

17 • Acid-Base Equilibria

BLUFFER'S GUIDE

- $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$
 $\text{pH} = -\log[\text{H}^+]$ $\text{pH} + \text{pOH} = 14$ $[\text{H}^+] = 10^{-\text{pH}}$
 Convert between pH, pOH, $[\text{H}^+]$, & $[\text{OH}^-]$
- Acid Ionization Constant (K_a):
 $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$
 Example: $\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$

$$K_a = \frac{[\text{F}^-][\text{H}_3\text{O}^+]}{[\text{HF}]}$$
- Typical question: Given K_a and the starting concentrations of acid, find concentrations (or pH) of $[\text{H}^+]$ at equilibrium.

 Example: K_a for acetic acid = 1.8×10^{-5} .
 Find the pH of 0.100M acetic acid.
- Polyprotic Acids: H_3PO_4 , H_2SO_4 , $\text{H}_2\text{C}_2\text{O}_4$, etc. The 1st dissociation is strong for H_2SO_4 .
 When using Hess's Law with a polyprotic acid: $K_{\text{overall}} = K_{a1} \times K_{a2}$
 Calculating pH, use K_{a1}
- Bronsted-Lowry Definitions.
 Acids = H^+ donors; Bases = H^+ acceptors
 Conjugate acid-base pairs.
- Base Ionization Constant (K_b):
 $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$
 Example: $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$

$$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]}$$
- Salt solns can have pH's $\neq 7$ (hydrolysis)
 ions from weak acids \rightarrow basic solutions
 $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^-$
 ions from weak bases \rightarrow acidic solutions
 $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$
- $K_a \times K_b = K_w = 10^{-14}$
 only applies for **conjugate** acids & bases!

 Example: $K_a \text{HC}_2\text{H}_3\text{O}_2 = 1.8 \times 10^{-5}$
 $K_b \text{C}_2\text{H}_3\text{O}_2^- = 10^{-14} / 1.8 \times 10^{-5}$
- Percent ionization =

$$\frac{[\text{H}^+]_{\text{equilibrium}}}{[\text{HA}]_{\text{initial}}} \times 100$$
- Acid Strength-know the 6 strong acids: HCl, HBr, HI, HNO_3 , HClO_4 , and H_2SO_4 (removal of the first H^+ only)
 - binary acids - acid strength increases with increasing size and electronegativity of the "other element". (NOTE: Size predominates over electronegativity in determining acid strength.)
 Examples: $\text{H}_2\text{Te} > \text{H}_2\text{O}$ & $\text{HF} > \text{NH}_3$
 - Oxoacids - Acid strength increases with increasing:
 - electronegativity
 - number of bonded oxygen atoms
 - oxidation state of the "central atom".
 Example: HClO_4 or $[\text{O}_3\text{Cl}(\text{OH})]$
 is very **acidic**
 NaOH is very **basic**
 Acid strength also increases with **decreasing** radii of the "central atom".
 Example:
 HOCl (bond between Cl and OH is covalent--making **HOCl acidic**)
 HOI (bond between I and OH is ionic--making **HOI basic**)
- Lewis Acids and Bases:
(This applies to coordinate covalent bonds.)
 Lewis Acid--electron pair acceptor
 Lewis Base--electron pair donor
 "Have Pair... Will Share" – Lewis Base

 In complex ion formation, metal ions are Lewis acids, and ligands are Lewis bases.
 Example: $\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$
 Cu^{2+} acts as an acid; NH_3 acts as a base.
- Strong Bases: amide ion, NH_2^-
 hydride ion, H^- , methoxide ion, CH_3O^-

18 • Acid-Base Reactions

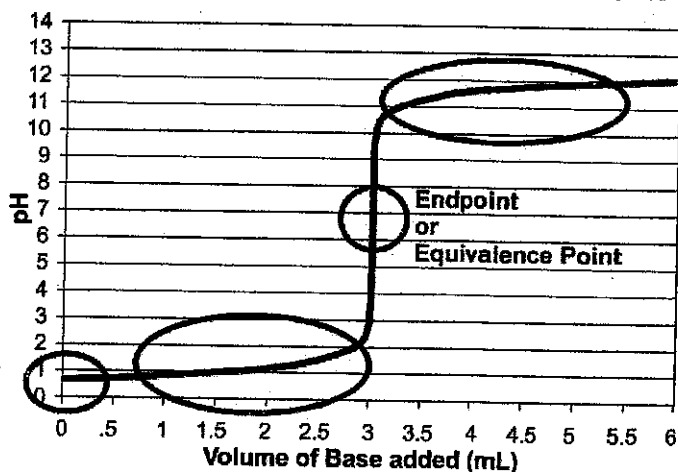
TITRATION CURVE CALCULATIONS

Strong Acid – Strong Base Titrations

When a strong acid (such as HCl) and a strong base (such as NaOH) are used for a titration, the pH change looks like the graph on the right. You can calculate the volume of base needed to reach the equivalence point using the formula: $V \underline{M} = V \underline{M}$ or a line equation.

There are three situations in which you determine pH.

- initial strong acid concentration (this is simply the $-\log[H^+]$ which is based on the [Acid].)
- equivalence point (or endpoint) when moles of OH^- = moles of H^+ . The pH is 7 (due to the auto-ionization of water.)
- before and after the endpoint (calculate excess moles of H^+ or OH^- , divide by the total volume, and calculate the pH based on this value.)



Weak Acid – Strong Base Titrations

When a weak acid (such as $HC_2H_3O_2$) is neutralized by a strong base (such as NaOH), the graph varies in *two* ways:

- the equivalence point is *not* at $pH = 7$ and
- a *buffer region* exists as you approach the endpoint.

You can still calculate the volume of base needed to reach the equivalence point using the formula: $V \underline{M} = V \underline{M}$. Weak acids require the same amount of base for neutralization as strong acids because they dissociate as they are neutralized.

There are five situations in which you need to be able to calculate the pH.

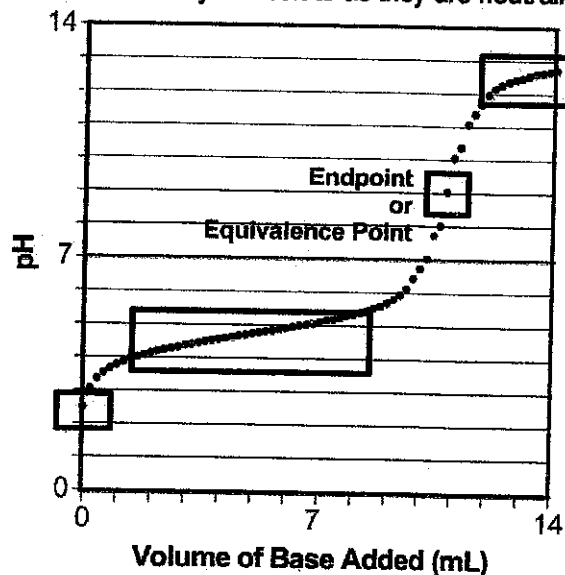
- **initial weak acid concentration** (this is an ICE box calculation.) The shortcut can be used here.
- **equivalence point** (endpoint) is when all of the weak acid has been neutralized and turned into the conjugate base ($C_2H_3O_2^-$ in this case.) This is a hydrolysis problem. Calculate the $[C_2H_3O_2^-]$ and then do an ICE box problem

knowing that $K_b = \frac{K_w}{K_a}$. Calculate the $[OH^-]$, the pOH,

and then the pH.

- **Halfway to the equivalence point** (as in a half-titration) the $pH = pK_a$. This is because at this point, there is a perfect buffer as the $[HA] = [A^-]$. At this point, you can determine the K_a of an unknown weak acid... very useful.
- **before and after the half-way point**, the pH can be calculated using the Henderson-Hasselbach equation (or an ICE box, if you want.) Use stoichiometry to determine

$$\text{the } [HA] \text{ and } [A^-]. \quad pH = pK_a + \log \frac{[A^-]}{[HA]}$$



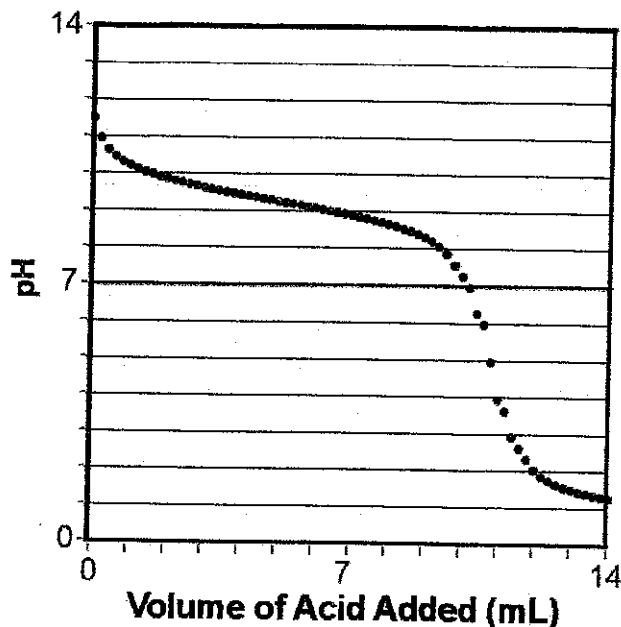
- finally, **after the equivalence point**, the pH depends on the excess strong base that has been added. As in the strong acid-strong base titration, calculate excess moles of OH^- , divide by the total volume, and calculate the pOH and then pH based on this value. The effect on the pH by the A^- is negligible compared to the excess OH^- .

Weak Base – Strong Acid Titrations

When a sample of a weak base is titrated with a strong acid, the curve resembles an inverted Weak Acid – Strong Base titration curve.

Note that the pH at the equivalence point is **less than 7**. An indicator such as phenolphthalein that changes at pH of 9 would change when only 6 mL of acid had been added even though the equivalence point is reached at around 11 mL.

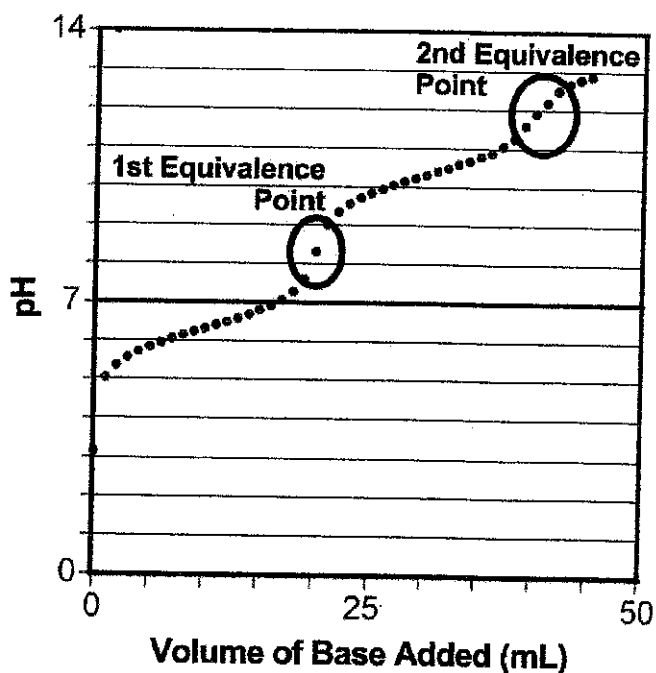
The acid-base indicator must be chosen with a K_a near to the $[H^+]$ of the equivalence point; that is the pK_a of the indicator must match the pH of the equivalence point.



Weak Diprotic Acid – Strong Base Titrations

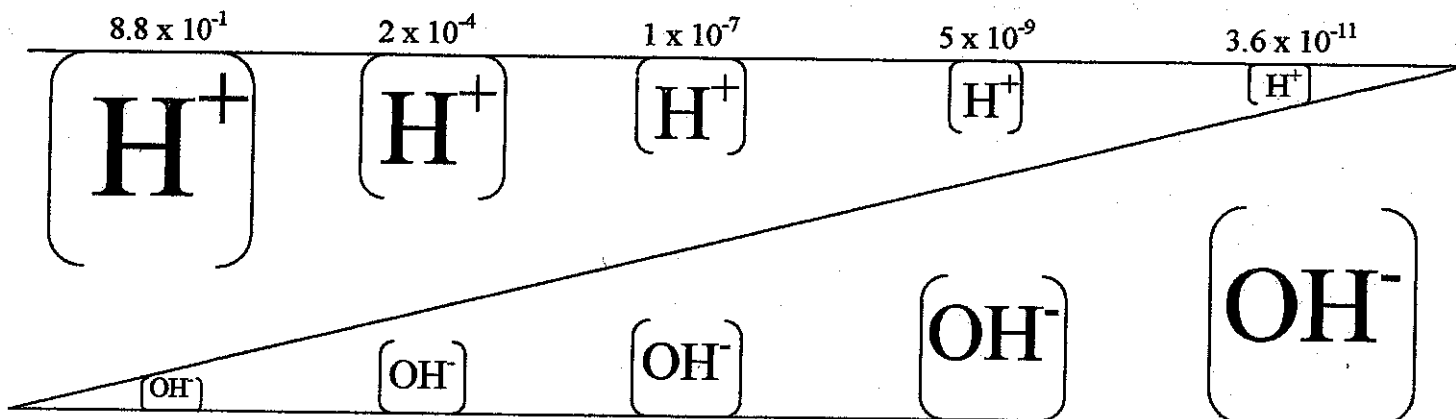
When a weak diprotic acid (examples: $H_2C_2O_4$ or H_2CO_3) is titrated, there are two equivalence points. The curve is not as distinct because of the various proton donors and proton acceptors in solution.

I believe that simply knowing the general shape of the titration curve and being able to identify the two equivalence points is sufficient for the AP exam.



17 • Acid-Base Equilibria

pH PRACTICE



- Write the pH of each solution above the $[H^+]$'s. $pH = -\log[H^+]$
- Label the "Z" diagram as "Acidic", "Basic" and "Neutral."
- Knowing that the $[H^+] \times [OH^-]$ always equals 1×10^{-14} , fill in the $[OH^-]$ for each of the five solutions in the "Z" Diagram. (1×10^{-14} is called the Dissociation Constant for water, K_w) ($1 \times 10^{-14} = 10 \times 10^{-15}$)
- Write the "pOH" of each solution below the $[OH^-]$'s.
- $pH + pOH$ always equals _____.
- A solution of acid has $[H^+] = 3.0 \times 10^{-3} M$
 - Calculate the $[OH^-]$ _____
 - Calculate the pH _____ the pOH _____
- A solution of base has an $[OH^-] = 4.25 \times 10^{-5} M$
 - Calculate the $[H^+]$ _____
 - Calculate the pH _____ the pOH _____
- Calculate the pH's of the following solutions:

$2.53 \times 10^{-3} M HCl$ $pH =$

$2.53 \times 10^{-6} M HCl$ $pH =$

$2.53 \times 10^{-9} M HCl$ $pH =$

A pH with 3 significant figures is written with _____ numbers after the decimal place.

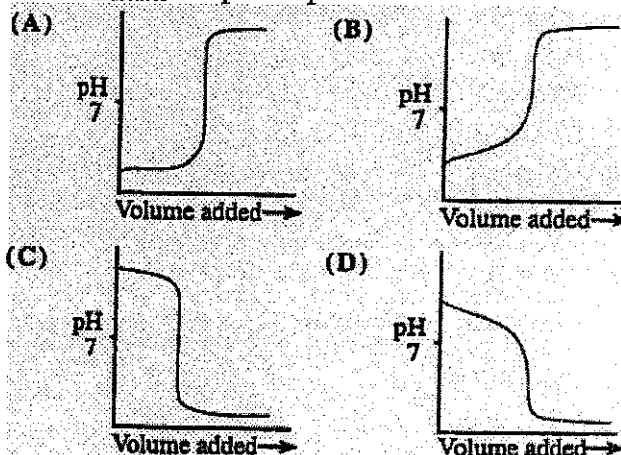
18 • Acid-Base Reactions

- HCN is a weak acid ($K_a = 6.2 \times 10^{-10}$). NH_3 is a weak base ($K_b = 1.8 \times 10^{-5}$). A 1.0 M solution of NH_4CN would be
 (A) strongly acidic (C) neutral
 (B) weakly acidic (D) weakly basic
- How many moles of HCOONa must be added to 1.0 L of 0.10 M HCOOH to prepare a buffer solution with a pH of 3.4? ($\text{HCOOH } K_a = 2 \times 10^{-4}$)
 (A) 0.01 (C) 0.1
 (B) 0.05 (D) 0.2
- The acid-base indicator methyl red has a K_a of 1×10^{-4} . Its acidic form is red while its alkaline form is yellow. If methyl red is added to a colorless solution with a pH = 7, the color will be
 (A) pink (C) orange
 (B) red (D) yellow
- Which mixture forms a buffer when dissolved in 1.0 L of water?
 (A) 0.2 mol NaOH + 0.2 mol HBr
 (B) 0.2 mol NaCl + 0.3 mol HCl
 (C) 0.4 mol HNO_2 + 0.2 mol NaOH
 (D) 0.5 mol NH_3 + 0.5 mol HCl
- A buffer solution is prepared in which the concentration of NH_3 is 0.30 M and the concentration of NH_4^+ is 0.20 M. What is the pH of this solution? The equilibrium constant, K_b for NH_3 equals 1.8×10^{-5} .
 (A) 8.73 (C) 9.43
 (B) 9.08 (D) 11.72

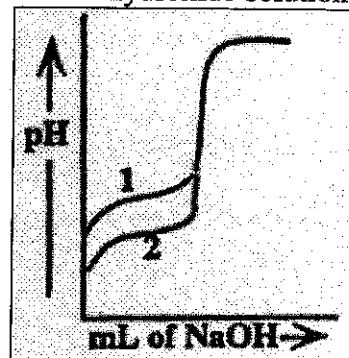
PRACTICE TEST

- For which titration would the use of phenolphthalein introduce a significant error?

$K_{\text{indicator}}$ for phenolphthalein = 1×10^{-9}



- The titration curves labeled 1 and 2 were obtained by titrating equal volumes of two different acid samples with portions of the same sodium hydroxide solution.



What conclusions can be drawn about the relative concentrations and strengths of acids 1 and 2 from these curves?

- The concentrations are the same but acid 1 is weaker than acid 2.
- The concentrations are the same but acid 1 is stronger than acid 2.
- Acid 1 is the same strength as acid 2, but it is less concentrated.
- Acid 1 is the same strength as acid 2, but it is more concentrated.

8. A 0.100 M solution of acetic acid ($K_a = 1.8 \times 10^{-5}$) is titrated with a 0.1000 M solution of NaOH. What is the pH when 50% of the acid has been neutralized?
- (A) 2.38 (C) 5.70
(B) 4.74 (D) 7.00

9. The pK_a values for several acid-base indicators are given in the table. Which indicator should be used in the titration of a weak base with a strong acid?

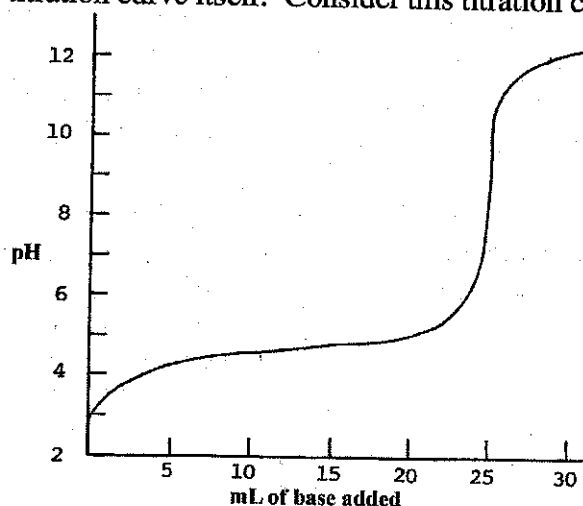
Indicator, pK_a	
2,4-dinitrophenol	3.5
bromthymol blue	7.0
cresol red	8.0
alizarin yellow R	11.0

- (A) 2,4-dinitrophenol
(B) bromthymol blue
(C) cresol red
(D) alizarin yellow R

18 • Acid-Base Reactions

Information from the Curve:

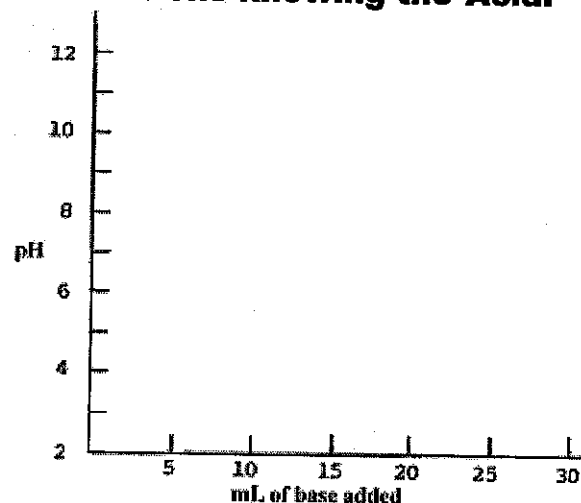
There are several things you can read from the titration curve itself. Consider this titration curve.



- This is a _____ (strong/weak) acid titrated with a strong base. The acid is _____ (monoprotic/diprotic). How would the other strength of acid look?
- Place a dot (•) on the curve at the equivalence point. The pH at the equivalence point is _____. Choose a good indicator for this titration from Figure 17.11 on page 810 of your textbook.
- What volume of base was used to titrate the acid solution? _____ mL.
- Place a box (■) on the curve where the pH of the solution = the pK_a of the acid.
 What is the pH at this point? _____
 What is the pK_a of the acid? _____
 What is the K_a of the acid? _____

CALCULATIONS

Calculations knowing the Acid:



- Hydrofluoric acid, HF, has a $K_a = 7.2 \times 10^{-4}$. Calculate the pH of 10.0 mL of a 0.050 M solution of HF. Plot this point on the axes.
- A 0.020 M solution of NaOH is used for the titration. What volume will be needed to reach the equivalence point?
- Write the net reaction for the neutralization of a solution of HF with a solution of NaOH.

- Calculate the moles of F^- at the equivalence point. What is the total volume? _____ L
 The $[F^-]$ at the equivalence point is _____
- Calculate the pH of the solution at the equivalence point. Use this information and the answer to question 6 to plot the equivalence point on your graph. Choose a good indicator for this titration from Figure 17.11 on page 810 of your textbook.

10. What is the pH halfway to the equivalence point? Plot this point on your graph.
11. How many moles of HF are in the original 10.0 mL sample of HF? _____
12. When only 5.0 mL of 0.020 M NaOH has been added, calculate the moles of HF left and F⁻ produced.

	HF	OH ⁻	H ₂ O	F ⁻
<i>i</i>			-----	
<i>c</i>			-----	
<i>e</i>			-----	

13. Use the Henderson-Hasselbach equation or an icebox to calculate the pH when 5.0 mL of base has been added. Plot this point on your graph.

14. When 20.0 mL of 0.020 M NaOH has been added, calculate the moles of HF left and F⁻ produced.

	HF	OH ⁻	H ₂ O	F ⁻
<i>i</i>			-----	
<i>c</i>			-----	
<i>e</i>			-----	

15. Use the Henderson-Hasselbach equation or an icebox to calculate the pH when 20.0 mL of base has been added. Plot this point on your graph.

16. When 30.0 mL of base is added, how many moles of OH⁻ is in excess? _____

The total volume is _____ L.

[OH⁻] = _____

pOH = _____ pH = _____

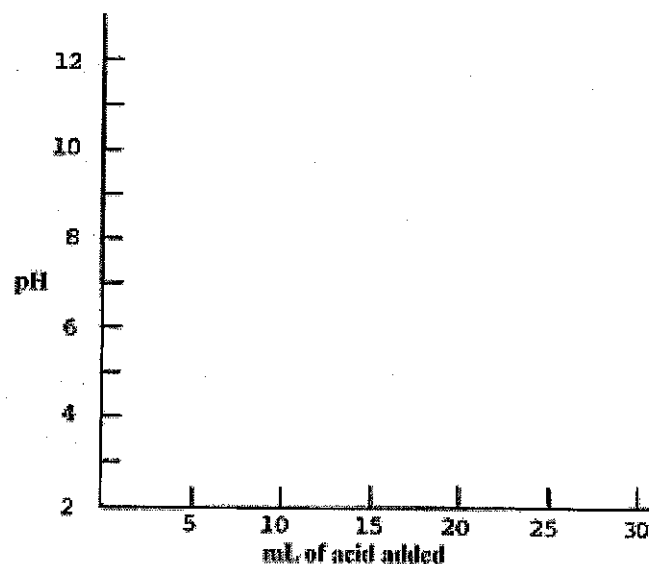
Plot this point on your graph.

17. Sketch the titration curve on your graph.

Weak Base-Strong Acid Curve:

A 20.0 mL sample of 0.10 M CH₃NH₂ (methyl amine) is titrated with 0.15 M HCl. The K_b for CH₃NH₂ = 4.2 × 10⁻⁴.

Do the appropriate calculations to sketch a titration curve for this titration.



Formulas from the AP Exam:

EQUILIBRIUM

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

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [OH^-][H^+] = 1.0 \times 10^{-14} \text{ @ } 25^\circ\text{C}$$

$$= K_a \times K_b$$

$$\text{pH} = -\log [H^+], \text{ pOH} = -\log [OH^-]$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[HB^+]}{[B]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

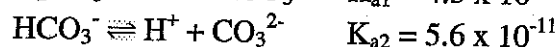
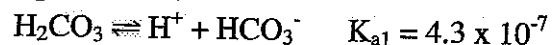
$$K_p = K_c(RT)^{\Delta n}$$

where Δn = moles product gas - moles reactant gas

17 • Acid-Base Equilibria**PRACTICE TEST**

- What is the $[H^+]$ when $[OH^-] = 8.1 \times 10^{-5}$?
 - $8.1 \times 10^{-5} \text{ M}$
 - $1.0 \times 10^{-7} \text{ M}$
 - $1.2 \times 10^{-10} \text{ M}$
 - $3.6 \times 10^{-6} \text{ M}$
 - $8.1 \times 10^{-5} \text{ M}$
- What is the $[H^+]$ when $[OH^-] = 3.3 \times 10^{-9}$?
 - $3.0 \times 10^{-6} \text{ M}$
 - $1.0 \times 10^{-7} \text{ M}$
 - $3.3 \times 10^{-5} \text{ M}$
 - $6.6 \times 10^{-5} \text{ M}$
 - $3.3 \times 10^{-9} \text{ M}$
- What is the $[H^+]$ in a 0.0025 M HCl solution?
 - $1.0 \times 10^{-7} \text{ M}$
 - $4.0 \times 10^{-12} \text{ M}$
 - $2.5 \times 10^{-3} \text{ M}$
 - $3.6 \times 10^{-5} \text{ M}$
 - need more info
- What is the $[OH^-]$ in a 0.0050 M HCl solution?
 - $5.0 \times 10^{-3} \text{ M}$
 - 1.0 M
 - $1.0 \times 10^{-7} \text{ M}$
 - $6.6 \times 10^{-5} \text{ M}$
 - $2.0 \times 10^{-12} \text{ M}$
- A solution in which $[H^+] = 10^{-8}$ has a pH of ____ and is _____.
 - 8, acidic
 - 6, basic
 - 6, basic
 - 8, neutral
 - 8, basic
- What is the pH of a 0.00030 M HNO_3 solution?
 - 8.11
 - 3.00
 - 3.52
 - 4.48
 - none of these
- What is the pH of a 0.0060 M KOH solution?
 - 5.12
 - 2.22
 - 11.78
 - 8.88
 - 7.00
- A sample of lemon juice is found to have a pH of 2.55. What is the H^+ concentration of the juice?
 - 0.0035 M
 - 0.0028 M
 - 11.6 M
 - 0.0080 M
 - 355 M
- A sample of milk is found to have a pH of 6.60. What is the OH^- concentration of the milk?
 - $2.5 \times 10^{-21} \text{ M}$
 - $1.0 \times 10^{-7} \text{ M}$
 - $5.0 \times 10^{-7} \text{ M}$
 - $4.0 \times 10^{-8} \text{ M}$
 - $2.5 \times 10^{-7} \text{ M}$
- What is the concentration of OCl^- in a 0.60 M solution of $HOCl$? $K_a = 3.1 \times 10^{-8}$.
 - $1.8 \times 10^{-4} \text{ M}$
 - $7.1 \times 10^{-11} \text{ M}$
 - 0.40 M
 - $1.4 \times 10^{-4} \text{ M}$
 - $1.1 \times 10^{-4} \text{ M}$
- What is the pH of a 0.020 M solution of hydrosulfuric acid, a diprotic acid? $K_{a1} = 1.1 \times 10^{-7}$ $K_{a2} = 1.0 \times 10^{-14}$
 - 7.00
 - 9.67
 - 7.84
 - 4.33
 - 3.05

12. What is the concentration of CO_3^{2-} in a 0.010 M solution of carbonic acid? The relevant equilibria are,



- a) $6.6 \times 10^{-5} \text{ M}$ d) $7.5 \times 10^{-7} \text{ M}$
b) $5.6 \times 10^{-11} \text{ M}$ e) $7.9 \times 10^{-7} \text{ M}$
c) $6.7 \times 10^{-11} \text{ M}$

13. What is the S^{2-} concentration in a saturated solution (0.10 M) of H_2S , in which the pH has been adjusted to 6.00 by the addition of HCl?

For H_2S , $K_{a1} = 1.1 \times 10^{-7}$ and $K_{a2} = 1.0 \times 10^{-14}$.

- a) $1.1 \times 10^{-16} \text{ M}$ d) $3.2 \times 10^{-8} \text{ M}$
b) $1.1 \times 10^{-10} \text{ M}$ e) $3.2 \times 10^{-6} \text{ M}$
c) $1.0 \times 10^{-2} \text{ M}$

14. Which of the following salts will result in a basic solution when it is dissolved in water?

- a) KCl d) MgBr_2
b) NH_4I e) none of these
c) NaCN

15. What is the pH of a 0.50 M solution of NaNO_2 ?

For HNO_2 , $K_a = 4.5 \times 10^{-4}$.

- a) 12.18 d) 8.52
b) 5.48 e) 7.00
c) 1.82

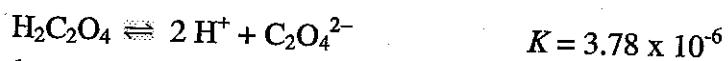
16. What is the pH of a 1.0 M solution of NaOCl?

For HOCl, $K_a = 3.1 \times 10^{-8}$.

- a) 10.75 d) 10.25
b) 3.25 e) 7.00
c) 3.75

17 • Acid-Base Equilibrium**AP PROBLEM PRACTICE**

The overall dissociation of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, is represented below. The overall dissociation constant is also indicated.



- (a) What volume of 0.400-molar NaOH is required to neutralize completely a 5.00×10^{-3} mole sample of pure oxalic acid?
- (b) Give the equations representing the first and second dissociations of oxalic acid.

Calculate the value of the first dissociation constant, K_1 , for oxalic acid if the value of the second dissociation constant, K_2 , is 6.40×10^{-5} .

- (c) To a 0.015-molar solution of oxalic acid, a strong acid is added until the pH is 0.5. Calculate the $[\text{C}_2\text{O}_4^{2-}]$ in the resulting solution. (Assume the change in volume is negligible.)
- (d) Calculate the value of the equilibrium constant, K_b , for the reaction that occurs when solid $\text{Na}_2\text{C}_2\text{O}_4$ is dissolved in water.

