*
4. pH = 8.54; pOH = 5.46; $[OH^-] = 2.9 \times 10^{-9}$ *M*

Conjugates

Some Conjugate Acid–Base Pairs

Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

$K_a \times K_b = ?$

$K_a \times K_b = K_w$

Conjugates

$K_a \times K_b = K_w$

HF
$K_a = 3.5 \times 10^{-4}$

Click to see conjugate base.

What do pK_a and pK_b refer to?

$pK_a + pK_b = ?$

$pK_a + pK_b = pK_w$

QUESTION

TABLE 14.2 Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a*
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloracetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
HOCl	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

↑ Increasing acid strength

Use information on this table to determine which of the following bases would have the weakest conjugate acid:

$OC_6H_5^-$; $C_2H_3O_2^-$; OCl^-; NH_3

1. $OC_6H_5^-$
2. $C_2H_3O_2^-$
3. OCl^-
4. NH_3

Strong vs.Weak Acids
pH Estimations/ Calculations

What are the respective pH values for a 0.100M solution of HCl ($K_a = \infty$) and a 0.100M solution of HF ($K_a = 3.53 \times 10^{-4}$)?

- *What are the respective equilibrium concentrations of H^+ (H_3O^+)?*
- *pH is calculated from the equilibrium concentration of H^+ (H_3O)*
- *Using K_a, and the starting molarity of acid, the equilibrium concentration of H^+ (H_3O^+) can be estimated and then pH)*; Strong acids 100%, ***pH=1.00***, Weak: less than 100%

Strong vs.Weak Acids
pH Estimations/ Calculations

What are the respective pH values for a 0.100M solution of HCl ($K_a = \infty$) and a 0.100M solution of HF ($K_a = 3.53 \times 10^{-4}$)?

- *Using K_a, and the starting molarity of the weak acid, the equilibrium concentration of H^+ (H_3O^+) can be estimated using an ICE approach and then the pH.*

$K_a = [H^+][A^-] / [HA - x] = x^2/(0.100\text{ M} - x)$

$3.53 \times 10^{-4} = x^2/0.100$; estimate @ $x \cong (10^{-5})^{1/2}$ representing the $[H^+]$, taking –log yields a *pH* >2 and <3.

QUESTION

Which of the following correctly compares strength of acids, pH, and concentrations?

1. A weak acid, at the same concentration of a strong acid, will have a lower pH.
2. A weak acid, at the same concentration of a strong acid, will have the same pH.
3. A weak acid, at a high enough concentration more than a strong acid, could have a lower pH than the strong acid.
4. A weak acid, at a concentration below a strong acid, could have a lower pH than a strong acid.

Weak Acids
K_a and Calculating pH

- *Write the balanced chemical equation clearly showing the equilibrium.*
- *Write the equilibrium expression. Use the value for K_a*
- *Let x = $[H^+]$; substitute into the equilibrium constant expression and solve.*
- *Convert $[H^+]$ to pH.*

Equilibrium Concentration Calculations
pH from Initial Concentrations and K_a

What is the pH value for a 0.100M solution of HF ($K_a = 3.53 \times 10^{-4}$)?

$$HF_{(aq)} \rightleftarrows H^+_{(aq)} + F^-_{(aq)}$$

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

Equilibrium Concentration Calculations

$HF_{(aq)} \leftrightarrows H^+_{(aq)} + F^-_{(aq)}$

Concentration (M)	HF	H^+	F^-
Initial	0.100	0	0
Change	0.100-x	+x	+x
Final	0.100-x	x	x

$$K_c = \frac{[H^+][F^-]}{[HF]} = 3.53 \times 10^{-4} = \frac{x^2}{(0.100 - x)}$$

$$3.53 \times 10^{-4}(0.100 - x) = x^2$$

Quadratic:

$0 = x^2 + 3.53 \times 10^{-4}x - 3.53 \times 10^{-5}$

$x = [H^+] = 0.00805\ M$; *pH= 2.09*

Simplified:

$$3.53 \times 10^{-4} = \frac{x^2}{(0.100)}$$

$3.53 \times 10^{-4}(0.100) = x^2$

$x = [3.53 \times 10^{-4}(0.100)]^{1/2}$

$x = [H^+] = 0.00594\ M$; *pH= 2.23*

QUESTION

Butyric acid is a weak acid that can be found in spoiled butter. The compound has many uses in synthesizing other flavors. The K_a of $HC_4H_7O_2$ at typical room temperatures is 1.5×10^{-5}. What is the pH of a 0.20 *M* solution of the acid?

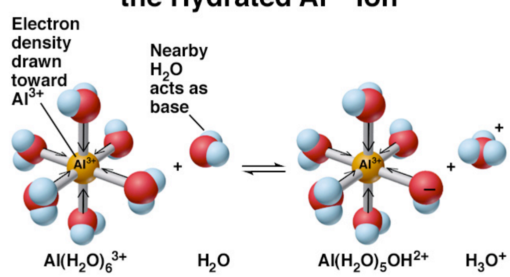
1. 5.52
2. 4.82
3. 2.76
4. –0.70

QUESTION

A 0.35 *M* solution of an unknown acid is brought into a lab. The pH of the solution is found to be 2.67. From this data, what is the K_a value of the acid?

1. 6.1×10^{-3}
2. 1.3×10^{-5}
3. 7.5×10^{-4}
4. 2.1×10^{-3}

Acidic Behavior of the Hydrated Al^{3+} Ion



K_a Values of Some Hydrated Metal Ions at 25°C

Ion	K_a
Fe^{3+} (aq)	6×10^{-3}
Sn^{2+} (aq)	4×10^{-4}
Cr^{3+} (aq)	1×10^{-4}
Al^{3+} (aq)	1×10^{-5}
Be^{2+} (aq)	4×10^{-6}
Cu^{2+} (aq)	3×10^{-8}
Pb^{2+} (aq)	3×10^{-8}
Zn^{2+} (aq)	1×10^{-9}
Co^{2+} (aq)	2×10^{-10}
Ni^{2+} (aq)	1×10^{-10}

QUESTION

The following salts were all placed in separate solutions at the same temperature so that their concentrations were all equal. Arrange them in order from lowest pH to highest pH.

$NaCl$; NH_4NO_3; $Ca(C_2H_3O_2)_2$; $AlCl_3$

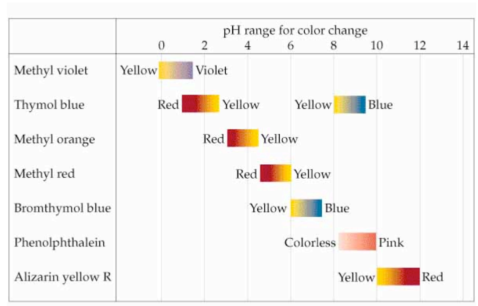
Additional information: K_b for $NH_3 = 1.8 \times 10^{-5}$; K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$; K_a for $Al(H_2O)^{3+} = 1.4 \times 10^{-5}$.

1. $NaCl$; NH_4NO_3; $Ca(C_2H_3O_2)_2$; $AlCl_3$
2. $AlCl_3$; $NaCl$; NH_4NO_3; $Ca(C_2H_3O_2)_2$
3. $AlCl_3$; NH_4NO_3; $NaCl$; $Ca(C_2H_3O_2)_2$
4. NH_4NO_3; $AlCl_3$; $NaCl$; $Ca(C_2H_3O_2)_2$

Indicators

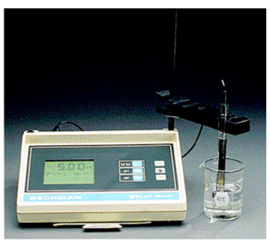
Natural Indicators

Acid-Base Indicators



Methods for Measuring the pH of an Aqueous Solution

(a) pH paper



(b) Electrodes of a pH meter

Structure and Acid-Base Properties

- *Two important factors that effect acidity in binary compounds:*
  - *Bond Polarity (smaller e.n. differences favor higher acidities)*
  - *Bond Strength (weak bonds favor higher acidity: more protons [hydronium ions] in solution)*
  - *Select & explain which is the stronger acid: HBr vs. HF.*

Oxides

- *Acidic Oxides (Acid Anhydrides):*
  - *O–X bond is strong and covalent.*

    SO_2, NO_2, CrO_3
- *Basic Oxides (Basic Anhydrides):*
  - *O–X bond is ionic.*

    K_2O, CaO

Behavior of Salts in Water

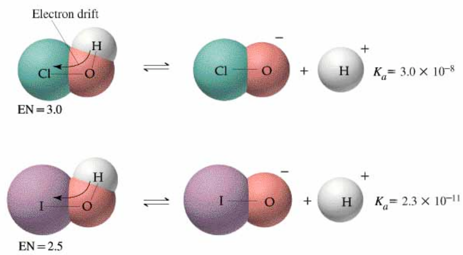
Table 18.8 The Behavior of Salts in Water

Salt Solution (Examples)	pH	Nature of Ions	Ion That Reacts with Water	
Neutral [$NaCl$, KBr, $Ba(NO_3)_2$]	7.0	Cation of strong base Anion of strong acid	None	
Acidic [NH_4Cl, NH_4NO_3, CH_3NH_3Br]	<7.0	Cation of weak base Anion of strong acid	Cation	
Acidic [$Al(NO_3)_3$, $CrCl_3$, $FeBr_3$]	<7.0	Small, highly charged cation Anion of strong acid	Cation	
Basic [CH_3COONa, KF, Na_2CO_3]	>7.0	Cation of strong base Anion of weak acid	Anion	

$LiNO_2$ NH_4Cl $Ca(NO_3)_2$

$MgSO_4$ $AgClO_3$ $CsCN$

Strength of Oxyacids



Strength of Oxyacids

- Name the acids:
  - *HBrO* , $K_a = 2.1 \times 10^{-8}$
  - *HIO* , $K_a = 2.3 \times 10^{-11}$
  - *HClO* , $K_a = 3.0 \times 10^{-8}$
  - $HClO_2$, $K_a = 1.2 \times 10^{-2}$

Is $HBrO_4$ a stronger or weaker acid than $HClO_4$?

QUESTION

- Rank 1.0M solutions of *HBrO, HIO* and *HClO* in order of increasing acidity.

HBrO , $K_a = 2.1 \times 10^{-8}$
HIO , $K_a = 2.3 \times 10^{-11}$
HClO , $K_a = 3.0 \times 10^{-8}$

1) HBrO < HIO < HClO *2) HIO < HBrO < HClO*

3) HClO < HBrO < HIO *4) HIO < HClO < HBrO*

QUESTION

- Rank 1.0M solutions of *HBrO, HIO* and *HClO* in order of increasing pH

HBrO , $K_a = 2.1 \times 10^{-8}$
HIO , $K_a = 2.3 \times 10^{-11}$
HClO , $K_a = 3.0 \times 10^{-8}$

1) HBrO < HIO < HClO *2) HIO < HBrO < HClO*

3) HClO < HBrO < HIO *4) HIO < HClO < HBrO*

Strength of Acids

Acid	Formula	K_a (25°C)
Acetic	CH_3COOH	1.8×10^{-5}
Chloroacetic	$CH_2ClCOOH$	1.4×10^{-3}
Dichloroacetic	$CHCl_2COOH$	3.3×10^{-2}
Trichloroacetic	CCl_3COOH	2×10^{-1}

Strength of Acids

Br-CH_2COOH, I-CH_3COOH, CH_3COOH

- *pKa= 2.69 pKa=3.12 pKa=4.75*

Is chloroacetic acid more or less acidic than bromoacetic acid?

Will its pKa be higher or lower than bromoacetic acid?

QUESTION

- Rank the following acids in order of increasing acidity.

A) Br-CH_2COOH, B) I-CH_3COOH, C) CH_3COOH

pKa= 2.69 pKa=3.12 pKa=4.75

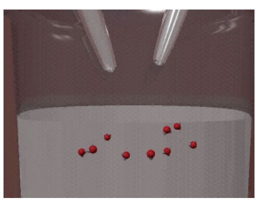
1) A > B > C 2) C > B > A 3) B > C > A

QUESTION

Ascorbic acid, also known as vitamin C, has two hydrogen atoms that ionize from the acid. $Ka_1 = 7.9 \times 10^{-5}$; $Ka_2 = 1.6 \times 10^{-12}$. What is the pH, and $C_6H_6O_6^{2-}$ concentration of a 0.10 *M* solution of $H_2C_6H_6O_6$?

1. 2.55; $[C_6H_6O_6^{2-}] = 0.050$ *M*
2. 2.55; $[C_6H_6O_6^{2-}] = 1.6 \times 10^{-12}$ *M*
3. 1.00; $[C_6H_6O_6^{2-}] = 1.6 \times 10^{-12}$ *M*
4. 5.10; $[C_6H_6O_6^{2-}] = 0.050$ *M*

Neutralization Reactions



Would there be a difference in the titration of HF versus HCl? ….mass wise?…. pH wise?