Acid-Base Equilibrium

Chem 120 Prep

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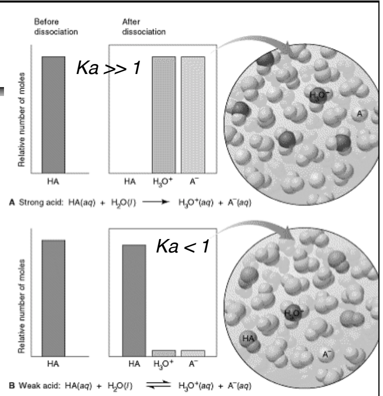
Strong & Weak Acids: Dissociation Constant ($\boldsymbol{K}_a$)

- $HA_{(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + A^-_{(aq)}$

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

- $HA_{(aq)} \leftrightarrows H^+_{(aq)} + A^-_{(aq)}$

The Extent of Dissociation for Strong and Weak Acids



Percent Ionization

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

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

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

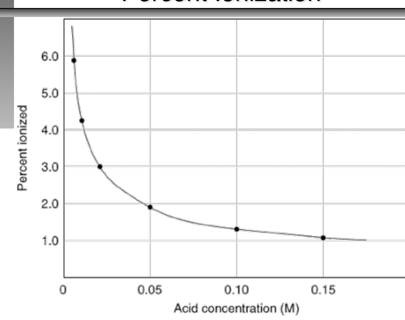
- *Percent ionization relates the* H_3O^+ *(aq) equilibrium concentration,* $[H^+]_{eqm}$*, to the initial* $HA(aq)$ *concentration,* $[HA]_0$.

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

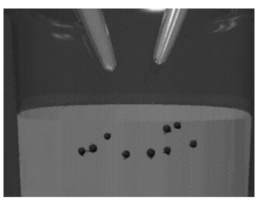
Nitric acid, HNO_3, is considered to be a strong acid whereas nitrous acid, HNO_2, is considered to be a weak acid. Which of the statements here is fully correct?

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

ANSWER

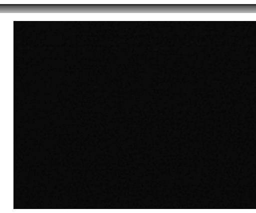
A) correctly compares equilibrium and conjugate base characteristics. The conjugate base of a strong acid is considered to be weak. The stronger the acid, the more reaction in water. Therefore, a weak acid's equilibrium is favored to the left.

Neutralization Reactions



Would there be a difference in the reaction of HF versus HCl?

Neutralizations / Titrations

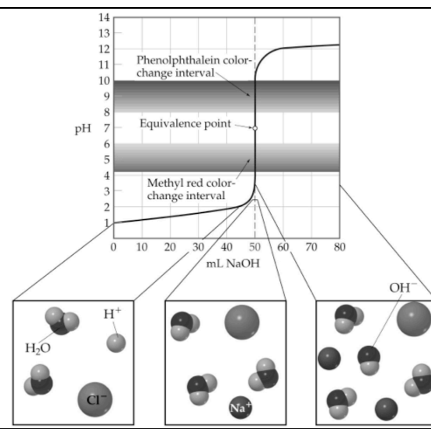


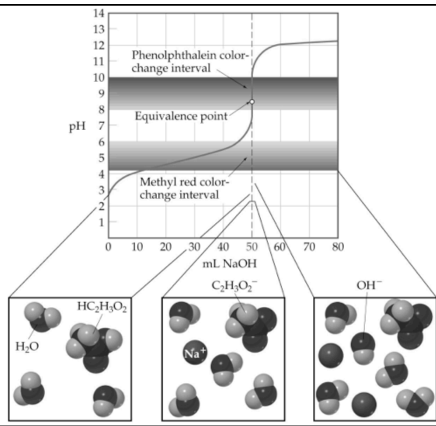
Are there differences in the titration of HF versus HCl? ….1) mass wise? …. 2) pH wise?

A) 1.NO 2.NO B) 1.YES 2.YES C) 1.YES 2.NO D) 1.NO 2.YES

Titrations: Indicators & (pH) Curves

- *pH Curve is a plot of pH of the solution being analyzed as a function of the amount of titrant added.*
- *Equivalence (stoichiometric) point: Enough titrant has been added to react exactly with the solution being analyzed. An indicator provides a visible color change to determine an (end point) volume of titrant.*

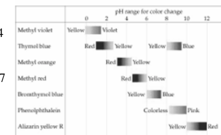




QUESTION

Most acid-base indicators are weak acids. In a titration of 0.50 *M* acetic acid (at 25°C, $K_a = 1.8 \times 10^{-5}$) with KOH, which indicator would best indicate the pH at the equivalence point? The approximate K_a for each choice is provided.

A. Bromophenol blue; $K_a \sim 1 \times 10^{-4}$
B. Methyl red; $K_a \sim 1 \times 10^{-5}$
C. Bromothymol blue; $K_a \sim 1 \times 10^{-7}$
D. Alizarin yellow; $K_a \sim 1 \times 10^{-10}$



ANSWER

D. provides the best choice although there may also be better choices available than these four. The equivalence point pH should be as close as possible to the pK_a of the indicator. As acetic acid is a fairly weak acid and NaOH is a strong base, the pH at the equivalence point will be above 7. The only choice above 7 in the list was Alizarin yellow. Without a more detailed calculation, this would be the best choice.

QUESTION

The acid-base indicator bromocresol purple has an interesting yellow-to-purple color change. If the approximate K_a of this indicator is 1.0×10^{-6}, what would be the ratio of purple [A^-] to yellow [HA] at a pH of 4.0?

A. 100:1
B. 1:100
C. 1:1
D. This choice indicates that I don't know.

ANSWER

B. shows the [A^-]/[HA] ratio at pH 4.0 for bromocresol purple. The pH can be converted to [H^+] and divided into the K_a value to reveal the [A^-]/[HA] ratio at pH 4.0.

$K_a/[H^+] = [A^-]/[HA]$.

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)

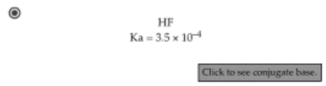
$K_a \times K_b = ?$

$K_a \times K_b = K_w$

http://chemconnections.org/general/movies/Ka-KbActivity.swf

Conjugates

$K_a \times K_b = K_w$



What do pK_a and pK_b refer to?
$pK_a + pK_b = ?$
$pK_a + pK_b = pK_w$

QUESTION

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 <u>weakest</u> conjugate acid:

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

A. $OC_6H_5^-$
B. $C_2H_3O_2^-$
C. OCl^-
D. NH_3

ANSWER

A. correctly identifies the base, among these four, with the weakest conjugate acid. The K_a's in the table can be used to compare conjugate acid strength. The higher the K_a value, the stronger the acid.

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%

Weak Acids

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

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

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

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

- ***K_a*** *is the acid dissociation constant.*

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.*

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

$3.53 \times 10^{-4} = x^2/0.100$; 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?

A. A weak acid, at the same concentration of a strong acid, will have a lower pH.
B. A weak acid, at the same concentration of a strong acid, will have the same pH.
C. A weak acid, at a high enough concentration more than a strong acid, could have a lower pH than the strong acid.
D. A weak acid, at a concentration below a strong acid, could have a lower pH than a strong acid.

ANSWER

C. correctly predicts that it is possible to have a high enough concentration of the weak acid compared to a strong acid, and that the pH of the weaker acid would be lower (more acidic) than the more dilute stronger acid. Strength of an acid refers to its dissociation. The pH of a solution depends on the concentration, regardless of source, of the H^+ ion.

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 x 10^{-4})?

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

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

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?

A. 5.52
B. 4.82
C. 2.76
D. –0.70

ANSWER

C. is correct assuming that the amount of dissociation of this weak acid is negligible when compared to its molarity.

$$K_a = [H^+][A^-] / [HA - x] = x^2/(0.20\text{ M} - x)$$

becomes $1.5 \times 10^{-5} = x^2/0.20$; once $\boldsymbol{x}$ is found, representing the $[H^+]$, taking –log of that yields the pH.

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?

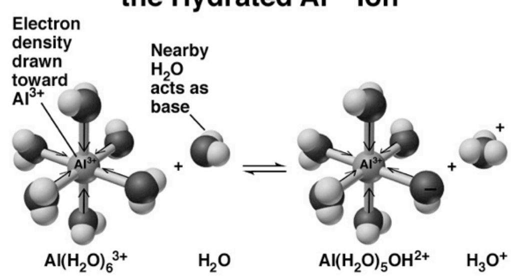
A. 6.1×10^{-3}
B. 1.3×10^{-5}
C. 7.5×10^{-4}
D. 2.1×10^{-3}

ANSWER

B. shows the unknown acid's K_a value. The pH could be used to find the $[H^+]$ concentration , $10^{-2.67}$, then the K_a expression only has one unknown:

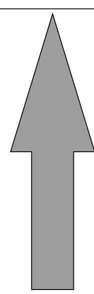
$$K_a = [0.00214][0.00214]/(0.35–0.00214)$$

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



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

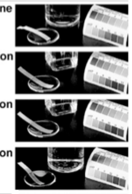
Structure and Acid-Base Properties

- *Two important factors that effect acidity in **binary** compounds, eg. HCl (aq):*
  - *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.*

Behavior of Salts in Water

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 $Ca(NO_3)_2$

http://chemconnections.org/general/movies/pHofSaltSolutions.swf

$MgSO_4$ $AgClO_3$ CsCN

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

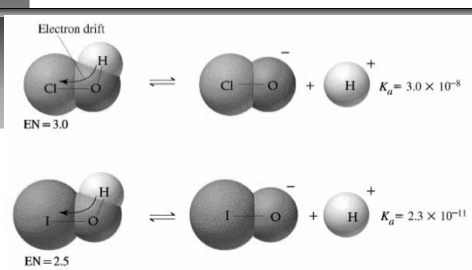
Additional information: K_b for NH_3 = 1.8×10^{-5}; K_a for $HC_2H_3O_2$ = 1.8×10^{-5}; K_a for $Al(H_2O)^{3+}$ = 1.4×10^{-5}.

A. NaCl; NH_4NO_3; $Ca(C_2H_3O_2)_2$; $AlCl_3$
B. $AlCl_3$; NaCl; NH_4NO_3; $Ca(C_2H_3O_2)_2$
C. $AlCl_3$; NH_4NO_3; NaCl; $Ca(C_2H_3O_2)_2$
D. NH_4NO_3; $AlCl_3$; NaCl; $Ca(C_2H_3O_2)_2$

ANSWER

C. correctly ranks the salt solutions from lowest pH (most acidic solution) to highest pH. The ranking is based on production of H^+ from the salt ions interacting with water. Highly charged small metal ions such as Al^{3+} can produce H^+ as can NH_4^+. However, the K_a of the aluminum's reaction is larger than the K_a for NH_4^+. NaCl is neutral and the acetate ion undergoes a reaction that produces OH^-, so it has a high pH.

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 $HBrO_3$ stronger or weaker than $HClO_3$?
A) stronger or B) weaker

Strength of Oxyacids

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  - *HClO*, $K_a = 3.0 \times 10^{-8}$
  - $HClO_2$, $K_a = 1.2 \times 10^{-2}$

Is $HBrO_3$ stronger or weaker than $HClO_3$?

A) stronger or **B) weaker**

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, $K_a = 3.0 \times 10^{-8}$

A) HBrO < HIO < HClO *B) HIO < HBrO < HClO*

C) HClO < HBrO < HIO *D) HIO < HClO < HBrO*

ANSWER: B) HIO < HBrO < HClO
(Increasing Ka values)

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, $K_a = 3.0 \times 10^{-8}$

A) HBrO < HIO < HClO *B) HIO < HBrO < HClO*

C) HClO < HBrO < HIO *D) HIO < HClO < HBrO*

ANSWER: C) HClO < HBrO < HIO
(pH ~ -log Ka values)

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_2COOH, CH_3COOH

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

1) Is chloroacetic acid more or less acidic than bromoacetic acid?
2) Will its pKa be higher or lower than bromoacetic acid?

A) 1.more 2.higher B) 1.less 2.lower C) 1.less 2.higher D) 1.more 2.lower

Strength of Acids

Br-CH_2COOH, I-CH_2COOH, CH_3COOH

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

1) Is chloroacetic acid more or less acidic than bromoacetic acid?
2) Will its pKa be higher or lower than bromoacetic acid?

D) 1.more 2.lower

QUESTION

- *Rank the following acids in order of decreasing acidity.*

1) Br-CH_2COOH, 2) I-CH_3COOH, 3) CH_3COOH

pKa= 2.69 pKa=3.12 pKa=4.75

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

ANSWER: B) 3 > 2 > 1; LOWER pKa HIGHER Acidity

QUESTION

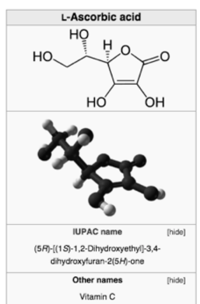
Ascorbic acid, also known as vitamin C, has two hydrogen atoms that ionize from the acid. $Ka_1 = 7.9 \times 10^{-5}$; $Ka_2 = 1.6 \times 10^{-12}$. What is the pH, and $C_6H_6O_6^{2-}$ concentration of a 0.10 *M* solution of $H_2C_6H_6O_6$?

A.2.55; $[C_6H_6O_6^{2-}] = 0.050$ *M*
B.2.55; $[C_6H_6O_6^{2-}] = 1.6 \times 10^{-12}$ *M*
C.1.00; $[C_6H_6O_6^{2-}] = 1.6 \times 10^{-12}$ *M*
D.5.10; $[C_6H_6O_6^{2-}] = 0.050$ *M*

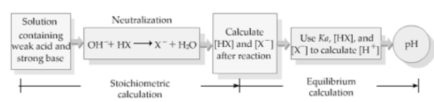
ANSWER

B.

In a diprotic acid with two small, widely separated K_a values the pH of a solution can be obtained from using the first K_a and the molarity. Eg. H_2SO_4. The concentration of the dianion can be closely approximated by assuming very little dissociation of the second acidic hydrogen, so that Ka_2 is very close to the molarity.

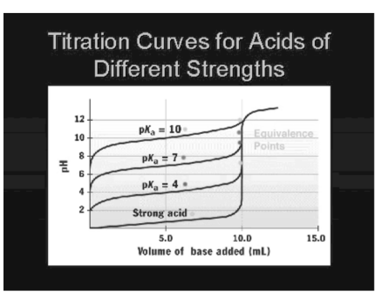


Neutralizations / Titrations



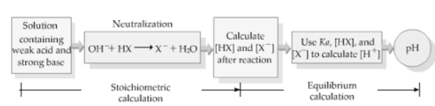
Are there differences in the titration of HF versus HCl? ….1) mass wise? …. 2) pH wise?

D) 1.NO 2.YES



QUESTION

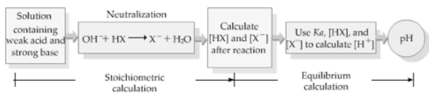
What is the pH of a solution made from adding 500. mL of 1.00 M HOAc$_{(aq)}$ (Ka = 1,8 x 10 $^{-5}$) to 100. mL of 5.00M NaOH $_{(aq)}$?
(This question relates to the titration of acetic acid.)



A) 4.74 B) 4.76 C) 9.24 D) 9.26

QUESTION

What is the pH of a solution made from adding 500. mL of 1.00 M $HOAc_{(aq)}$ (Ka = 1,8 x 10^{-5}) to 100. mL of 5.00M NaOH $_{(aq)}$?

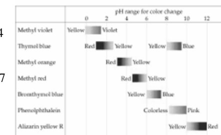


A) 4.74 B) 4.76 C) 9.24 D) 9.26

QUESTION

Most acid-base indicators are weak acids. In a titration of 0.50 *M* acetic acid (at 25°C, $K_a = 1.8 \times 10^{-5}$) with KOH, which indicator would best indicate the pH at the equivalence point? The approximate K_a for each choice is provided.

A. Bromophenol blue; $K_a \sim 1 \times 10^{-4}$
B. Methyl red; $K_a \sim 1 \times 10^{-5}$
C. Bromothymol blue; $K_a \sim 1 \times 10^{-7}$
D. Alizarin yellow; $K_a \sim 1 \times 10^{-10}$



ANSWER

D. is best. (C. is marginal.)

A. Bromophenol blue; $K_a \sim 1 \times 10^{-4}$
B. Methyl red; $K_a \sim 1 \times 10^{-5}$
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