Calculations In Chemistry

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Module 32: pH of Salts
Module 33: Buffers
Module 34: pH During Titration

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Module 32 — pH of Salts

Prerequisites: Complete Modules 30 and 31 before starting this module.

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Lesson 32A: The Acid-Base Behavior of Salts

Timing: Do this lesson *if* you are assigned problems that ask you to predict the acidity or basicity of salt solutions.

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Salts

Historically in chemistry, **salt** is a term that has been used to describe the ionic compounds that are a product in acid-base neutralization**.** In current usage, "salt" can refer to any ionic compound.

Salt = Ionic Compound

As with all ionic compounds, salts are solids at room temperature. All salts dissolve to some extent in water. All particles that dissolve will be present as ions that can move about freely in the solution. In water, some salts form pH neutral solutions, but others react with water (hydrolyze) to form acidic or basic solutions.

Distinguishing the Types of "Neutral"

To describe acidic and basic ions, it is necessary to distinguish between the two uses in chemistry for the word *neutral*.

- Particles that have a zero overall charge are termed *electrically neutral*. Positive or negative *ions* are particles that are *not* electrically neutral.
- Whether a particle is electrically neutral *or* is an ion, in an aqueous solution the particle can also be
  - *pH neutral*, also termed *acid-base neutral* (such particles include H_2O and Na^+ and Cl^-), *or*
  - *not* pH neutral and can be acidic (such as HF or NH_4^+), basic (such as NH_3 or F^-), or amphoteric (can react as acids or bases, such as HCO_3^-).

To avoid confusion, the terms *electrically neutral* and *pH neutral*, rather than simply *neutral*, are preferred in situations where the meaning of "neutral"may not be clear.

Soluble Salts

Some ionic compounds are quite soluble in water, but others are only slightly soluble. Recall from Lesson 13A that if compounds contain these ions, they are nearly always *soluble* in water:

- NH_4^+ , the row 3-7 alkali metal ions (Na^+, K^+, Rb^+, Cs^+, Fr^+), NO_3^-, and CH_3COO^- except when combined with Ag^+.

Other ion combinations are also soluble, but the ions above are the most frequently encountered in problems.

To solve problems in this module, it is especially important to be able to recall from memory the ion combinations that are *soluble*: those combinations that dissolve and *separate* into ions essentially *100%* at substance concentrations of 0.10 M or less.

When a soluble ionic compound dissolves, if the moles of solid dissolved per liter of solution is known, the concentration of the ions in solution can be found by the *REC* steps (Lessons 7C and 12B). To briefly review, try this problem.

Q. Write the chemical formula and concentration for each particle formed when 0.10 M $Ca(NO_3)_2$ dissolves in water.

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Answer

Nitrates are ionic compounds that are soluble in water: in dilute solutions, they dissolve and separate into ions essentially 100%. Write the *REC* steps (Lesson 12B) by inspection.

Reaction and ***E***xtent: $\mathbf{1}\ Ca(NO_3)_2(aq) \rightarrow \mathbf{1}\ Ca^{2+}(aq) + \mathbf{2}\ NO_3^-(aq)$ (goes ~100%)

^ ^ ^

Concentrations: 0.10 M → **0 M** **0.10 M** and **0.20 M** formed

In this solution are *no* $Ca(NO_3)_2$ particles, 0.10 M Ca^{2+} ions, and 0.20 M NO_3^- ions.

Coefficients represent the *mole* ratios that react and form. However, if the reaction goes to completion and all of the particles in the same solution, the coefficients will also represent the *mole per liter* (concentration) ratios of the particles used up and formed.

Practice A: (For additional review, see Module 7 and Lessons 12B and 13A.)

1. In dilute aqueous solutions, will these dissolve ~100% *and* dissociate ~100% into ions? State your reasoning.

   a. KCl
   b. CH_4
   c. $Ra(NO_3)_2$
   d. Sodium acetate
   e. Cl_2
   f. Calcium phosphate
   g. Ammonium bromide
   h. HCl
   i. RbOH
   j. Silver chloride
   k. $PbCl_2$
   l. Lead nitrate

2. Which compound above is

   a. A strong base?
   b. An element?
   c. Radioactive?

3. Write symbols for the ions formed, then beside or below, write the concentration for each ion formed in solution when these salts dissolve in water.

   a. 0.20 M NH_4Cl →

   b. 0.50 M $Ba(NO_3)_2$ →

   c. 0.25 M potassium cyanide →

   d. 0.10 M sodium sulfate →

Ions in Aqueous Solution: Acidic, Basic, or Neutral?

When mixed with water, an *ion* has a characteristic acidic, basic, or neutral behavior. An ion that is acidic, when combined in a salt with an ion that is pH-neutral, forms an acidic aqueous solution. A basic ion, in combination with a pH-neutral ion, forms a basic solution in water.

To predict whether a salt will form an acidic, basic, or pH-neutral solution, the first step is to classify each of its *ions* as acidic, basic, or pH neutral. For many ions, whether they have acidic, basic or pH-neutral behavior can be predicted with a Table of Acid Strengths and the following

Rules for Identifying Ions As pH-Neutral, Acidic, or Basic

The ions in **bold** below are those encountered most often in problems.

1. **pH-neutral ions** include

a. In rows 3-7 of the periodic table, the column 1 **alkali metal ions** (**Na^+, K^+**, Rb^+, Cs^+, Fr^+) plus the **column 2** metal ions: Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}.

b. Conjugates of *strong* acids, such as **Cl^-** and **NO_3^-**.

HCl and HNO_3 are strong acids. Conjugates of strong acids or bases are very weak**.** *Very weak* acids and bases are considered to be essentially pH *neutral* in water.

2. If an *ion* formula is listed in an acid-strength table, its position in the table will identify whether it has acidic, basic, or neutral behavior when dissolved in water.

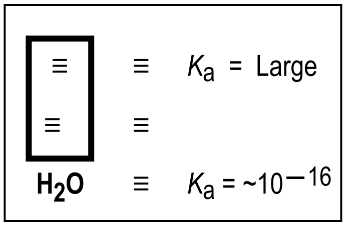
For an acid-strength table (see Lesson 31B), the rules include:

- Each line in the table includes a conjugate acid-base pair.
- Acids are listed in the left column and bases after the H^+ in the right column.
- The strongest acids are at the top left, and strongest bases at the bottom right.
- If one acid or base particle is strong (K>1), its conjugate is *very* weak (K<10^{-16}).
- If one member of a conjugate pair is moderately *weak* (with its K_a or K_b between 1 and ~10^{-16}), the other will also be moderately weak.
- The stronger is one, the weaker is its conjugate.

a. **Acidic ions** are those that are

- stronger acids than H_2O in an acid-strength table →
- which are those with a K_a larger than ~10^{-16}.

The acidic *ions* encountered most frequently are **NH_4^+** and $R\text{-}NH_x^+$ ions, where R is a group containing carbon and hydrogen.



b. Another type of *acidic* ion is the highly charged ion of a small-radius metal atom, such as Fe^{3+}, Al^{3+}, and Sn^{4+}. These ions, when dissolved in water, form **hydrated complexes** that can bind to the hydroxide ions formed by the auto-ionization of water. This results in a solution that is acidic because it has more free H^+ ions than OH^- ions.

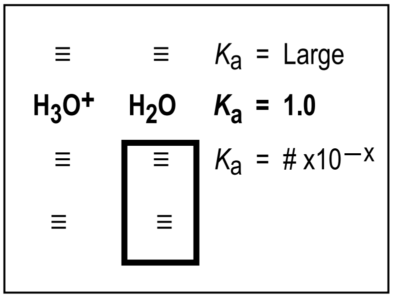
c. **Basic ions** are listed in the right-side column.

Ions at the top right are conjugates of very strong acids, and those bases are so weak that they are essentially pH neutral.

The strongest bases are at the bottom right: the conjugates of the weakest acids.

The ions that have basic behavior in water are

- ions listed below H_2O on the *base* side.
- which are also the conjugate bases of acids that have a K_a *below* 1.0. →
- which are also bases with K_b *larger* than ~10^{-16} .



Basic ions include $\mathbf{F^-}$, $\mathbf{CN^-}$, $\mathbf{CH_3COO^-}$, and $C_6H_5COO^-$.

Any ion which is the conjugate of a weak acid has basic behavior.

Practice B: First learn the rules, *then* do these problems.

1. Using the acid-strength table in Lesson 31B, but applying the *rules* in this lesson from memory, label these ions as acidic (A), basic (B), or pH-neutral (N).

   a. CH_3COO^- b. K^+ c. NH_4^+ d. Al^{3+} e. F^- f. Cl^- g. Ca^{2+}

2. Which of the ions in Problem 1, if present in a compound, will always result in the compound to be soluble?

3. In this problem, do *not* consult the acid-strength table.

   In the *partial* acid-strength table at the right.

   a. Fill in the blanks with the conjugate formulas.

   b. After the conjugate formula, label it as an acid (A) or base (B).

   c. What is the formula for the table *ion* (other than H^+) that is the strongest acid?

HCl	→	H^+	+	________ ( )
_________ ( )	→	H^+	+	SO_4^{2-}
________ ( )	→	H^+	+	F^-
C_6H_5COOH	→	H^+	+	________ ( )
HCN	→	H^+	+	________ ( )
________ ( )	→	H^+	+	NH_3
H_2O	→	H^+	+	________ ( )
NH_3	→	H^+	+	________ ( )

   d. Which ion in the table is the weakest acid?

   e. Which ion in the table is the strongest base?

   f. Which ion in the table is the weakest base?

4. These acids are listed strongest to weakest: $HBr > HF > HCO_3^{-} > H_2O > CH_3CH_2OH$

   Arrange these bases strongest to weakest: CO_3^{2-}, $CH_3CH_2O^{-}$, F^{-}, Br^{-}, OH^{-}

Salt Solutions: Acidic or Basic?

Salts must contain both positive and negative ions. To predict the acidity or basicity of salt solutions, both ions must be considered. This results in 4 possibilities, but the rules are logical. In a salt solution, if

- *Both* ions are pH-neutral, the salt solution will be pH-neutral: close to a pH of 7.
- *One ion* is *acidic*, and the other is pH-*neutral*, the solution will be *acidic* (pH < 7).
- *One* is *basic*, and the other is *neutral*, the salt solution will be *basic* (pH > 7).
- One is acidic and one is basic: compare K_a for the acidic to the K_b for the basic ion. If K_a is a larger number, the salt solution will be *acidic*. If K_b is larger, it will be *basic*.

  The reaction with the higher K value is the dominant reaction: this K is used to predict the ion concentrations in the solution.

Apply those rules to this problem, then check your answer below.

Q. Is a solution of ammonium chloride acidic, basic, or neutral?

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Answer: Ammonium chloride contains NH_4^{+} and Cl^{-} ions. NH_4^{+} is in the left column of the acid-strength table; it is acidic. Cl^{-} ion is at the top right, the conjugate of the strong acid HCl: a very weak base that is essentially pH *neutral*.

An acidic ion combined with a neutral ion form a compound that results in an *acidic* solution when the compound is dissolved in water.

Practice C: Consult the acid-strength table in Lesson 31B as needed to answer these. Check and do half now, and save the rest for your next practice session.

1. Predict whether aqueous solutions of these salts will be acidic (A), basic (B), or neutral (N).

   a. NaCl b. NH_4NO_3 c. KCN d. Sodium acetate

   e. Barium Chloride f. Cesium fluoride g. Ferric Nitrate

   h. Ammonium Fluoride i. Ammonium Cyanide

ANSWERS

Practice A

1. a. KCl **YES.** Compounds with alkali metals dissolve and ionize ~100% in dilute aqueous solutions.
   b. CH_4 **NO**. Two non-metals form a covalent, not ionic, compound.
   c. $Ra(NO_3)_2$ **YES**. It is ionic (Ra is metal atom) and it is soluble (NO_3^- compounds).
   d. Sodium acetate **YES**. Is ionic (sodium is metal atom). Is soluble (Na^+ = soluble).
   e. Cl_2 **NO.** May dissolve, but two non-metal atoms form a covalent, not ionic, compound.
   f. Calcium phosphate **NO.** It is ionic, but by solubility rules for phosphate ions, it is insoluble. It will dissolve only slightly in water.
   g. Ammonium bromide **YES.** All ammonium (NH_4^+) compounds are soluble.
   h. HCl **YES**. HCl is a strong acid. Strong acids dissolve and ionize ~100% in water.
   i. RbOH **YES**. All compounds with alkali metal atoms dissolve and ionize ~100%.
   j. Silver chloride **NO.** AgCl is a well-known precipitate: if it precipitates in water, it is insoluble.
   k. $PbCl_2$ **NO.** By solubility rules is insoluble. l. Lead nitrate **YES**. Nitrates are ionic and soluble.
2. a. A strong base? **RbOH** Alkali metal compounds ionize ~100%, hydroxide ion is formed.
   b. An element? **Cl_2** Only one kind of atom.
   c. Radioactive? **$Ra(NO_3)_2$** Ra is radium; all atoms with more than 83 protons are radioactive.
3. a. 0.20 M NH_4Cl **1** NH_4Cl → **1** NH_4^+ + **1** Cl^- ; **0.20** M NH_4^+ and **0.20** M Cl^-
   b. 0.50 M $Ba(NO_3)_2$ **1** $Ba(NO_3)_3$ → **1** Ba^{2+} + **2** NO_3^- ; **0.50** M Ba^{2+} and **1.0** M NO_3^-
   c. 0.25 M potassium cyanide **1** KCN → **1** K^+ + **1** CN^-; **0.25** M K^+ and **0.25** M CN^-
   d. 0.10 M sodium sulfate **1** Na_2SO_4 → **2** Na^+ + **1** SO_4^{2-}; **0.20** M Na^+ and **0.10** M SO_4^{2-}

Practice B

1. a. CH_3COO^- **B** Appears in table on right, in the base column. The conjugate of an acid is a base.
   b. K^+ **N** Ions of alkali metals in rows 3-7 are pH neutral.
   c. NH_4^+ **A** Appears in the acid column as a weak acid.
   d. Al^{3+} **A** Metals ions with a 3+ or 4+ charge form acidic solutions in water.
   e. F^- **B** Appears in table on right side: the base column.
   f. Cl^- **N** Appears in table on right side base column, but Cl^- is the conjugate of a strong acid, so is very weak base – essentially pH neutral.
   g. Ca^{2+} **N** Ions of column 2 metals in rows 3-7 are pH neutral.
2. Compounds containing row 3-7 alkali metals (including **b. K^+**) and compounds containing ammonium ion (**c. NH_4^+**) always dissolve more than 0.1 mol/L in water, which is the general definition for "soluble." *Except* for silver acetate, acetate compounds (a. **CH_3COO^-**) are also soluble.

3. a, b.

HCl → H^+ + **Cl^- (B)**
HSO_4^- (A) → H^+ + SO_4^{2-}
HF (A) → H^+ + F^-
C_6H_5COOH → H^+ + **$C_6H_5COO^-$ (B)**
HCN → H^+ + **CN^- (B)**
NH_4^+ (A) → H^+ + NH_3
H_2O → H^+ + **OH^- (B)**
NH_3 → H^+ + **NH_2^- (B)**

   c. Strongest acid ion? **HSO_4^-** is the ion closest to top left. Ions are *charged* particles.
   d. Weakest acid ion? **NH_4^+** Ion closest to the bottom left.
   e. Strongest basic ion? **NH_2^-** Strongest bases are at bottom right.
   f. Weakest base ion? **Cl^-** Weakest bases are at top right. **Cl^-** is so weak it is pH neutral.

4. The conjugate of the strongest acid is the weakest base, the conjugate of the weakest acid is the strongest base. From strongest to weakest base: **$CH_3CH_2O^- > OH^- > CO_3^{2-} > F^- > Br^-$**

Practice C

1. a. NaCl Both are neutral ions = **Neutral**
   b. NH_4NO_3 NH_4^+ is acidic in the acid-strength table, NO_3^- is pH-neutral, combined: **Acidic**
   c. KCN pH-neutral K^+, basic CN^- in table = **Basic**
   d. Sodium acetate Neutral Na^+, basic CH_3COO^- = **Basic**
   e. Barium Chloride Both are neutral ions = **Neutral**
   f. Cesium fluoride Neutral Cs^+, basic F^- = **Basic**
   g. Ferric Nitrate Acidic Fe^{3+} (highly charged metal ion), neutral NO_3^- = **Acidic**
   h. Ammonium Fluoride Acidic NH_4^+, basic F^-; must **compare** K_a and K_b

      NH_4^+, from the acid-strength table, has $\boxed{K_a = 5.6 \times 10^{-10}}$

      Don't know K_b for F^-, but know K_a for its conjugate HF from acid-strength table. For conjugates,

$$\boxed{K_w = K_b \times K_a} = 1.0 \times 10^{-14}, \quad K_b \text{ of } F^- = \frac{K_w}{K_a \text{ of HF}} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = \boxed{1.5 \times 10^{-11}}$$

      Since the K_a of the acid is *larger* than the K_b of the base, the solution will be *acidic*.

   i. Ammonium Cyanide NH_4^+ is acidic and CN^- is basic, so we must *compare* K_a and K_b

      NH_4^+, from the acid-strength table, has a **K_a = 5.6 x 10^{-10} =** $\boxed{0.000\,000\,000\,56 = K_a}$

      To find K_b for CN^-, use K_a for its conjugate acid HCN. For conjugates,

$$\boxed{K_w = K_b \times K_a}\ ;\ \mathbf{K_b}\text{ for CN}^- = \frac{K_w}{K_a\text{ of HCN}} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = \mathbf{1.6 \times 10^{-5}} = \boxed{\mathbf{0.000\ 016} = \mathbf{K_b}}$$

Since K_b for CN^- is a *larger number* than K_a for NH_4^+, the solution is *basic*.

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Lesson 32B: Will A Salt Acid-Base React?

Applying Brønsted-Lowry Rules With Spectators Present

In Lesson 31B, we learned *two* ways to predict whether an acid or a base, when mixed in roughly equal proportions, will react.

1. **Labeling**: Using the acid-strength table, label each particle in the reactants and products as strong**er** acid (sA), sB, wA, or wB. Equilibrium favors the side with the wA and wB: sA and sB react, wA and wB form, and wA and wB will not react.

   Recall that we use the **s**A to label the strong***er*** acid when comparing two acids, and use **S**A to label an acid that is strong in absolute terms (with $K_a > 1$, such as HCl.)

2. **The Diagonal Rule**: In the acid-strength table, a particle in the left column (the acids) will react with a particle in the right column (the bases) below it.

   This means: Particles \ diagonal react to form / diagonals; particles / do not react.

These two rules are simply different ways to state that when an acid and base are combined, equilibrium favors the side with the weaker acid and base.

So far, all of our acid-base prediction problems have involved particles found in the acid strength table, where many of the particles are ions. We also need to be able to predict whether acid-base reactions *go* when the equations include *salts* rather than the ions in the table. To make these predictions, we will use what we will call Brønsted-Lowry Rule

13. If *salt* formulas are used in acid-base equations, to predict whether a reaction will go and what the products will be,

- Re-write ionic solids (salts) as their *separated* ions;
- Label each particle as A, B, or N, using the acid-strength table and N rules.
- Apply the Brønsted-Lowry *labeling* or *diagonal* rule to A and B particles, ignoring N's, to decide whether the reaction will go, and if so, which products form.
- Rewrite the products as solid formulas, with the N spectators added back in.

A short way to state this rule:

> 13. When predicting whether acid-base reactions with salt formulas will go, take out the pH-neutral spectators, apply the Brønsted-Lowry rules, put the spectators back in.

These rules are consistent with our general rule:

> To predict the behavior of ionic solids, re-write substance formulas as separated ions.

Try Rule 13 on this example.

Q. Will these reactions go? If so, write the products using molecular/ionic solid formulas. Use the acid-strength table in Lesson 31B.

a. $HCl + NaCN \rightarrow$

b. $KNO_3 + HCN \rightarrow$

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Answers

a. **$HCl + NaCN \rightarrow$**

$HCl + Na^+ + CN^- \rightarrow$ (re-write, separating the salt into its ions)
A N B (to label, use the table and rules for pH-neutrals)

Use the table to write the conjugates, then label sA, sB, wA, wB, and *go* or *no*.

$HCl + Na^+ + CN^- \rightarrow Cl^- + HCN$
sA N sB **wB** **wA** (*will go* to the right)

Add the products, including spectators, after the initial reactants, then balance.

$HCl + NaCN \rightarrow$ **$NaCl + HCN$** **(Will Go)**

b. **$KNO_3 + HCN \rightarrow$**

$K^+ + NO_3^- + HCN \rightarrow$ (re-write, separating the salt into its ions)
N VwB/N A (use the table and rules for neutrals)

Nitrate ion is a *very* weak base (VwB): essentially pH neutral. Using the table:

$K^+ + NO_3^- + HCN \rightarrow HNO_3 + CN^-$ (write conjugates; label sA, sB…)
N V**wB** **wA** **sA** **sB** (will *not* go to the right)

$KNO_3 + HCN \rightarrow$ Will Not Acid-Base React

If NO_3^- is labeled as neutral (very weak bases are essentially neutral), the combination of N, N, and A is also predicted to *not* react.

Practice: Put a check by and do every other letter. Save the rest for your next practice session. Use the table of acid strengths in Lesson 31B as needed. Check answers as you go.

1. Rewrite these reactions with the *salts* separated into ions, then write a letter below each particle to label it as acidic (A), basic (B), or pH-neutral (N).

   a. $CH_3COOH + NaCN \rightarrow CH_3COONa + HCN$

   b. $HF + NaCl \rightarrow NaF + HCl$

c. $NaHSO_4 + C_6H_5COOH \rightarrow H_2SO_4 + C_6H_5COONa$

2. In the above reactions, label each A or B particle as the stronger acid (sA), the stronger base (sB), the weaker acid (wA), or the weaker base (wB). Then label the reaction as "will go to the right" or "won't go."
3. Complete these reactions, using molecular/ionic solid formulas, then label the reaction as *will go* or *won't go*.

a. $HF + KCN \rightarrow$

b. $KHSO_4 + KF \rightarrow$

c. $KCN + K_2HPO_4 \rightarrow$

d. $NaF + NH_4NO_3 \rightarrow$

e. $HNO_3 + RbH_2PO_4 \rightarrow$

f. $NaHCO_3 + NaHSO_4 \rightarrow$

g. $NaOH + NH_4NO_3 \rightarrow$

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ANSWERS

1,2 a. $CH_3COOH + Na^+ + CN^- \rightarrow CH_3COO^- + Na^+ + HCN$

sA N sB wB N wA (Will go)

b. $HF + Na^+ + Cl^- \rightarrow Na^+ + F^- + HCl$

wA N wB N sB sA (Will NOT go)

c. $Na^+ + HSO_4^- + C_6H_5COOH \rightarrow H_2SO_4 + C_6H_5COO^- + Na^+$

N wB wA sA sB N (Will NOT go)

3. a. $HF + KCN = HF + K^+ + CN^- \rightarrow K^+ + F^- + HCN =$ **$KF + HCN$**

sA N sB N wB wA **(Will go)**

b. $= K^+ + HSO_4^- + K^+ + F^- \rightarrow SO_4^{2-} + 2\,K^+ + HF =$ **$K_2SO_4 + HF$**

N wA N wB sB N sA **(Will NOT go)**

(F^- must be a base, so HSO_4^- , which can be an acid or a base, must be acting as an acid)

c. $= K^+ + CN^- + 2\,K^+ + HPO_4^{2-} \rightarrow PO_4^{3-} + 3\,K^+ + HCN =$ **$K_3PO_4 + HCN$**

N wB N wA sB N sA **(Will NOT go)**

(CN^- *must* be a base, so HPO_4^{2-} , which can be an acid or a base, must be acting as an acid)

d. $= Na^+ + F^- + NH_4^+ + NO_3^- \rightarrow HF + NH_3 + Na^+ + NO_3^- =$ **$HF + NH_3 + NaNO_3$**

N wB wA N sA sB N N **(Will NOT go)**

e. $= HNO_3 + Rb^+ + H_2PO_4^- \rightarrow H_3PO_4 + Rb^+ + NO_3^- =$ **$H_3PO_4 + RbNO_3$**

sA N sB wA N wB **(Will go)**

(HNO_3 is a strong acid. Its conjugate NO_3^- must be a very weak base.)

f. Hint: Try the diagonal rule, and look for both non-N reactants on both *sides*.

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f. $= Na^+ + HCO_3^- + Na^+ + HSO_4^- \rightarrow [\,H_2CO_3\,] + 2\,Na^+ + SO_4^{2-} =$ **$H_2O + CO_2\uparrow + Na_2SO_4$**

N sB N sA wA N wB **(Will go)**

(HSO_4^-as A and HCO_3^- as B are \ . H_2CO_3 decomposes to **$H_2O + CO_2$** (see Lesson 14E).)

g. $= Na^+ + OH^- + NH_4^+ + NO_3^- \rightarrow H_2O + NH_3 + Na^+ + NO_3^- =$ **$H_2O + NH_3 + NaNO_3$**

N sB sA N wA wB N N **(Will go)**

NH_3 is the conjugate of NH_4^+.

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Lesson 32C: Calculating the pH of a Salt Solution

Timing: Some courses ask you to predict whether a salt solution will be acidic or basic (as in Lesson 32A), but do not assign calculations of the *pH* of salt solutions. Do this lesson only *if* you are asked to calculate the $[H^+]$ or pH of a salt solution.

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In solutions of *soluble* ionic compounds (salts), there are four possible types of mixtures of ions. We can easily calculate the $[H^+]$ or pH for three of them:

- If all ions in a salt are pH-neutral, assume the pH of the solution is 7.
- If a salt consists of a *neutral* ion plus an *acidic* ion, calculate $[H^+]$ or pH based on the *acidic* ion data and its K_a.
- If a salt consists of a neutral ion plus a basic ion, calculate $[H^+]$ or pH using the basic ion reaction with water and its K_b.
- If the salt consists of one acidic and one basic ion, the pH can be calculated, but most first-year courses defer those calculations until a more advanced course in chemistry.

For the first three types of salts above, when a soluble acidic or basic salt dissolves in water, *two* reactions take place:

- First, the ionic solid separates into ions,
- then, one of the ions ionizes or hydrolyzes, behaving as a weak acid or base.

In an aqueous solution, to calculate $[H^+]$, $[OH^-]$, or pH of a soluble salt that includes one acidic or basic ion, we solve in three logical steps.

- First determine the [salt ions]: apply the ***REC*** steps to the salt.

  The ***REC*** steps calculate the salt ion concentrations after the ions separate, but before they react as an acid or base with water.
- **Identify and label** each ion as *acidic* (A), *basic* (B) *or pH neutral* (N).
- Treat the *acidic* or *basic* ion as a weak acid or base that reacts with water. Solve by using the ***WRRECK*** steps for ionization (K_a) or hydrolysis (K_a or K_b).

We will summarize these steps as the "***REC*, label, *WRRECK***" rule for salts:

For **salt** solutions, to calculate $[H^+]$ or pH,

- ***REC*** the salt to find the concentration of each ion.
- **Label** each ion as A, B, or N.
- To the A or B ion, apply its K_a or K_b ***WRRECK*** steps.

Using the above rule, try this calculation.

Q. What would be the pH of a 0.25 M solution of NH_4Cl? (K_a $NH_4^+ = 5.6 \times 10^{-10}$)

* * * * *

Answer

WANT: pH . Find $[H^+]$ first.

DATA: $[NH_4Cl]_{\text{as mixed}} = 0.25$ M

pH prompt: $\boxed{pH \equiv -\log [H^+] \quad \text{and} \quad [H^+] \equiv 10^{-pH}}$

Strategy: Ammonium compounds are salts that are soluble in water: they separate 100% into ions.

To calculate $[H^+]$ or pH when a salt dissolves, analyze the *two* reactions that take place: the salt separating into ions, then the non-pH-neutral ion ionizing as an acid or hydrolyzing as a base.

For salt pH: REC the salt, **label** the ions A, B, or N, ***WRRECK*** the A or B ion.

***REC* steps**:

$$\begin{array}{llcll}
 & & & \textbf{A}\text{cidic} & \textbf{N}\text{eutral} \\
 & & & \wedge & \wedge \\
\textit{R\&E}: & 1\ NH_4Cl & \rightarrow & 1\ NH_4^+ & +\ 1\ Cl^- \qquad \text{(goes 100\%)} \\
 & \quad\wedge & & \quad\wedge & \quad\wedge \\
\textit{C}\text{onc}: & 0.25\text{ M} \rightarrow 0\text{ M} & & \mathbf{0.25\ M} & 0.25\text{ M}
\end{array}$$

***Label* the ions as *A, B,* or *N*:** According to the acid-strength table, the NH_4^+ ion is acidic, and the Cl^- ion is so weakly basic that it is pH-neutral.

WRECK: To find $[H^+]$, apply the ***WRRECK*** steps to the *non*-pH-neutral ion.

*W*ANT $\mathbf{[H^+]} = x$

Since the non-pH-neutral ion is *acidic*, write its ***R***eaction as an acid and its K as a $K_{\mathbf{a}}$.

$$\begin{array}{lccccl}
\text{Specific } \mathbf{R}: & NH_4^+ & \leftarrow\leftarrow\rightarrow & H^+ & + \ NH_3 & \text{(goes slightly)} \\
\text{General } \underline{\mathbf{R}} \ \& \ \underline{\mathbf{E}}: & WA & \leftarrow\leftarrow\rightarrow & H^+ & + \ CB & \text{(goes slightly)} \\
 & \wedge & & \wedge & \wedge & \\
\underline{C}\text{onc. at Eq}: & [WA]_{\text{mixed}} - x & & x & x &
\end{array}$$

$$K_{\mathbf{a}} \equiv \frac{[H^+]_{\text{eq.}}[CB]_{\text{eq.}}}{[WA]_{\text{at eq.}}} \equiv \frac{x^2}{[WA]_{\text{mixed}} - x} \qquad \boxed{\approx \frac{x^2}{[WA]_{\text{mixed}}}}$$

^ Definition ^ Exact ^ Approximate

SOLVE the K_a approximation for the WANTED symbol.

$$x^2 = (5.6 \times 10^{-10})\,(0.25) = 1.4 \times 10^{-10}$$

$$x = \text{estimate } 1\text{-}2 \times 10^{-5} = \boxed{\mathbf{1.2 \times 10^{-5}\ M = [H^+]}}$$

To see if the approximation is acceptable, apply the 5% test.

$$\textbf{\% Dissociation} = \frac{x}{[\textbf{WA or WB}]_{\textbf{mixed}}} \bullet \textbf{100\%} = \frac{1.2 \times 10^{-5}}{0.25} \bullet \mathbf{10^2}\ \% =$$

$$= \mathbf{4.8 \times 10^{-3}\ \%} = \mathbf{0.0048\%} = \text{less than 5\%, so the approximation is OK.}$$

Done? After long calculations, look back at the WANTED unit or symbol to make sure you have completed the problem.

WANT: **pH** $= -\log [H^+] = -\log(1.2 \times 10^{-5}) = \mathbf{4.?} = \boxed{4.92}$ (estimate, *then* calculate.)

Check: this mildly acidic pH is consistent with a salt composed of one acidic and one neutral ion.

Practice: Problem 3 is more challenging.

1. Which of these solutions passes the 5% test by the quick rule?
   a. For a weak base solution, [WB] = 0.020 M and $[OH^-] = 5.0 \times 10^{-5}$ M
   b. For a weak acid solution, [WA] = 0.0010 M and $[H^+] = 4.0 \times 10^{-5}$ M
2. Calculate the pH in a 0.10 M C_6H_5COOK solution (K_b of $C_6H_5COO^- = 1.6 \times 10^{-10}$).
3. Calculate the $[OH^-]$ in a 0.20 M calcium acetate solution.

ANSWERS

1a. In scientific notation, [WB] = 0.020 M = 2.0×10^{-2} M and $[OH^-] = \boldsymbol{x} = 5.0 \times 10^{-5}$ M . The difference in the exponents is 3 or greater. The ionization is less than 5% and passes the 5% test.

1a. In scientific notation, [WA] = 0.0010 M = 1.0×10^{-3} M and $[OH^-] = \boldsymbol{x} = 4.0 \times 10^{-5}$ M . The difference in the exponents is 2 or less. Use the dissociation equation for the 5% test. (4% -- *barely* passes)

2. WANT: **pH**

DATA: 0.10 M C_6H_5COOK

K_b of $C_6H_5COO^- = 1.6 \times 10^{-10}$

pH prompt: $\boxed{pH \equiv -\log [H^+] \text{ and } [H^+] = 10^{-pH}}$

Analysis: C_6H_5COOK (potassium benzoate) is an ionic compound (a salt). In all compounds that contain column one metals, the metal atoms are +1 ions. Compounds with column one metal atoms are soluble in water and separate ~100% into ions. In any [ion] calculation where a compound separates ~100% into ions, begin by writing the *REC* steps.

To find pH in salt solutions, ***REC*** the salt, **label** ions A, B, or N, ***WRRECK*** the A or B ion.

REC: Neutral **Basic**

R&E: 1 C_6H_5COOK → 1 K^+ + 1 $C_6H_5COO^-$ (goes 100%)

^ ^ ^

Conc: 0.10 M → 0 M 0.10 M (N) **0.10 M (B)**

Label ions. K^+ is neutral and in the acid-strength table, $C_6H_5COO^-$ is *basic*.

Because $C_6H_5COO^-$ is *basic,* the dominant pH-related reaction is $C_6H_5COO^-$ *base* hydrolysis governed by K_b . Apply the K_b prompt: write the *WRRECK* steps.

* * * * *

WRRECK:

WANT: **pH** For a *basic* ion, use K_b steps to find **[OH⁻]** first.

R and E: specific: $C_6H_5COO^- + H_2O \leftleftarrows\rightarrow$ **OH^-** + C_6H_5COOH (goes slightly)

(K_b reactions always have base and water on left and **OH^-** + conjugate acid on right.)

R and E general: **weak base + H_2O** $\leftleftarrows\rightarrow$ **OH^- + conjugate acid** (goes slightly)

^ ^ ^

Conc. at Eq: $[WB]_{mixed.} - x$ x x (*rice* bottom row)

K_b: $K_b = \dfrac{[OH^-][\text{conjugate}]}{[WB]_{mixed} - x} \approx \boxed{\dfrac{x^2}{[WB]_{mixed}} \approx K_b}$

Remember that K_a solves for $x = [H^+]$ and K_b solves for $x = [OH^-]$.

Make a DATA TABLE to match the *symbols* in the approximation; solve the approximation for *x*.

DATA: **$x = [OH^-] = ?$**

K_b of $C_6H_5COO^- = 1.6 \times 10^{-10}$

$[WB]_{mixed} = [C_6H_5COO^-] = 0.10$ M based on the *REC* steps above,

SOLVE: WANT: **$[OH^-] = x = ?$** Solving the **K_b** approximation:

$x^2 = K_b \cdot [WB] = K_b \cdot [C_6H_5COO^-] = (1.6 \times 10^{-10})(0.10) = 16 \times 10^{-12}$

$\boxed{x = 4.0 \times 10^{-6}\text{ M} = [OH^-]}$ But after solving with the approximation, do the

Quick 5% test : $x = 4.0 \times 10^{-6}$ M, **[WB]** = 0.10 M = 1.0×10^{-1} M

Since the difference in the exponents is 3 or more, the ionization passes the 5% test, and the approximation may be used.

WANT: **pH**. Since we just found **[OH⁻],** one option is to find pOH then use $\boxed{\textbf{pH} + \text{pOH} = 14.00 \text{ at } 25^\circ\text{C}}$

pOH = — log [**OH⁻**]) = —log(**4.0 x 10⁻⁶**)) = 5.? = **5.40** (estimate, *then* calculate.)

pH = 14.00 — **pOH** = 14.00 — **5.40** = $\boxed{\textbf{8.60}}$, which is a mildly basic pH, as expected.

3. WANT: **$[OH^-]$**

DATA: 0.20 M calcium acetate = 0.20 M $Ca(CH_3COO)_2$

Analysis: $Ca(CH_3COO)_2$ is a salt. Acetates (except silver acetate) are soluble in water.

> To find pH (or $[H^+]$ or **$[OH^-]$**) in salt solutions, ***REC*** salt, **label** ions, ***WRRECK*** A or B ion.

In calculations where a compound separates 100% into ions, begin by writing the *REC* steps.

$$\begin{array}{llllll} & & \textbf{N}\text{eutral} & & \textbf{B}\text{asic} & \\ \textit{\textbf{R\&E}}: & \mathbf{1}\ Ca(CH_3COO)_2 \rightarrow 1 & Ca^{2+} & + & \mathbf{2}\ CH_3COO^- & \text{(goes } \mathbf{100\%}) \\ & \wedge & \wedge & & \wedge & \\ \textbf{C}\text{onc}: & 0.20\ M \rightarrow 0\ M & 0.20\ M\ (N) & & \mathbf{0.40\ M\ (B)} & \end{array}$$

Label: Ca^{2+} is neutral, CH_3COO^- is mildly *basic* in the acid-strength table.

WRRECK: Because CH_3COO^- is *basic,* use K_b and the CH_3COO^- *base* hydrolysis reaction when you write the *WRRECK* steps.

WANT: **$[OH^-]$**

R and E specific: $CH_3COO^- + H_2O \leftarrow\leftarrow\rightarrow CH_3COOH + \mathbf{OH^-}$ (goes slightly)

(K_b reactions have base on left and **OH^-** + conjugate acid on right.)

R and E general: **weak base + H_2O $\leftarrow\leftarrow\rightarrow$ OH^- + conjugate acid** (goes slightly)

$$\begin{array}{llll} & \wedge & \wedge & \wedge \\ \textbf{C}\text{onc. at Eq}: & [WB]_{mixed} - x & x & \boldsymbol{x} \end{array}$$

K : $K_b = \dfrac{[OH^-][\text{conjugate}]}{[WB]_{mixed} - x} \approx \boxed{\dfrac{x^2}{[WB]_{mixed}} \approx K_b}$

To solve, make a DATA TABLE to match the *symbols* in the approximation:

DATA: **$x = [OH^-] = ? =$** $[CH_3COOH]$

K_b = **?** We don't have a K_b of CH_3COO^-, but can solve from table K_a of its conjugate.

$\boxed{K_w = K_b \times K_a}$, $\mathbf{K_b} = \dfrac{K_w}{K_a \text{ of } CH_3COOH} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \mathbf{5.6 \times 10^{-10}}$

K_b for CH_3COO^- = **5.6×10^{-10}**

$[WB]_{mixed}$ = from the *REC* steps: $\boxed{\mathbf{[CH_3COO^-] = 0.40\ M}}$

SOLVE: WANT: **$[OH^-] = x =$?**

Solving the ***K_b*** *approximation* for the WANTED *symbol*:

$$\boldsymbol{x^2} = K_b \cdot [WB]_{mixed} = (5.6 \times 10^{-10})(0.40) = 2.24 \times 10^{-10}$$

$x = \boxed{1.5 \times 10^{-5}\text{ M} = [OH^-]}$ Since we used the approximation, do the

Quick 5% test : $x = 1.5 \times 10^{-5}$ M, [**WB**] = 0.40 M = 4.0×10^{-1} M

Since the difference in the exponents is 4 = 3 or more, the ionization passes the 5% test, and the approximation may be used.

* * * * *

Lesson 32D: Salts That Contain Amphoteric Ions

Timing: Do this lesson *if* you are assigned problems that ask you to predict whether an amphoteric salt will be acidic or basic.

Pre-requisite: Complete Lesson 30G on polyprotic acids.

* * * * *

Recognizing Amphoteric Ions

Particles that are **amphoteric** can react as acids when mixed with bases, and bases when mixed with acids. Compounds that are amphoteric include water, amino acids, and many metal oxides.

Ions, as well as compounds, can be amphoteric. An ion that is amphoteric will be listed in an acid-strength table *twice*. The ion will be listed in the *right* column as a *base*, and then on a *lower* line in the table on the left side as an acid.

For example: find these amphoteric ions in two places in the acid-strength table in Lesson 31B: $\mathbf{HPO_4^{2-}}$ $\mathbf{HSO_4^-}$ $\mathbf{H_2PO_4^-}$

Polyprotic acids, when they ionize, always form one or more amphoteric ions.

- Diprotic acids (with two acidic hydrogens) form one amphoteric ion when they lose their first proton.

  Examples: Sulfuric acid forms one amphoteric ion: the hydrogen sulfate ion.

  $$H_2SO_4 \rightarrow H^+ + \mathbf{HSO_4^-}$$

  The $\mathbf{HSO_4^-}$ ion can react as an acid with a base, or as a base with an acid:

  $$H^+ \text{ from acid } + \mathbf{HSO_4^-} \rightarrow H_2SO_4$$

  $$OH^- \text{ from base } + \mathbf{HSO_4^-} \rightarrow SO_4^{2-} + H_2O$$

- Triprotic acids such as H_3PO_4 can successively ionize to form *two* amphoteric ions.

  $$H_3PO_4 \rightarrow \mathbf{H_2PO_4^-} \rightarrow \mathbf{HPO_4^{2-}} \rightarrow PO_4^{3-}$$

  The two *middle* ions in the series above can react as an acid or a base.

When the successive ionizations of a polyprotic acid are written in a series, all of the middle particles in the series (between the first and last particles) will be amphoteric.

Amphoteric Salt Solutions

Whether an amphoteric substance will react as an acid or a base will depend on what it is mixed with.

A frequent question is: If a *salt* that includes a *neutral* ion and an *amphoteric* ion is dissolved in water, will it form a solution that is acidic or basic? The rule is

An Amphoteric Salt: Acidic or Basic?

To determine whether a salt composed of an amphoteric and a neutral ion will form an acidic or basic solution, compare the K_a of the amphoteric ion acting as an acid to its K_b acting as a base.

If K_a is a *larger number*, the solution will be *acidic*, if K_b is larger, it will be *basic*.

The K_b of an amphoteric ion will often need to be calculated from the K_a of its conjugate acid using $\boxed{K_w = K_a \text{ x } K_b}$

Use those rules and the acid-strength table in Lesson 31B on the following problem.

Q. For a solution of sodium hydrogen carbonate ($NaHCO_3$),

a. What is the K_a value for HCO_3^-?

b. What is the K_b value for HCO_3^-?

c. Will the solution be acidic or basic?

* * * * *

Answer

a. The table lists K_a values for *acids* in the *left* column. Find HCO_3^- in the left column. $\boxed{K_a = \mathbf{5.6 \text{ x } 10^{-11}}}$

b. K_b may be found from the K_a of its conjugate acid. The conjugate acid of HCO_3^- is H_2CO_3, with $K_a = 4.3 \text{ x } 10^{-7}$.

For conjugate acid-base pairs: $K_w = \boxed{K_a \text{ x } K_b = 1.0 \text{ x } 10^{-14}}$

$$\mathbf{K_b} = \frac{1.0 \text{ x } 10^{\mathbf{-14}}}{K_a} = \frac{1.0 \text{ x } 10^{-14}}{\mathbf{4.3 \text{ x } 10^{-7}}} = 0.23 \text{ x } 10^{-7} = \boxed{\mathbf{2.3 \text{ x } 10^{-8} = K_b}}$$

c. $NaHCO_3$ ionizes to form Na^+ and HCO_3^-. Na^+ is an alkali metal ion in rows 3 -7; those ions are pH neutral. Because HCO_3^- is amphoteric, to determine if HCO_3^- is acidic or basic in water, its K_a is compared to its K_b. Since its K_b is higher (above), HCO_3^- is basic, and the $NaHCO_3$ solution has a **basic** pH.

* * * * *

Practice: Learn the rules for amphoteric salts above, then use the acid-strength table in Lesson 31B or a textbook to answer these.

1. Which of these are amphoteric particles?

   a. HSO_3^- b. NH_4^+ c. $H_2PO_4^-$ d. H_2SO_4 e. PO_4^{3-} f. H_2O

2. The K_a value of H_2SO_3 is 1.2×10^{-2}. The K_b value of SO_3^{2-} is 6.0×10^{-8}. What is the K_a value for HSO_3^- ?
3. Predict whether a solution of a salt composed of $H_2PO_4^-$ and a pH neutral atom will be acidic (A), basic (B), or neutral (N).
4. Will a solution of K_2HPO_4 be acidic (A), basic (B), or neutral (N)?
5. For citric acid, $H_3C_6H_5O_7$, $K_{a_1} = 7.1 \times 10^{-4}$, $K_{a_2} = 1.7 \times 10^{-5}$, and $K_{a_3} = 4.0 \times 10^{-7}$. Will a solution of $NaH_2C_6H_5O_7$ be acidic or basic?

ANSWERS

1. An amphoteric particle can act as both an acid and a base. If a particle is listed in both columns of the acid-strength table, it is amphoteric. The particle will be listed higher in the base column than in the acid column. Particles in this problem that meet those conditions are **a. HSO_3^-**, **c. $H_2PO_4^-$** and **f. H_2O**.

   H_2SO_4 and PO_4^{3-} can participate in reactions that *form* amphoteric ions, but they are not amphoteric, since H_2SO_4 cannot react as a base, and PO_4^{3-} cannot react as an acid.

2. The K_a for HSO_3^- can be calculated if you know the K_b of its conjugate base. Its conjugate base is SO_3^{2-}, with $K_b = 6.0 \times 10^{-8}$.

   For conjugate acid-base pairs: $K_w = \boxed{K_a \times K_b = 1.0 \times 10^{-14}}$

   $$\mathbf{K_a} = \frac{1.0 \times 10^{-14}}{K_b} = \frac{1.0 \times 10^{-14}}{\mathbf{6.0 \times 10^{-8}}} = 0.17 \times 10^{-6} = \boxed{\mathbf{1.7 \times 10^{-7}} = K_a}$$

   Quick check: $K_b \times K_a$ must estimate to = $\mathbf{K_w} = \mathbf{10.0} \times 10^{\mathbf{-15}}$ or 1.0×10^{-14}.

3. Since $H_2PO_4^-$ is amphoteric, its K_a as an acid and K_b as a base must be compared.

   The acid-strength table lists the K_a for $H_2PO_4^-$ as $\boxed{\mathbf{6.3 \times 10^{-8}}}$

   To find the K_b of $H_2PO_4^-$, write its conjugate acid formula: H_3PO_4

   Find the K_a of that conjugate acid in the acid-strength table: 7.2×10^{-3}

   And apply the rule for conjugate pairs: $K_w = \boxed{K_a \times K_b = 1.0 \times 10^{-14}}$

   SOLVE: $$\mathbf{K_b} = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{\mathbf{7.2 \times 10^{-3}}} = \boxed{\mathbf{1.4 \times 10^{-12}} = \mathbf{K_b} \text{ for } H_2PO_4^-}$$

Since the K_a of 6.3×10^{-8} is larger than the K_b of 1.4×10^{-12}, $H_2PO_4^-$ is **acidic**.

4. For ionic compounds dissolving in water, write the reaction for ions separating.

$K_2HPO_4 \rightarrow\rightarrow 2\ K^+ + HPO_4^{2-}$ That's two pH-neutral K^+ ions and one amphoteric ion.

Since HPO_4^{2-} is amphoteric, compare its K_a as an acid and K_b as a base.

The acid-strength table lists the K_a for HPO_4^{2-} as $\boxed{\mathbf{4.2 \times 10^{-13}}}$

To find the K_b of HPO_4^{2-}, write its conjugate acid formula: $H_2PO_4^-$,

find the K_a of that conjugate acid in the acid-strength table: 6.3×10^{-8}

And apply the rule for conjugates: $K_w = \boxed{K_a \times K_b = 1.0 \times 10^{-14}}$

SOLVE: $\mathbf{K_b} = \dfrac{\mathbf{1.0 \times 10^{-14}}}{K_a} = \dfrac{1.0 \times 10^{-14}}{\mathbf{6.3 \times 10^{-8}}} = \boxed{\mathbf{1.6 \times 10^{-7}} = \mathbf{K_b} \text{ for } HPO_4^{2-}}$

Since the K_a of 4.2×10^{-13} is smaller than the K_b of 1.6×10^{-7}, the solution is **basic**.

5. For ionic compounds dissolving in water, write the reaction for the ions separating.

$NaH_2C_6H_5O_7 \rightarrow Na^+ + H_2C_6H_5O_7^-$

Since there are three K values for citric acid, there are 3 H's that can be lost. This reaction therefore produces one pH-neutral Na^+ ion and one amphoteric ion.

Because $\mathbf{H_2}C_6H_5O_7^-$ is amphoteric, to determine if the salt solution will be acidic or basic, compare its K_a as an acid and K_b as a base.

When successive numeric K_a values are given, it helps to write out the ionization equations.

For: $\mathbf{H_3}C_6H_5O_7 \rightarrow H^+ + \mathbf{H_2}C_6H_5O_7^-$ $K_{a_1} = 7.1 \times 10^{-4}$

For: $\mathbf{H_2}C_6H_5O_7^- \rightarrow H^+ + \mathbf{H}C_6H_5O_7^{\mathbf{2-}}$ $K_{a_2} = 1.7 \times 10^{-5}$

For: $\mathbf{H}C_6H_5O_7^{\mathbf{2-}} \rightarrow H^+ + C_6H_5O_7^{\mathbf{3-}}$ $K_{a_3} = 4.0 \times 10^{-7}$

For $\mathbf{H_2}C_6H_5O_7^-$ acting as an acid, $\boxed{\mathbf{K_a = 1.7 \times 10^{-5}}}$

We need to compare that value to its K_b when acting as a base.

To find that value, we need to use the K_a of its conjugate acid and $\boxed{K_a \times K_b = 1.0 \times 10^{-14}}$

The *conjugate acid* of $\mathbf{H_2}C_6H_5O_7^-$ is $\mathbf{H_3}C_6H_5O_7$ with a $K_{a_1} = 7.1 \times 10^{-4}$

SOLVE: $\mathbf{K_b} = \dfrac{\mathbf{1.0 \times 10^{-14}}}{K_a} = \dfrac{1.0 \times 10^{-14}}{\mathbf{7.1 \times 10^{-4}}} = \boxed{\mathbf{1.3 \times 10^{-11} = K_b} \text{ for } \mathbf{H_2C_6H_5O_7^-}}$

Since the K_a is larger than the K_b for this amphoteric ion, the solution is **acidic**.

* * * * *

SUMMARY – pH of Salts

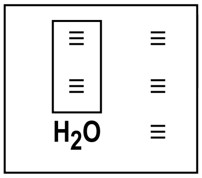
1. In salt solutions, for ions that are *not* amphoteric:

<u>**Neutral ions**</u> include

- In Rows 3-7, column 1 and 2 ions: **Na^+, K^+**, Rb^+, Cs^+; Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}.
- Plus conjugates of strong acids and bases, including **Cl^-**, **NO_3^-**.

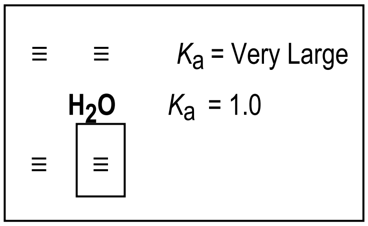
<u>**Acidic ions**</u> are

- Stronger acids than H_2O in an acid-strength table→
- OR have a K_a larger than 1.0 x 10^{-14}.
- Include **NH_4^+**, other $R\text{-}NH_x^+$, Fe^{3+}, Al^{3+}, and Sn^{4+}.



<u>**Basic ions**</u> are

- Conjugate bases of acids *below* K_a= 1.0; bases below H_2O as base OR with a K_b larger than 1.0 x 10^{-14} .
- include **F^-, CN^-, CH_3COO^-**, $C_6H_5COO^-$.



2. When predicting whether acid-base reactions with salt formulas will go to the right, take out the pH-neutral spectators, apply the Brønsted-Lowry labeling or diagonal rules, then put the spectators back in.
3. **For the pH of salt solutions**, ***if***
   - *Both* ions are neutral ions, pH ≈ 7.
   - *One ion* is *acidic*, and the other is *neutral*, solution will be *acidic* (pH <7).
   - *One* is *basic*, and the other is *neutral*, solution will be *basic* (pH>7).
   - One is acidic and one is basic: Compare the K_a and K_b for the two ions. If K_a is larger, solution will be acidic. If K_b is larger, it will be basic.
4. An amphoteric compound reacts as an acid when mixed with a base, and as a base when mixed with an acid.
5. To determine whether a salt with both amphoteric and neutral ions will form an acidic or basic solution, compare the numeric value of the K_a of the amphoteric ion as an acid to its K_b as a base. If K_a is larger, the solution is acidic, if K_b is larger, it is basic.
6. To calculate the pH of salt solutions, if the salt contains:
   - One *neutral* ion *plus* one *acidic* ion, apply K_a rules to the *acidic*-ion hydrolysis.
   - One *neutral* ion *plus* one *basic* ion, apply K_b rules to the *basic*-ion hydrolysis.

# # #

Module 33 — Buffers

Prerequisites: Complete Modules 29, 30, and 32 before starting this module.

Lesson 33A: Acid-Base Common-Ions; Buffers

Buffer Solutions

In chemical and biological systems, it is often important to **buffer** solutions to resist a change in pH when acids or bases are added. A buffer contains both an acid to react with bases and a base to react with acids.

Blood is one example of a buffered solution. As chemicals are added and removed during digestion and metabolism, the buffers in blood assure that its pH stays relatively constant, and the important pH-sensitive reactions that occur in blood can continue to take place.

Common-Ion Buffers

A **common-ion buffer** solution is a mixture of two components: a weak acid or base and its conjugate. One component may be ionic and one covalent, or both may be ionic. Both components must be substantially soluble in water.

One way to prepare a common-ion buffer is to mix

- a *weak acid* (K_a between 1 and 10^{-16}) or a *weak base* (K_b between 1 and 10^{-16}) with
- a soluble *salt* composed of a pH-neutral ion and the *conjugate* of the acid or base.

Each of the two components of the buffer reacts with water: the weak acid or base hydrolyzes slightly, while the soluble salt separates ~100% into ions. The reactions are:

(Weak acid or base) + H_2O $\leftarrow\leftarrow\rightarrow$ (H_3O^+ or OH^-) + *conjugate ion* (goes slightly)

Conjugate salt in water $\rightarrow\rightarrow\rightarrow$ pH-neutral ion + *same conjugate* (goes ~ 100%)

This mixture is called a *common-ion* buffer because the two reactions have one product in common: the same conjugate ion is formed in both the reaction of the weak acid or base with water, *and* the dissolving of the salt in water.

In a common-ion buffer, the common ion = the conjugate ion

How Buffers Differ From Weak Acid or Weak Base Solutions

Weak acid or base solutions contain both the weak acid or base and its conjugate. Buffer solutions also contain both a weak acid or base and its conjugate, but the two types of solutions are different.

- In a weak acid or weak base solution, the [weak acid or base] is much *higher* than the [conjugate], because a weak acid or base reacts only slightly with water to form its conjugate.
- In a buffer solution, the [weak acid or base] and [conjugate] are relatively close, because to create the buffer, substantial amounts of the conjugate particles are *added* to the solution of the weak acid or base.

For example,

Acetic acid is a weak acid: it ionizes only slightly and forms only a *small* concentration of hydrogen and acetate ions.

$$1\ \mathrm{CH_3COOH}(l) \leftarrow\leftarrow\rightarrow\ 1\ \mathrm{H^+}(aq) + 1\ \mathbf{CH_3COO^-}(aq) \qquad \text{(goes slightly)}$$

In 0.10 M acetic acid, $[\mathrm{CH_3COOH}] \approx \mathbf{0.10\ M}$ and $[\mathrm{CH_3COO^-}] = \mathbf{0.0013\ M}$

In a *buffer* solution that contains 0.10 M acetic acid *and* 0.10 M acetate ions, $[\mathrm{CH_3COOH}] \approx \mathbf{0.10\ M}$ and $[\mathrm{CH_3COO^-}] \approx \mathbf{0.10\ M}$

The acetic acid concentration is approximately the same in both solutions, but in the buffer, the concentration of the conjugate ion is much higher.

In a buffer, the moles and concentrations of the weak acid and the conjugate do not need to be the same, but they need to be relatively high and close, preferably differing by a ratio of less than 3 to 1. Why? For a buffer to be effective at limiting pH changes, it needs a relatively high number of moles of acid to neutralize base added, and a relatively high number moles of base to neutralize acid added.

Selecting Buffer Components

A buffer is a mixture of the acid and base of a conjugate pair. Since the acid in the conjugate pair must have one more positive charge than the base, *if* one particle in the pair is electrically neutral, the other must have a charge. *Both* particles in the conjugate pair can also be charged, so long as their charges differ by the +1 charge on a proton.

For example, in the conjugate pair $\mathrm{HSO_4^-}$ and $\mathrm{SO_4^{2-}}$, both particles are ions.

In short, *one* or *both* of the particles in a conjugate pair must be an *ion*.

A buffer may be *described* as either

- the two particles in the conjugate pair, in which at least one is an ion, *or*
- as two electrically neutral compounds that *contain* the particles in the conjugate pair, in which one or both of the compounds is a soluble salt.

For example: The acetic acid/acetate buffer can be represented as

$\mathrm{CH_3COOH}$ and $\mathbf{CH_3COO^-}$ *or as* $\mathrm{CH_3COOH}$ and $\mathrm{CH_3COO\mathbf{Na}}$

The first is the weak acid and its conjugate ion, the second is the weak acid and a salt that contains the conjugate ion.

To select a *conjugate particle* that will buffer a weak acid or weak base solution,

- find the weak acid or base in a table of acid strength (see Lesson 31B).
- The conjugate particle in the opposite column will buffer the solution.
- If one of the buffer components is amphoteric, two substances can buffer the solution: the conjugate acid will buffer to a lower (more acidic) pH, and the conjugate base will buffer to a higher pH.

If a problem asks for the formula for a neutral substance that will buffer an acid or base, first write the formulas for the conjugate pair. Then, for each particle that is an ion, pair the *ion* with a *pH-neutral* ion that will form a *soluble* combination, then write formula for that combination in a molecular formula (ionic solid) format. An ionic solid (salt) that will buffer a solution may contain either the acid *or* the base component of the conjugate acid-base pair.

Using the acid-strength table in Lesson 31B if needed, apply those rules to this problem.

Q. Write formulas for *two* ionic solids that would buffer the weak acid HF.

* * * * *

Answer: The conjugate base is F^-. Soluble salts that include F^- include NaF, KF, and RbF. The ion that you pair with F^- must be both pH-neutral and result in a soluble compound. All row 3-7 alkali metal ions are pH neutral, and all compounds that include those ions are water soluble.

To determine whether an ionic compound will buffer a weak acid or base solution,

- Write the reaction for the ionic solid separating into its *ions*.
- If one ion is pH neutral, the other ion is a conjugate of the weak acid or base, and the combination is water soluble, then the salt will buffer the solution.

Practice. Use the acid-strength table in Lesson 31B as needed.

1. Write the formula for the conjugates of

    a. NH_4^+ b. HNO_3 c. F^-

    d. HCO_3^- acting as a base e. HCO_3^- acting as an acid

2. Write the formula for an *ion* that would buffer solutions of these particles.

    a. C_6H_5COOH b. HCN

3. Write the formula for a *compound* that would buffer solutions of these particles.

    a. $C_6H_5COO^-$ b. CH_3COOH

4. Answer the following questions using these letters. Each question may have multiple letters for its answer.

    a. KF b. NH_4NO_3 c. NH_3 d. NaCN e. NH_4Cl

    i. Which compound(s) above will serve as a common-ion buffer for an HF solution?

    ii. Which compound(s) above will serve as a common-ion buffer for NH_3 solution?

    iii. Which compound(s) will form a buffer if mixed into an NH_4Cl solution?

ANSWERS

1. In the acid-strength table, the conjugate of a. NH_4^+ is **NH_3** b. HNO_3 is **NO_3^-** c. F^- is **HF**
   d. HCO_3^- if acting as a base, is the acid **H_2CO_3** e. HCO_3^- as an acid is the base **CO_3^{2-}**.
2. a. **$C_6H_5COO^-$** is an ion. Since it is also the conjugate base of the acid, it will buffer the solution.
   b. **CN^-** is the conjugate base of the acid HCN; it buffers an HCN solution.
3. a. The acid-strength table shows that $C_6H_5COO^-$ is the conjugate base of **C_6H_5COOH**. A buffer is a mixture of a conjugate acid-base pair, so C_6H_5COOH buffers $C_6H_5COO^-$.
   b. The acid-strength table shows that for CH_3COOH, CH_3COO^- is the conjugate base ion that would buffer the solution. A compound must have a neutral overall charge. Compounds that would buffer the solution include any pH–neutral ion that combines with the acetate ion to form a soluble combination, such as Na^+ to form **CH_3COONa**, or Mg^{2+} to form **$(CH_3COO)_2Mg$** . (Except for silver acetate, metal-acetate combinations are soluble).
4. i. **(a). KF** is a soluble salt with pH-neutral ion K^+ and basic F^-. F^- is the conjugate base of HF.
   ii. **(b)** and **(e)**. Both are soluble salts that contain the acid-conjugate NH_4^+ of the base NH_3.
   iii. **(c)**. NH_4Cl contains the *acidic* NH_4^+ ion and the pH-neutral Cl^- ion. The particle needed as a buffer is the base-conjugate of the acid, which is **NH_3** .

* * * * *

Lesson 33B: Buffer Example

Simplifying Buffer Calculations

Buffers are a mixture of an acid and a base. Buffer calculations can be solved based on *either* the K_a of the acid or the K_b of the base.

One way to simplify buffer calculations is to choose to solve based on K_a of the acid or the K_b and to use this approach consistently. We will use that method in these lessons. Our fundamental rule will be

> **Treat buffer** solutions as a weak *acid* ionization equilibrium to which *conjugate base* has been *added* and solve buffer calculations using K_a equations.

Reactions in a Buffer

An example of a common-ion buffer solution is the combination of aqueous acetic acid (CH_3COOH) and the *salt* sodium acetate. Let's describe the mixing of an acetic acid/acetate buffer, developing the equations for buffer calculations as we go.

1. First, mix 0.10 moles of the weak acid CH_3COOH and about 950 mL of water. Acetic acid is highly soluble and ionizes slightly ($K_a = 1.8 \times 10^{-5}$).

2. Next, add 0.20 moles of the solid but soluble salt *sodium acetate* (CH_3COONa) to the acetic acid solution. Dissolve the salt, then add a bit more water, with mixing, until the total volume is 1.0 L.

Write the concentrations of the two substances, as *mixed* into this solution, but before any reactions take place.

* * * * *

Since the moles of both compounds are dissolved in 1.0 liters of solution,

$[CH_3COOH]_{\text{as mixed}} = \mathbf{0.10\ M}$ and $[CH_3COONa]_{\text{as mixed}} = \mathbf{0.20\ mol/L}$

Those are concentrations "as mixed." However, those values do not represent the actual concentrations in the solution, because both substances react with water.

Write the *REC* steps for the reaction of CH_3COOH in water, then CH_3COONa in water, and then check your answers below.

* * * * *

<u>For the weak acid:</u>

Rxn. & ***E***xtent:	1 CH_3COOH	←←→	1 H^+	+	1 $\mathbf{CH_3COO^-}$	(goes slightly)
	^		^		^	
Conc@Eq. *symbols* =	$[WA]_{mixed} - x$	▌	x	|	x	
Conc@Eq.	$\underline{\mathbf{0.10\ M} - x}$	▌	$\underline{x}$	|	$\underline{x}$	

Because the weak acid ionizes *slightly*, its concentration is written as 0.10 M $- x$.

<u>For the salt:</u>

Rxn. & ***E***xtent:	**1** CH_3COONa	→→	**1** Na^+	+	**1** $\mathbf{CH_3COO^-}$	(goes ~ 100%).
	^		^		^	
Conc@Eq. *values*:	$\underline{\mathbf{0\ M}}$ ~~0.20 M~~	▌	0.20 M		$\underline{\mathbf{\mathit{0.20\ M}}}$	

The actual $[CH_3COO\mathbf{Na}]$ = 0 M, because in dilute aqueous solutions, all Na compounds dissolve and separate into ions essentially 100%.

Na^+ is a pH-neutral ion. CH_3COO^- is the conjugate base of the weak acid CH_3COOH. This solution is a buffer because it combines substantial amounts of both a weak acid and its conjugate base. CH_3COO^- is a *common ion* because it is formed in both reactions above that occur in the solution.

<u>Ion Concentrations In Buffers</u>

Adding the *numbers* and *x's* underlined in the two "***c***oncentration at equilibrium" rows above, fill in the chart below with the *total values* for the concentrations at equilibrium.

<u>Totals</u>:		<u>Exact</u>		<u>Approximate</u>
$[CH_3COOH]_{\text{at eq.}} = [WA]_{\text{eq.}}$	=	____________________	≈	______________
$[H^+]_{\text{at equilibrium}}$	=	____________________	≈	______________
$[CH_3COO^-]_{\text{at eq.}} = [CB]_{\text{eq.}}$	=	____________________	≈	______________

* * * * *

<u>Totals</u> in the buffer solution are — <u>Exact</u> — <u>Approx</u>. — <u>Approx. Symbol</u>

$[CH_3COOH]_{\text{at eq.}} = [WA]_{\text{eq.}} = \mathbf{0.10\ M} - x \approx \mathbf{0.10\ M} = \_\_\_\_\_\_\_\_\_\_$

$[H^+]_{\text{at equilibrium}} = x \approx x$

$[CH_3COO^-]_{\text{at eq.}} = [CB]_{\text{eq.}} = x + \mathbf{0.20\ M} \approx \mathbf{0.20\ M} = \_\_\_\_\_\_\_\_\_\_$

The [CB] at equilibrium includes the concentration formed when the weak acid ionizes (x), plus the concentration added by the salt used to form the buffer. However, in the *approximate* concentrations, the small x values that are added or subtracted from larger numbers are ignored.

Based on the *symbols* for WA and CB concentrations used in point 2 above, in the two *blanks* above, write what you think is an appropriate symbol for each approximate concentration.

* * * * *

$[CH_3COOH]_{\text{at eq.}} = [WA]_{\text{eq.}} = 0.10\text{ M} - x \approx \mathbf{0.10\ M} = \mathbf{[WA]_{as\ mixed}}$

$[CH_3COO^-]_{\text{at eq.}} = [CB]_{\text{eq.}} = 0.20\text{ M} + x \approx \mathbf{0.20\ M} = \mathbf{[CB]_{as\ mixed}}$

To summarize:

In buffer calculations: $[WA]_{\text{eq.}} \approx \mathbf{[WA]_{as\ mixed}}$ *and* $[CB]_{\text{eq.}} \approx \mathbf{[CB]_{as\ mixed}}$ and both are large compared to $[H^+] = x$.

The Buffer Equations

In buffer solutions, we are most often interested in the $[H^+]$.

For a weak acid alone, the reaction that occurs is

$$\mathbf{1\ WA}(aq) \leftleftarrows\rightarrow \mathbf{1\ H^+}(aq) + \mathbf{1\ CB}(aq) \qquad \text{(goes slightly)}$$

and the K equation that governs the reaction is:

$$K_a \equiv \frac{[H^+]_{eq.}[CB]_{eq.}}{[WA]_{\text{at eq.}}} \equiv \frac{x \cdot x}{[WA]_{\text{mixed}} - x} \approx \boxed{\frac{x^2}{[WA]_{\text{mixed}}} \approx K_a}$$

^ Definition — ^ Exact — ^ Approximation

After conjugate base is added to a weak acid solution to create a buffer, the weak-acid-ionization reaction continues to govern the formation of H^+. The K_a equation that allows us to calculate the $[H^+]$ has the same *definition*.

However, once additional conjugate is added, the two *top* terms in the three ratios are *no longer equal*. In a buffer, the K_a equations become

$$K_a \equiv \frac{[H^+]_{eq.}[CB]_{eq.}}{[WA]_{\text{at eq.}}} \equiv \frac{x \cdot (x + [CB]_{\text{mixed}})}{[WA]_{\text{mixed}} - x} \approx \boxed{\frac{x \cdot [CB]_{\text{mixed}}}{[WA]_{\text{mixed}}} \approx K_a}$$

^ Definition — ^ Exact — ^ Approximate

Calculations for both a weak acid ionization and a buffer solution are based on the same definition, but the exact and approximate equations are different. Note how they are different.

Now *calculate* the $[H^+]$ in this 0.10 M acetic acid/0.20 M acetate buffer solution. To do so, solve the boxed *buffer* approximation equation above. Use the **C**onc@Eq. *approximate* data in the totals table above, plus the K_a for $CH_3COOH = 1.8 \times 10^{-5}$.

* * * * *

$$K_a \approx \frac{x \bullet [CB]_{mixed}}{[WA]_{mixed}}$$

DATA:

$\mathbf{K_a} = 1.8 \times 10^{-5}$

$x = [H^+] = \mathbf{?}$

$[CB]_{mixed} = \mathbf{0.20\ M}$

$[WA]_{mixed} = \mathbf{0.10\ M}$

SOLVE:

* * * * *

$$\mathbf{?} = x = \mathbf{[H^+]} \approx \frac{K_a \bullet [WA]_{mixed}}{[CB]_{mixed}} \approx \frac{1.8 \times 10^{-5}\,(0.10)}{0.20} \approx \boxed{\mathbf{9.0 \times 10^{-6}\ M\ H^+}}$$

As always, units are omitted *during K* calculations, but concentrations that are calculated are labeled mol/L (or M).

Finally, apply the 5% test to see if the exact buffer equation needs to be solved.

* * * * *

Quick 5% test: $x = \mathbf{[H^+]} = 9.0 \times 10^{-6}$ M, $\mathbf{[WA]} = 0.10\ M = 1.0 \times 10^{-1}$ M

Since the difference in the exponents is 3 or more, the approximation may be used.

Done! We won't need to do all those steps for future buffer calculations. However, exploring in detail the impact of *common ions* on solution concentrations will be useful in several types of reactions where common ions are added to solutions.

Summary

1. A common-ion buffer solution is composed of a conjugate acid-base *pair* in which
   - each particle is a weak acid or base;
   - both particles in the pair have relatively high, but often different, concentrations;
   - one or both of the particles is an ion.
2. A buffer solution can be viewed as
   - A weak acid with conjugate base added, with reactions governed by K_a , or
   - A weak base with conjugate acid added, with reactions governed by K_b .

   To simplify calculations, these lessons will treat buffers as a weak *acid* ionization equilibrium to which *conjugate base* has been *added*, and solve using K_a equations.

3. For a buffer, the K_a ratios are

$$K_a \equiv \frac{[H^+]_{eq.}[CB]_{eq.}}{[WA]_{at\ eq.}} \equiv \frac{x \bullet (x + [CB]_{mixed})}{[WA]_{mixed} - x} \approx \boxed{\frac{x \bullet [CB]_{mixed}}{[WA]_{mixed}} \approx \mathbf{K_a}}$$

^ Definition ^ Exact ^ Approximate

In the buffer equations, $x = [H^+]$ = small, but [WA] and [CB] are large and often differ.

4. In a buffer solution,

$[WA]_{at\ eq.} \approx [WA]_{as\ originally\ mixed}$ *and*

$[CB]_{at\ eq.} \approx [CB]_{as\ originally\ mixed}$ into the buffer solution.

These “concentration as originally mixed” are easily measured and are usually the data supplied in problems.

5. In buffer equations, the [conjugate base] may be abbreviated as

$[CB]_{at\ eq.} \approx [CB]_{mixed}$ *or* $[CB]_{added}$ *or* [CB] *or* [base]

and the [weak acid] may be abbreviated in equations as

$[WA]_{at\ eq.} \approx [WA]_{mixed}$ *or* [WA] *or* [acid]

Practice

1. The general reaction for the ionization of a weak acid is

1 weak acid(aq) ←← → **1** $\mathbf{H^+}(aq)$ + **1 conjugate base**(aq) (goes slightly)

The ***K*** definition and exact equations for that reaction are

$$\mathbf{K_a} \equiv \frac{[H^+]_{eq.}\,[CB]_{eq.}}{[WA]_{at\ eq.}} \equiv \frac{x \bullet x}{[WA]_{mixed} - x} \approx \boxed{}$$

^Definition ^ Exact ^ Approximation

a. Modify the *exact* equation above to reflect the changes when conjugate base particles are added to make a buffer solution.

b. Based on the buffer exact equation, write the *approximate* buffer equation.

2. Which concentrations are small

a. In a weak acid approximation equation?

b. In a buffer approximation equation?

3. Which concentrations are equal

a. In a weak acid approximation equation?

b. In a buffer approximation equation?

4. For this reaction, write the ***K*** definition and exact equations.

Rxn. & ***E***xtent: $\mathbf{1\ A_2B}\ (aq) \leftarrow\leftarrow\rightarrow \mathbf{2\ A^{+}}(aq) + \mathbf{1\ B^{2-}}(aq)$ (goes slightly)

$\wedge \qquad \wedge \qquad \wedge$

Conc@Eq. = $[\mathbf{A_2B}]_{\text{mixed}} - x \quad | \quad 2x \quad | \quad x$

5. Write the *K* definition, exact, and approximation equations for the Problem 2 reaction, modified by adding a substantial amount of $\mathbf{B^{2-}}$ to the solution.

ANSWERS

1. $$K_a \equiv \frac{[H^+]_{eq.}\,[CB]_{eq.}}{[WA]_{at\ eq.}} \equiv \frac{x \bullet (x + [\text{CB } \textit{mixed}])}{[WA]_{mixed} - x} \approx \frac{x \bullet [CB]_{mixed}}{[WA]_{mixed}}$$

^Definition ^ Exact ^ Approximation

2. In the weak acid approximation equation, $\mathbf{x} = [H^+] = [CB]$ = small,

In the buffer approximation equation, $[H^+]$ is the only concentration that is small,

3 In the weak acid approximation equation, $[H^+] = [CB]$

In the buffer approximation equation, $[H^+]$ is small, and [WA] and [CB] are large and may be equal, but none of the concentrations are required to be equal.

4. $$K \equiv \frac{[A^+]^{\mathbf{2}}_{eq.}\,[B^{2-}]_{eq.}}{[A_2B]_{eq.}} \equiv \frac{(2x)^2 \bullet x}{[A_2B]_{mixed} - x} \text{ or } \frac{4x^2 \bullet x}{[A_2B]_{mixed} - x}$$

^Definition ^ Exact

5. $$K \equiv \frac{[A^+]^2_{eq.}\,[B^{2-}]_{eq.}}{[A_2B]_{eq.}} \equiv \frac{(2x)^2 \bullet (x + \mathbf{[B^{2-}]\ as\ mixed})}{[A_2B]_{mixed} - x} \approx \boxed{\frac{4x^2 \bullet \mathbf{[B^{2-}\ mixed]}}{[A_2B]_{mixed}}}$$

^Definition ^ Exact ^ Approximate

* * * * *

Lesson 33C: Buffer Components

Identifying Buffer Components

A key step that we will use to simplify buffer calculations is to fill in the following

Buffer Chart: **WA** *formula* = _________ **CB** *formula* = ___________

mol or $[WA]_{mixed}$ = _______ mol or $[CB]_{mixed}$ = _________

You need to be able to write the four *labels* for the blanks in the chart from memory.

The two formulas, WA and CB, must be a conjugate pair: the acid particle formula must have one more H and one more + charge than the base formula.

For some problems, you can fill in the buffer chart by inspection. Let's try an example.

Q. For a buffer that consists of 0.10 M HF and 0.20 M F^-, fill in the

Buffer Chart: **WA** *formula* = ______________ **CB** *formula* = ________________

mol *or* $[WA]_{mixed}$ = _________ mol *or* $[CB]_{mixed}$ = ___________

* * * * *

Buffer Chart: **WA** *formula* = **HF** **CB** *formula* = $\mathbf{F^-}$

mol or $[WA]_{mixed}$ = **0.10 M HF** mol or $[CB]_{mixed}$ = **0.20 M** $\mathbf{F^-}$

The buffer is a mixture of the weak acid HF and ions of its conjugate base F^-.

Salts In Buffers

In buffer problems, the ion or the two ions in the conjugate pair may be written as a part of a soluble ionic solid (salt). In problems that supply the concentration of the salt, you will need to write in the buffer chart the concentrations of the ions that form when the salt dissolves.

To do so, you must be able to recall from memory the formulas for ions that tend to form. It helps that most salts will include familiar ions that are always soluble. Recall that if a substance formula includes one or more of these groups:

- **Na K $\mathbf{NO_3}$ $\mathbf{NH_4}$**

then the compound is both soluble and will separate ~100% into ions in dilute aqueous solutions. Other combinations of ions are soluble as well (see solubility rules, Lesson 13A), but the four atoms/groups above are those encountered most frequently.

For some calculations in which salt formulas are supplied, you will be able to identify the ions and fill in the buffer chart by inspection. However, if the salts in a buffer solution are complex, it helps to write out the *REC* steps to list the ions and ion concentrations that form when ionic solids separate, and *then* fill in the buffer chart.

The rule is: If you cannot fill in a buffer chart by inspection, *REC* the salt(s).

Try this problem.

Q. For a buffer consisting of 0.20 M Na_2HPO_4 and 0.10 M NaH_2PO_4 , write and fill in the buffer chart.

* * * * *

Since both buffer components contain Na, both are ionic compounds (salts) that separate in water ~ 100% into ions. The *REC* steps for those t*w*o reactions are

***R**xn. & **E**xtent:*	$\mathbf{1\ Na_2H}PO_4$	→→	$\mathbf{2}\ Na^+$	+	$\mathbf{1\ H}PO_4^{2-}$	(goes ~ 100%)
	^		^		^	
***C**onc@Eq.*	0 M ~~0.20 M~~	▌	0.40 M		***0.20 M***	
***R**xn. & **E**xtent:*	$\mathbf{1\ NaH_2}PO_4$	→→	$\mathbf{1}\ Na^+$	+	$\mathbf{1\ H_2}PO_4^-$	(goes ~ 100%)
	^		^		^	
***C**onc@Eq.*	0 M ~~0.10 M~~	▌	0.10 M		***0.10 M***	

Identify the conjugate pair in the two dissolved salts, then complete the buffer chart.

* * * * *

In a buffer chart, the two *formulas* must be a conjugate pair. One or both formulas may be an ion. In this problem, based on the *REC* steps above,

Buffer Chart:	**WA** *formula* = $\mathbf{H_2PO_4^-}$	**CB** *formula* = $\mathbf{HPO_4^{2-}}$
	mol *or* $[WA]_{mixed}$ = **0.10 M** $H_2PO_4^-$	mol *or* $[CB]_{mixed}$ = **0.20 M** HPO_4^{2-}

Practice: Try to solve these by inspection first, but if you are not certain of your answer, *REC* the salt(s) and/or consult the acid-strength table in Lesson 31B.

1. From the list of ions below, write the formula(s) for the ions that are

   a. pH-neutral b. Acidic

   c. Always result in a compound containing the ion to be soluble.

   (1) Na^+ (2) NO_3^- (3) NH_4^+ (4) Cl^- (5) K^+

2. The following pairs of compounds can be mixed to make aqueous buffer solutions. Circle the compounds that are soluble salts.

   a. NaF and HF b. HCN and KCN c. NH_3 and NH_4Br

   d. C_6H_5COOH and C_6H_5COOK e. $NaHCO_3$ and Na_2CO_3

3. For each of the following buffer solutions, write and fill in this *first line* of the buffer chart.

   Weak acid (**WA**) formula = _________ Conjugate base (**CB**) formula = ________

   a. 0.20 M CN^- and 0.40 M HCN b. 0.10 M $NaHCO_3$ and 0.20 M Na_2CO_3

4. For each of the following buffer solutions, write and fill in a complete *buffer chart.*

   a. 0.25 M NH_3 and 0.30 M NH_4Cl

b. 0.10 M CH_3COOH and 0.15 M $(CH_3COO)_2Ca$

c. 0.40 mol Na_3PO_4 and 0.20 mol Na_2HPO_4

d. 0.15 M $C_6H_5NH_2$ and 0.25 M $C_6H_5NH_3Cl$

ANSWERS

1a. pH-neutral: (1) **Na^+** (2) **NO_3^-** (4) **Cl^-** (5) **K^+** (For review, see Lesson 31A)

1b. Acidic: **(3) NH_4^+** **1c.** Always soluble: (1) Na^+ (2) NO_3^- (3) NH_4^+ (5) K^+ (see Lesson 13A)

2. Salts are compounds composed of ions. In buffers, one or both components will be salts that are soluble in water, and one ion in the salt will be acidic or basic.

a. NaF -- is a **soluble salt**. The two ions are Na^+ and F^-. HF is composed of two non-metal atoms and will have less ionic character. According to the acid-strength table, HF behaves as a weak acid, which means that it ionizes only slightly.

b. KCN -- is a **salt**. Potassium atoms in compounds are always ions, and all potassium compounds are **soluble** and ionize 100% in dilute aqueous solutions. The two ions are K^+ and CN^-.

c. NH_4Br -- is ammonium bromide, a compound composed of ions, which makes it a **salt**. One ion formed is the ammonium ion **NH_4^+**. Ammonium compounds are soluble in water and ionize ~ 100%. NH_3 is weak base composed of two non-metals and has primarily covalent character.

d. C_6H_5COOK -- All potassium compounds are ionic, and ionic compounds are salts. K compounds are soluble in water and ionize ~100%. The ions formed are K^+ and CH_3COO^-.

e. $NaHCO_3$ and Na_2CO_3 -- Both contain Na. **Both** are therefore **soluble salts**.

3a. Weak acid (WA) formula = **H**CN Conjugate base (CB) formula = **CN^-**

3b. Weak acid (WA) formula = **H**CO_3^- Conjugate base (CB) formula = **CO_3^{2-}**

4a. Buffer Chart:	WA formula = **NH_4^+**	CB formula = **NH_3**
	mol *or* $[WA]_{mixed}$ = **0.30 M NH_4^+**	mol *or* $[CB]_{mixed}$ = **0.25 M NH_3**

If needed, **REC** the **salt(s)**:	**R&E**:	NH_4Cl	→→	NH_4^+	+	Cl^-	(goes ~ 100%)
		^		^		^	
	Conc.@Eq.	0.30 M → 0		**0.30 M**		0.30 M	

NH_3 is a covalent compound and a base, but not a salt. Treat the buffer as WA ionization of NH_4^+ with conjugate base **NH_3** added.

4b. Buffer Chart: WA formula = **CH_3COOH** CB formula = **CH_3COO^-**

mol *or* $[WA]_{mixed}$ = **0.10 M CH_3COOH** mol *or* $[CB]_{mixed}$ = **0.30 M CH_3COO^-**

If needed, **REC** salt(s): **R&E**: **1** $(CH_3COO)_2Ca$ →→ 1 Ca^{2+} + **2** **CH_3COO^-** (goes ~ 100%)
^ ^ ^
Conc.@Eq. 0.15 M → 0 0.15 M **0.30 M**

$(CH_3COO)_2Ca$ separates into calcium ion and acetate ions: it is a salt. Acetates (except silver acetate) are soluble in water. CH_3COOH is a weak acid and not a salt.

4c. Buffer Chart: WA formula = **HPO_4^{2-}** CB formula = **PO_4^{3-}**

mol *or* $[WA]_{mixed}$ = **0.20 mol HPO_4^{2-}** mol *or* $[CB]_{mixed}$ = **0.40 mol PO_4^{3-}**

If needed, **REC** salt(s): **R&E**: **1 Na_2**HPO_4 → → **2** Na^+ + **1 H**PO_4^{2-} (goes ~ 100%)
^ ^ ^
Conc@Eq. 0 M ~~0.20 M~~ ▌ 0.40 M ***0.20 M***

R&E: **1 Na_3**PO_4 → → **3** Na^+ + **1** PO_4^{3-} (goes ~ 100%)
^ ^ ^
Conc@Eq. ~~0.40 M~~ 0 M ▌ 1.20 M ***0.40 M***

4d. Buffer Chart: WA formula = **$C_6H_5NH_3^+$** CB formula = **$C_6H_5NH_2$**

mol *or* $[WA]_{mixed}$ = **0.25 M $C_6H_5NH_3^+$** mol *or* $[CB]_{mixed}$ = **0.15 M $C_6H_5NH_2$**

If needed, **REC** salt(s): **R&E**: $C_6H_5NH_3Cl$ → → **$C_6H_5NH_3^+$** + Cl^- (goes ~ 100%)
^ ^ ^
Conc.@Eq. 0.25 M → 0 **0.25 M** 0.25 M

* * * * *

Lesson 33D: Methodical Buffer Calculations

Buffer Steps

To solve buffer calculations methodically, we use the following steps.

1. **Fill in the buffer chart** using conjugate-pair formulas. If needed, ***REC* the *salt(s)*.**

   Buffer Chart: **WA** *formula* = ______________ **CB** *formula* = _________________

   mol *or* $[\text{WA}]_{mixed}$ = _______ mol *or* $[\text{CB}]_{mixed}$ = __________

2. ***WRECK* the *WA*,** adding conjugate base at step ***C***. Treat buffers as a weak acid ionizing, with CB mixed in.

   For all buffers, the *REC* steps will be

   $$\begin{array}{lcccccl} R \text{ and } E\text{:} & \textbf{WA} & \leftarrow\leftarrow\rightarrow & \textbf{H}^+ & + & \textbf{CB} & \text{(goes slightly)} \\ & \wedge & & \wedge & & \wedge & \\ C\text{onc@Eq.} & [\text{WA}]_{\text{mixed}} - x & \big| & x & \big| & x + [CB]_{mixed} & \end{array}$$

3. **At the *K* step,** write the **three *buffer* K_a equations.**

   $$K_{\mathbf{a}} \equiv \frac{[\text{H}^+]_{\text{eq.}}[\text{CB}]_{\text{eq.}}}{[\text{WA}]_{\text{at eq.}}} \equiv \frac{x \bullet (x + [\text{CB}]_{\text{mixed}})}{[\text{WA}]_{\text{mixed}} - x} \approx \boxed{\frac{x \bullet [\text{CB}]_{\text{mixed}}}{[\text{WA}]_{\text{mixed}}} \approx K_{\mathbf{a}}}$$

   ^ Definition ^ Exact ^ Approximation

   In a buffer, the two concentrations in the K_a numerators are *not* equal.

4. **Solve the K_a *approximation*** for the WANTED symbol.

   To solve the approximation, use the concentrations in the *buffer chart.*

5. **Calculate % dissociation.** If >5%, solve the *exact* K_a buffer equation as a quadratic.

> In short: To solve buffer calculations,
>
> - fill-in the buffer chart, *WRECK* the WA, solve the buffer approximation.

Let's practice on this example.

Q. Find the $[\text{H}^+]$ in a buffer solution composed of 0.10 M HF and 0.20 M NaF. (K_a of HF = 6.8×10^{-4})

Apply the steps, then check your answer below.

* * * * *

Answer

1. **Buffer Chart:** **WA** *formula* = **HF** **CB** *formula* = $\mathbf{F^-}$

   mol *or* $[\text{WA}]_{mixed}$ = **0.10 M** HF mol *or* $[\text{CB}]_{mixed}$ = **0.20 M** F^-

   If needed, *REC* salt(s):

   $$\begin{array}{lccccc} \textbf{R\&E:} & \textbf{NaF} & \rightarrow\rightarrow & \text{Na}^+ & + & \mathbf{F^-} \quad (\sim 100\%) \\ & \wedge & & \wedge & & \wedge \\ \text{Conc.@Eq.} & \cancel{0.20\text{ M}} \rightarrow 0 & & 0.20\text{ M} & & \mathbf{0.20\text{ M}} \end{array}$$

3. ***WRECK*** the WA, then add conjugate base.

   WANTED = $[H^+] = x$

   R and ***E***: $\quad \textbf{WA} \leftarrow\leftarrow\rightarrow \textbf{H}^{+} + \textbf{CB} \quad$ (goes slightly)

   $\qquad\qquad\qquad\qquad \wedge \qquad\quad \wedge \qquad\quad \wedge$

   Conc@Eq. $\quad [WA]_{mixed} - x \quad \| \quad x \quad | \quad x + [CB\ added]$

4. SOLVE the buffer approximation.

$$K_a \equiv \frac{[H^+]_{eq.}[CB]_{eq.}}{[WA]_{at\ eq.}} \equiv \frac{x \bullet (x + [CB]_{mixed})}{[WA]_{mixed} - x} \approx \boxed{\frac{x \bullet [CB]_{mixed}}{[WA]_{mixed}} \approx K_a}$$

   ^ Definition In Buffer: ^ Exact ^ Approximate

   Substitute K_a from the problem and the other values from the *buffer chart*, then solve for the WANTED symbol**.**

$$K_a = 6.8 \times 10^{-4} \approx \frac{x \bullet (0.20\text{ M})}{0.10\text{ M}}\ ; \qquad \boxed{x = \mathbf{3.4 \times 10^{-4}\ M = [H^+]}}$$

5. 5% test quick **:** $x = [H^+] = 3.4 \times 10^{-4}$ M, **[WA]** = 0.10 M = 1.0×10^{-1} M

   The exponent difference is 3 or greater. The % dissociation is **< 5%.** The approximation may be used.

Practice A: For these rules, you may consult the 6 steps above. Do one now and the other in your next practice session.

1. Calculate the $[H^+]$ in a solution containing 0.30 M HCN and 0.45 M KCN. (K_a of HCN = 6.2×10^{-10}).
2. In a solution containing 0.10 M NaH_2PO_4 and 0.20 M Na_2HPO_4, calculate the $[H^+]$. (K_a of $H_2PO_4^{-}$ = 6.7×10^{-8})

How the Conjugate Shifts the Equilibrium

In solution, a weak acid ionizes slightly, and the $[H^+]$ formed = [*conjugate base*] formed.

1 weak acid*(aq)* ←← → **1 H^+***(aq)* + **1 conjugate base***(aq)* (goes slightly)

When conjugate base is *added* to a weak acid solution, the [conjugate] becomes relatively large compared to that due to the weak acid ionization alone. The weak-acid-ionization reaction written above continues in both directions, but the concentrations of the reactants and products shift to new values at a new equilibrium. Try these questions.

Q1. According to Le Châtelier's Principle (Lesson 28A), how does increasing the [conjugate] change the $[H^+]$ in the reaction above?

* * * * *

Answer

Increasing the [conjugate], a particle on the right side of the equation, shifts the equilibrium to the left. This reduces the concentration of the other particle on the right, which is $\mathbf{H^+}$. As [conjugate] goes *up*, [H^+] goes *down*.

Q2. According to Le Châtelier's Principle, how does adding conjugate change the percent dissociation of the weak acid in the solution?

* * * * *

Answer

As the equilibrium shifts to the left, the [weak acid] goes up. That means less of the weak acid is ionizing (dissociating). The % dissociation becomes *lower*.

This smaller dissociation has an impact on buffer calculations. For dilute solutions of relatively strong weak acids ($K_a > 10^{-6}$), % dissociation is often >5%, and the exact *K* quadratic needs to be solved. However, if the same weak acid solution is buffered, the % dissociation is lower. The result is that buffer solutions are less likely to be dissociated > 5%, and you are less likely to need to solve a quadratic to solve a buffer calculation.

For buffers, the *approximation* equation nearly always gives an answer that is within the 5% uncertainty allowed in *K* calculations.

Practice B

1. In a weak acid solution, which will be higher: [H^+] or [conjugate]?
2. In a weak acid solution, which will be highest: [weak acid], [H^+], or [conjugate]?
3. In a weak acid solution to which a buffer salt has been added, which will be higher: [H^+] or [conjugate]?
4. In a weak acid solution, as a salt that buffers the solution is first added, what happens to the solution pH?

ANSWERS

Practice A

1. Strategy: A weak acid (HCN) and a salt with its conjugate = buffer solution. Use the 5 buffer steps.

1. Buffer Chart: **WA** *formula* = **HCN** **CB** *formula* = $\mathbf{CN^-}$

mol *or* $[\text{WA}]_{mixed}$ = **0.30 M** HCN mol *or* $[\text{CB}]_{mixed}$ = **0.45 M** CN^-

If needed, ***REC*** the salt: $\mathbf{1}\ \text{KCN} \rightarrow\rightarrow \mathbf{1}\ \text{K}^+ + \mathbf{1}\ \mathbf{CN^-}$ (separates 100%).

$\mathbf{0\ M}\ \cancel{0.45\ \text{M}} \rightarrow\rightarrow 0.45\ \text{M} \quad \mathbf{0.45\ M}$

2. ***WRECK*** the WA, then add additional conjugate base at step ***C***.

   WANTED = $[H^+] = x$

   R and ***E***: WA $\leftarrow\leftarrow\rightarrow$ H^+ + CB (goes slightly)
   ^ ^ ^
   Conc@Eq. $[WA]_{mixed} - x$ ▌ x | $x + [CB\ mixed\ in]$

3. At the WA ***K*** **step,** write the **three *buffer* K_a** equations**.**

$$K_a \equiv \frac{[H^+]_{eq.}[CB]_{eq.}}{[WA]_{eq.}} \equiv \frac{x \cdot (x + [CB]_{mixed})}{[WA]_{mixed} - x} \approx \boxed{\frac{x \cdot [CB]_{mixed}}{[WA]_{mixed}} \approx K_a}$$

^ Definition ^ Exact ^ Approximation

4. Solve the buffer approximation. Use values in the buffer chart.

   WANT: $[H^+] = x$

   SOLVE: $6.2 \times 10^{-10} \approx \dfrac{x \cdot 0.45\text{ M}}{0.30\text{ M}}$; $x \approx 6.2 \times 10^{-10} \cdot \dfrac{0.30}{0.45} \approx \boxed{4.2 \times 10^{-10}\text{ M} = [H^+]}$

   Check: the exponent of the K_a and the $[H^+]$ are within ± 1 .

   In buffers, you mix similar moles of acid and a base. Because the K_a of HCN is *smaller* than the K_b of its conjugate base (CN^-), the solution should be basic, and, since $[H^+] < 10^{-7}$, it is.

5. % Dissociation quick check: $x = [H^+] = 4.2 \times 10^{-10}$ M, [**WA**] = 0.30 M = 3.0×10^{-1} M
   = the dissociation is much less than 5%, so the approximation may be used.

2. Strategy: If the two substances include a conjugate pair, the solution is a buffer

   1. **Buffer Chart:** **WA** *formula* = $H_2PO_4^-$ **CB** *formula* = HPO_4^{2-}

      mol *or* $[WA]_{mixed}$ = **0.10 M** $H_2PO_4^-$ mol *or* $[CB]_{mixed}$ = **0.20 M** HPO_4^{2-}

      If needed, ***REC*** the salt(s):

      Rxn. & ***E***xtent: **1** NaH_2PO_4 $\rightarrow\rightarrow$ **1** Na^+ + **1** $H_2PO_4^-$ (goes ~ 100%).
      ^ ^ ^
      Conc@Eq. **0 M** ~~0.10 M~~ ▌ 0.10 M ***0.10 M***

      Rxn. & ***E***xtent: **1** Na_2HPO_4 $\rightarrow\rightarrow$ **2** Na^+ + **1** HPO_4^{2-} (goes ~ 100%).
      ^ ^ ^
      Conc@Eq. **0 M** ~~0.20 M~~ ▌ 0.40 M ***0.20 M***

   2. ***WRECK*** the weak acid ionization, then add additional conjugate base.

      WANTED = $[H^+] = x$

      $H_2PO_4^-$ is amphoteric, listed in the acid-strength table twice: on the right as a base, and on the left below as an acid. In this buffer, it is the weak *acid* in the conjugate pair. In water it will ionize slightly.

      R & ***E*** WA $\leftarrow\leftarrow\rightarrow$ H^+ + CB (goes slightly)
      ^ ^ ^
      Conc@Eq. $0.10\text{ M} - x$ ▌ x | $x + [0.20\text{ M CB}]$

3. At the WA **K step,** write the **three *buffer K_a*** equations**.**

$$K_a \equiv \frac{[H^+]_{eq.}[CB]_{eq.}}{[WA]_{at\ eq.}} \equiv \frac{x \cdot (x + [CB]_{mixed})}{[WA]_{mixed} - x} \approx \boxed{\frac{x \cdot [CB]_{mixed}}{[WA]_{mixed}} \approx K_a}$$

^ Definition ^ Exact ^ Approximation

4. Solve the buffer approximation. Use values in the buffer chart.

   WANT: **$[H^+] = x$**

   SOLVE: $6.7 \times 10^{-8} \approx \frac{x \cdot 0.20\ M}{0.10\ M}$; $x \approx 6.7 \times 10^{-8} \cdot \frac{0.10}{0.20} \approx \boxed{3.4 \times 10^{-8}\ M = [H^+]}$

5. % Dissociation quick check: **$x = [H^+]$** $= 3.4 \times 10^{-8}$ M M, **[WA]** = 0.10 M = 1.0×10^{-1} M

   The exponent difference is 3 or greater; so dissociation is < 5% and the approximation may be used.

Practice B

1. In a weak acid solution, H^+ and conjugate are formed in a 1 to 1 ratio, so $[H^+]$ **=** [conjugate].
2. In a weak acid solution, the weak acid has a substantially higher concentration than H^+ or conjugate.
3. A buffer adds conjugate to the weak acid solution. [Conjugate] becomes higher than $[H^+]$ **.**
4. Adding conjugate ion shifts the weak acid ionization reaction to the left, using up H^+. As $[H^+]$ goes down, pH goes UP.

* * * * *

Lesson 33E: Quick Buffer Calculations

Buffer Calculations – the Quick Steps

In most cases, two factors allow us to solve buffer calculations in fewer steps than required in the methodical method above.

1. In *weak acid* solutions, except for a few moderately strong weak acids, ionization is usually less than 5%, and the approximation equation can be used in calculations.

   In *buffers*, as noted in the prior lesson, the weak acid ionization is even lower than for the weak acid alone. For this reason, calculations based on the buffer approximation equation pass the 5% test even more often than for weak acid solutions.

2. In most courses, instructors will require that you write out the methodical buffer steps at least once during an assignment to demonstrate that you understand how the buffer approximation is derived. However, for buffer calculations, the generic reaction and K_a equations are the same or very similar, and after those steps are written once, in the calculations that follow you are often permitted to omit those steps.

For these reasons, for most buffer calculations it is acceptable to solve by the following

Buffer Quick Steps

1. Write "WANTED = " and the *symbol* wanted.
2. As DATA, fill in the **buffer chart.** If needed, *REC* the salts.
3. SOLVE the buffer *approximation* $K_a \approx \frac{[H^+]\,[CB]_{mixed}}{[WA]_{mixed}}$ using the chart data.

Try the quick steps on the following problem, then check your answer below.

Q. In a buffer solution that contains 0.25 M CN^- and 0.50 M HCN, find $[H^+]$. (K_a of HCN = 6.2×10^{-10}).

* * * * *

Answer

1. WANT: $[H^+]$
2. **Buffer Chart:** **WA** *formula* = **HCN** **CB** *formula* = $\mathbf{CN^-}$
   mol or $[WA]_{mixed}$ = **0.50 M HCN** mol or $[CB]_{mixed}$ = $\mathbf{0.25\ M\ CN^-}$
3. SOLVE: $K_a \approx \frac{[H^+]\,[CB]_{mixed}}{[WA]_{mixed}} \approx 6.2 \times 10^{-10} \approx \frac{[H^+]\ (0.25\ M)}{0.50\ M}$;

$$[H^+] = \frac{6.2 \times 10^{-10}\,(0.50)}{0.25} \quad \boxed{= 1.2 \times 10^{-9}\ M = [H^+]}$$

Practice A. Use the buffer quick steps.

1. Calculate the $[H^+]$ in a solution of 0.60 M C_6H_5COOH and 0.40 M $C_6H_5COO^-$. (K_a of C_6H_5COOH = 6.3×10^{-5}).
2. Find $[H^+]$ in a mixture of 0.10 M NaOCN and 0.20 M HOCN (K_a HOCN = 3.5×10^{-4})

Buffer Calculations Based On Moles

The buffer approximation equation can be written as

$$K_a \approx [H^+] \bullet \frac{[CB]_{as\ mixed}}{[WA]_{mixed}}$$

In a buffer, because the acid and base are both in the same liters of solution, liters can be cancelled in the fraction of the equation above.

$$\frac{[CB]}{[WA]} = \frac{\text{mol CB}/\cancel{\text{L of soln.}}}{\text{mol WA}/\cancel{\text{L of soln}}.} = \frac{\textbf{mol}\text{ CB}}{\textbf{mol}\text{ WA}}$$

This converts the buffer approximation to the form

$$K_a \approx \frac{[H^+]\,[CB]_{mixed}}{[WA]_{mixed}} \qquad OR \qquad K_a \approx \frac{[H^+]\,(\text{base } moles \text{ as mixed})}{(\text{acid } moles \text{ as mixed})}$$

For most buffer calculations, the data for WA and CB is supplied in moles/liter, but the buffer approximation can be solved if the WA and CB as mixed are measured in mol/L *or moles*, as long as both terms have the same unit.

A Check On Buffer Calculations

In most buffer solutions, comparing [WA mixed] and [CB mixed]: one is no more than 10 times the other. In the buffer approximation equation, this means that the fraction [CB]/[WA] has a value of between 1/10 and 10.

$$K_a \approx [H^+] \bullet \frac{[CB]_{mixed}}{[WA]_{mixed}} \approx [H^+] \bullet (10^{-1} \text{ to } 10)$$

This result means that

Using in scientific notation, for solutions mixed to be buffers, the *exponent* of the $[H^+]$ is nearly always within $\pm$ **1** of the *exponent* of the K_a .

For example, in the previous calculation, $K_a = 6.2 \times 10^{-10}$; $[H^+] = 1.2 \times 10^{-9}$ M

Use this rule as a *quick check* on your $[H^+]$ calculations in buffers.

This rule also results in an important

General Rule for Buffers:

In common-ion buffer solutions, the $[H^+]$ will be *close* in value (within a factor of 10) to the K_a of weak acid component of the buffer.

A Special Case: Equal Moles or Equal Concentrations

For the special case of a buffer in which [WA as mixed] is the *same* as [CB as mixed], in the buffer approximation equation, those two terms cancel. This means that *if* [WA] = [CB], then $[H^+]$ can be written by inspection: it is the same as the K_a .

$$K_a \approx \frac{[H^+] \bullet \cancel{[CB]_{mixed}}}{\cancel{[WA]_{mixed}}} \qquad \text{so} \qquad \boxed{K_a \approx x = [H^+] \quad if \;\; [WA] = [CB]}$$

Similarly, if the *moles* of WA and CB are in the same, then $[H^+] \approx K_a$.

In buffer solutions, *if* either [WA] = [CB] *or* **moles** WA = **moles** CB, then $[H^+] \approx K_a$.

Limitations

The buffer approximation equations are reliable within 5% as long as the mol/L WA that ionizes = x = $[H^+]$ is *small* compared to [WA] and [CB]. In most buffers, this will be the case, but if the WA ionization is high, or the solution is very dilute, you may need to solve the buffer quadratic to obtain more accurate results.

Summary: Buffer Quick Steps

1. Write "WANTED = " and the *symbol* wanted
2. As DATA, fill in the **buffer chart.** If needed, *REC* the salts.
3. SOLVE the buffer *approximation:* using the chart data.

$$K_a \approx \frac{[H^+]\,[CB]_{mixed}}{[WA]_{mixed}} \qquad \text{OR} \qquad K_a \approx \frac{[H^+] \text{ moles CB mixed}}{\text{moles WA mixed}}$$

4. Check: If [WA] and [CB] differ by <10x, **$[H^+]$** and **K_a** *exponents* are within **$\pm$ 1**.
5. ***If*** [WA] **=** [CB] *or* **moles** WA **= moles** CB, **$[H^+] \approx K_a$** .
6. In a buffer, the **$[H^+]$** will be *close* to the **K_a** of the weak acid component.

Practice B. Do the odd numbers first, and the evens if you need more practice. Problem 6 is more challenging.

1. Estimate the $[H^+]$ for a. Problem 2 b. Problem 3

Use the Quick Steps for Problems 2-5.

2. Find $[H^+]$ for a buffer solution in which KF= 0.20 mol and HF = 0.20 mol. K_a of HF = 6.8×10^{-4}
3. Calculate $[H^+]$ in a mixture of 0.25 M NaOBr and 0.50 M HOBr (K_a HOBr =2.3×10^{-9})
4. In a solution of 0.25 M NH_3 and 0.75 M NH_4Cl, find the $[OH^-]$. (K_b NH_3 = 1.8×10^{-5}).
5. 8.10 g of HCN and 4.90 g of NaCN are mixed into about half a liter of water. What is the pH in this solution? (K_a of HCN = 6.2×10^{-10}).
6. To have a pH of 5.00 in a buffer solution of 0.10 M CH_3COOH and ? M CH_3COONa, what must be the $[CH_3COONa]$? (K_a for CH_3COOH = 1.8×10^{-5})

ANSWERS

Practice A

1. **1.** WANT: $\mathbf{[H^+]}$

   2. Buffer Chart: **WA** *formula* = C_6H_5COOH **CB** *formula* = $C_6H_5COO^-$

   mol or $[WA]_{mixed}$ = **0.60 M** C_6H_5COOH mol or $[CB]_{mixed}$ = **0.40 M** $C_6H_5COO^-$

   3. Solve the buffer approximation: $\boxed{K_a \approx \frac{[H^+]\,[CB]_{mixed}}{[WA]_{mixed}}}$

   $6.3 \times 10^{-5} \approx \frac{[H^+]\,0.40\text{ M}}{0.60\text{ M}}$; $[H^+] = 6.3 \times 10^{-5} \cdot \frac{0.60}{0.40} = \boxed{9.4 \times 10^{-5}\text{ M} = [H^+]}$

   4. Check: the exponent of the K_a and the $[H^+]$ are within ± 1 .

2. **1.** WANT: $\mathbf{[H^+]}$

   2. Buffer Chart: **WA** *formula* = HOCN **CB** *formula* = OCN^-

   mol or $[WA]_{mixed}$ = **0.20 M** HOCN mol or $[CB]_{mixed}$ = **0.10 M** OCN^-

   3. Solve the buffer approximation: $\boxed{K_a \approx \frac{[H^+]\,[CB]_{mixed}}{[WA]_{mixed}}}$

   $3.5 \times 10^{-4} \approx \frac{[H^+]\,0.10\text{ M}}{0.20\text{ M}}$; $[H^+] = 3.5 \times 10^{-4} \cdot \frac{0.20}{0.10} = \boxed{7.0 \times 10^{-4}\text{ M} = [H^+]}$

   4. Check: the exponent of the K_a and the $[H^+]$ are within ± 1 .

Practice B

1a. In problem 2, $K_a = 6.8 \times 10^{-4}$, so $[H^+]$ in scientific notation must end in " $\times 10^{-\mathbf{3,4,or\ 5}}$ " by the check rule. The $[H^+]$ must be close to the K_a .

1b. In problem 3, $K_a = 2.3 \times 10^{-9}$, so $[H^+]$ in scientific notation must end in " $\times 10^{-\mathbf{8,9,or\ 10}}$ "..

2. WANT: $\mathbf{[H^+]}$

   Quick method: since 0.20 mol HF = 0.20 mol F^-, *mol WA mixed* cancels *mol CB mixed* in the approximation,

   and $\boxed{K_a \approx [H^+] \approx 6.8 \times 10^{-4}\text{ M}}$

3. **1.** WANT: $\mathbf{[H^+]}$

   2. Buffer Chart: **WA** *formula* = HOBr **CB** *formula* = OBr^-

   mol or $[WA]_{mixed}$ = **0.50 M** HOBr mol or $[CB]_{mixed}$ = **0.25 M** OBr^-

   3. Solve the buffer approximation: $\boxed{K_a \approx \frac{[H^+]\,[CB]_{mixed}}{[WA]_{mixed}}}$

$$2.3 \times 10^{-9} \approx \frac{[H^+]\ 0.25\ M}{0.50\ M}\ ; \quad [H^+] = 2.3 \times 10^{-9} \cdot \frac{0.50}{0.25} = \boxed{\mathbf{4.6 \times 10^{-9}\ M} = [H^+]}$$

4. Check: the exponent of the K_a and the $[H^+]$ are within ± 1 .

4. A mixture of a weak acid (**NH_4^+**) and its conjugate (**NH_3**) = a buffer solution.

1. WANT: **$[OH^-]$** In buffer calculations, find $[H^+]$ first.

2. **Buffer Chart:** **WA** *formula* = **NH_4^+** **CB** *formula* = **NH_3**

mol or $[WA]_{mixed}$ = **0.75 M NH_4^+** mol or $[CB]_{mixed}$ = **0.25 M NH_3**

If needed, *REC* the salt: **1** NH_4Cl →→ **1 NH_4^+** + 1 Cl^- (separates ~100%).

^ ^ ^

0 M ~~0.75 M~~ →→ 0.75 M 0.75 M

3. Solve the buffer approximation: $K_a \approx \frac{[H^+]\ [CB]_{mixed}}{[WA]_{mixed}}$

Since you are given K_b and need K_a , first use $\boxed{K_a \times K_b = 1.0 \times 10^{-14}}$

$$? = K_a\ NH_4^+ = \frac{1.0 \times 10^{-14}}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \mathbf{5.6 \times 10^{-10}} = K_a \text{ of } NH_4^+$$

$$K_a = \mathbf{5.6 \times 10^{-10}} \approx \frac{x \cdot 0.25\ M}{0.75\ M}; \quad x \approx \mathbf{5.6 \times 10^{-10}} \cdot \frac{0.75}{0.25} \approx \boxed{\mathbf{1.7 \times 10^{-9}\ M} = [H^+]}$$

4. Check: the exponent of the K_a and the $[H^+]$ are within ± 1 .

But WANTED = **$[OH^-]$** . Use K_w = $\boxed{[H^+][OH^-] = 1.0 \times 10^{-14}}$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = \frac{1.0 \times 10^{-14}}{\mathbf{1.7 \times 10^{-9}}} = 0.59 \times 10^{-5} = \mathbf{5.9 \times 10^{-6}\ M\ OH^-}$$

(K_w check: $[H^+] \times [OH^-]$ (circled) must estimate to **10.0** x 10^{-15} or **1.0** x 10^{-14}).

5. In chemistry, given grams, we convert to moles. Once we know moles, we can fill in the buffer chart.

For *grams* and moles, need molar masses: HCN = 27.0 g/mol ; NaCN = 49.0 g/mol

$$\textbf{? mol HCN} = 8.10\text{ g HCN} \bullet \frac{1\text{ mol HCN}}{27.0\text{ g HCN}} = 0.300\text{ mol HCN}$$

$$\textbf{? mol NaCN} = 4.90\text{ g NaCN} \bullet \frac{1\text{ mol NaCN}}{49.0\text{ g NaCN}} = 0.100\text{ mol NaCN}$$

1. WANT: **$[H^+]$**

2. Buffer Chart**:** **WA** *formula* = HCN **CB** *formula* = CN^-

mol or $[WA]_{mixed}$ = **0.300 mol** HCN mol or $[CB]_{mixed}$ = **0.100 mol** CN^-

3. Solve the buffer approximation that uses moles: $\boxed{K_a \approx \frac{[H^+]\ (\text{moles of base})}{\text{moles of acid}}}$

$$6.2 \times 10^{-10} \approx \frac{[\mathbf{H^+}]\ 0.100 \text{ mol}}{0.300 \text{ mol}} \quad ; \quad [\mathbf{H^+}] = 6.2 \times 10^{-10} \bullet \frac{0.300}{0.100} = \boxed{\mathbf{1.9} \times \mathbf{10^{-9}\ M} = [\mathbf{H^+}]}$$

4. Check: the exponent of the K_a and the $[H^+]$ are within ± 1 .

Note that if the buffer approximation fraction has *moles* as units, we do *not* need to know the solution volume (unless the solution becomes *very* diluted, in which case the approximation assumption that ***x*** is much smaller than [WA] and [CB] may no longer be true.

6. **1.** ***W***ANTED: $\mathbf{[CH_3COONa]} =$ $[CB]_{\text{mixed}}$ (write specific and general *symbols* WANTED)

DATA: pH = 5.00

$\boxed{\text{pH prompt: } pH \equiv -\log [H^+] \text{ and } [H^+] = 10^{-pH}}$

So $\mathbf{[H^+] = 1.0 \times 10^{-5}}$

$[CH_3COOH]_{\text{mixed}} = 0.10$ M = [WA mixed]

Strategy: A weak acid (CH_3COOH) and a salt with its conjugate ion = buffer solution.

To find the original salt concentration, find the [CB] as mixed into the solution.

To find [CB mixed], use the buffer steps .

2. **Buffer Chart:** **WA** *formula* = $\mathbf{CH_3COOH}$ **CB** *formula* = $\mathbf{CH_3COO^-}$

$[WA]_{mixed}$ = $\mathbf{0.10\ M\ CH_3COOH}$ $[CB]_{mixed}$ = $\mathbf{??\ M\ C_6H_5COO^-}$

REC the salt: $\underline{1}\,CH_3COONa \rightarrow\rightarrow 1\,Na^+ + \underline{1}\,CH_3COO^-$ (separates ~100%).

^ ^ ^

0 M ~~? ? ?~~ $[CB]_{\text{mixed}}$ →→ ? ? ? M ? ? ? $[CB]_{\text{mixed}}$

* * * * *

3. Solve the buffer approximation: $\mathbf{K_a} \approx \frac{[H^+]\ \mathbf{[CB]_{mixed}}}{[WA]_{mixed}}$ for the WANTED symbol.

$$\textbf{? = [CB mixed]} = \frac{K_a \bullet [WA]_{\text{mixed}}}{[H^+]} = \frac{1.8 \times 10^{-5}\,(0.10)}{1.0 \times 10^{-5}} = \boxed{\mathbf{0.18\ M\ [CH_3COO^-]}}$$

To find the WANTED symbol, substitute back into the salt *REC* equation.

REC the salt: $\underline{1}\,CH_3COONa \rightarrow\rightarrow 1\,Na^+ + \underline{1}\,CH_3COO^-$ (separates ~100%).

^ ^ ^

0 M ~~**0.18 M**~~ →→ 0.18 M $\underline{\mathbf{0.18\ M}}$

$\boxed{\mathbf{[CH_3COONa]_{as\ mixed} = 0.18\ M}}$

* * * * *

Lesson 33F: The Henderson-Hasselbalch Equation

Solving For pH in Buffers

In buffer solutions, you are often asked to find the pH rather than $[H^+]$.

The pH can be calculated after an $[H^+]$ is solved by the buffer approximation, but it is convenient to have a formula that calculates pH directly. We can derive such a formula by the following steps. The buffer approximation equation can be written as

$$K_\mathbf{a} \approx [H^+] \bullet \frac{[CB]_{\text{as mixed}}}{[WA]_{\text{mixed}}}$$

Taking the log of both sides, applying the rule that "the log of a product is the sum of the logs," then multiplying both sides by **−1** results in

$$\mathbf{-log}\,(K_\mathbf{a}) \approx \mathbf{-\,log}\,[H^+] \mathbf{-\,log} \left(\frac{[CB]_{\text{mixed}}}{[WA]_{\text{mixed}}}\right)$$

In science, the symbol for **−log** is a lower case **p ,** as in **−log** $[H^+]$ **= pH.** The above equation can therefore be written as

$$\mathbf{p}K_\mathbf{a} \approx \mathbf{pH - log} \left(\frac{[CB]_{\text{mixed}}}{[WA]_{\text{mixed}}}\right)$$

Solving for pH, the equation becomes $\mathbf{pH} \approx \mathbf{p}K_\mathbf{a} + \mathbf{log}\left(\frac{[CB]_{\text{mixed}}}{[WA]_{\text{mixed}}}\right)$

This form of the equation that solves for pH is known as the **Henderson-Hasselbalch** equation. It is usually written as

$$\boxed{\mathbf{pH} \approx \mathbf{p}K_\mathbf{a} + \mathbf{log}\left(\frac{[\mathbf{base}]}{[\mathbf{acid}]}\right)}$$

since [CB] = [base]
and [WA] = [acid] in a buffer.

The Henderson-Hasselbalch equation is simply the buffer approximation equation modified mathematically to solve for pH.

If **1.** WANTED **= buffer pH**

2. Fill in the *buffer chart.*

3. Write and solve the **Henderson-Hasselbalch** equation using *buffer chart* values.

Try this example.

Q. In a buffer that contains 0.30 M acetic acid and 0.20 M acetate ion, find the pH. (K_a $CH_3COOH = 1.8 \times 10^{-5}$)

* * * * *

Answer

1. WANTED = pH of a buffer.
2. **Buffer Chart:** **WA** *formula* = CH_3COOH **CB** *formula* = CH_3COO^-

   $[WA]_{mixed}$ = **0.30 M** CH_3COOH $[CB]_{mixed}$ = **0.20 M** CH_3COO^-

3. $$\mathbf{pH \approx pK_a + \log\left(\frac{[base]}{[acid]}\right)} = \mathbf{-\log}\,(1.8 \times 10^{-5}) + \log\,(0.20/0.30)$$

   $$= \mathbf{-(-4.74)} + \log\,(\mathbf{0.67}) = \mathbf{4.74 - 0.18} = \boxed{\mathbf{4.56 = pH}}$$

   (To review taking logs with a calculator, see Lesson 27D).

Practice A:

Commit the Henderson-Hasselbalch equation and rule above to memory, then do these.

1. If $X = 2.0 \times 10^{-12}$, pX = ?
2. If $K_a = 4.5 \times 10^{-7}$, pK_a = ?
3. If $pK_a = 5.50$, K_a = ?
4. Find the pH in a solution that contains 0.15 M HCN and 0.25 M NaCN.
   (K_a of HCN = 6.2×10^{-10}).

The Henderson-Hasselbalch Fraction: Moles *Or* Mol/L

The acid and base in a buffer solution are usually measured in terms of their *concentrations*, and the Henderson-Hasselbalch equation is solved using the form

$$pH \approx pK_a + \log\,(\mathbf{[base]/[acid]})$$

However, as with the buffer approximation, since the acid and base are dissolved in the same solution, the liters in which both components are dissolved is the same, and liters can be cancelled in the fraction of the equation.

$$\frac{[base]}{[acid]} = \frac{\text{mol base}/\cancel{\text{L of soln.}}}{\text{mol acid}/\cancel{\text{L of soln}}.} = \frac{\textbf{mol}\text{ base}}{\textbf{mol}\text{ acid}}$$

This converts the Henderson-Hasselbalch equation to the form

$$pH \approx pK_a + \log\,(\boldsymbol{mol}\ \mathbf{base}\ /\ \boldsymbol{mol}\ \mathbf{acid})$$

In upcoming problems when we solve for pH during titration, measuring the acid and base in moles will speed our calculations.

To reflect this option, let us modify our buffer pH rule as follows.

***If* 1. WANTED = buffer pH,**

2. Fill in the *buffer chart* for moles or mol/L .

3. Solve the **Henderson-Hasselbalch** equation using the *buffer chart* values and either

$$\text{pH} \approx \text{p}K_a + \log\left([\text{base}]\,\mathbf{/}[\text{acid}]\right)$$

or

$$\text{pH} \approx \text{p}K_a + \log\left(\textit{mol}\text{ base}\,\mathbf{/}\textit{mol}\text{ acid}\right)$$

Pick the form of the equation that best matches the data supplied in the problem.

Henderson-Hasselbalch Relationships

From the Henderson-Hasselbalch equation, we can derive additional relationships that simplify buffer calculations. In a buffer solution,

1. ***If* [acid] = [base]**, or ***moles* acid = *moles* base**, then **pH ≈ pK_a** .

   Why? If *base/acid* in moles or mol/L = *1* , then log(1) = log (10^0) = 0 , and the Henderson-Hasselbalch equation becomes **pH** ≈ pK_a + 0 ≈ **pK_a**

2. For different solutions of the same conjugate pair, if the mole or mol/L ratio *base/acid* is the same, the pH is the same.

   For example, in a buffer that contains **0.10 M NaF** and **0.20 M HF**, the pH will be the same as in a buffer containing **0.30 mol NaF** and **0.60 mol HF**.

   Buffer pH is based on the particle ratio *base/acid* , and in both of these solutions, that ratio is the same.

3. In buffer solutions, the **pH will be close to the pK_a** of the weak acid component.

   Why? Most buffers are mixed so that the moles of the acid and base are close, in order for the buffer to be able to neutralize substantial amounts of both acids and bases that may be added to the buffer. For the base and acid in most buffers, the mol/L of the one will not be more than 10 times the other.

   - If a base/acid ratio is between 1/10 and 10, the log of those numbers is small: Log 1/10 = **— 1** , log 10 = **+ 1 .**
   - When one component is double the other, Log 2 = **0.3** , log 0.5 = **— 0.3 ,** and the difference between pK_a and pH is smaller: **± 0.3 .**

   Adding those numbers to the **pK_a** in the Henderson-Hasselbalch equation results in a small change in pH.

   The math above gives us the

   Buffer pH check rule: when the acid and base are mixed in close to equal moles or concentrations (as in most buffers), *check* that the pH is within ± 2 of the number after the negative sign of the K_a of the weak acid component of the buffer.

   For example, in the problem above Practice A, $K_a = 1.8 \times 10^{-5}$ **; pH = 4.56**

The check rule also leads to a

Summary of fundamentals for buffers.

- A buffer contains a weak acid and its conjugate base, both in substantial concentrations. A buffer resists a change in pH if acid or base is added.
- In a buffer, the $[H^+]$ is *close* to the K_a of the weak acid component, and the **pH** is *close* to the $\mathbf{p}K_a$ of the weak acid component.

Summary: To Calculate *pH* In A Buffer

1. Write WANTED = symbol wanted.
2. Fill in the *buffer chart* using *either* moles *or* mol/L.
3. Substitute into the **Henderson-Hasselbalch** equation in the form

$$\mathbf{pH} \approx \mathbf{p}K_a + \log\left(\mathbf{[base]/[acid]}\right)$$

or

$$pH \approx pK_a + \log(\mathit{mol}\ \mathbf{base}/\mathit{mol}\ \mathbf{acid})$$

4. In a buffer, if *either* [WA] = [CB] **or** *moles* WA = *moles* CB, then $[H^+] \approx K_a$ and $pH \approx pK_a$.
5. For a given conjugate pair in different buffer solutions, if the ratio [base]/[acid] **or** mol base/mol acid is the *same*, the **pH** is the same, and $[H^+]$ is the *same*, in the two solutions.
6. **Buffer pH check rule**: when the moles or concentrations of acid and base close to equal (as in most buffers), *check* that the *pH* is within **± 2** of the number after the negative sign of the K_a .

Practice B. Put a check by problem numbers as you do them. Save one or two for your next practice session.

1. In which solution in Questions 2-5 below will $pH = pK_a$?
2. Using the Check Rule, do a quick whole number *estimate* of the top and bottom of the range of possible pH values in these buffer solutions.
   a. 0.45 M HF and 0.15 M NaF (K_a of HF = 6.8×10^{-4})
   b. 0.15 mol HOCl and 0.30 mol KOCl (K_a of HOCl = 3.5×10^{-8})
3. Find the pH for the buffer solutions in Problem 2.
4. In a buffer consisting of 0.20 mol NH_3 and 0.20 mol NH_4Cl, what is the pH? (K_b of NH_3 = 1.8×10^{-5})
5. A solution consists of 0.30 M K_2CO_3 and 0.40 M $KHCO_3$. Calculate the pH. For H_2CO_3, $K_{a1} = 4.3 \times 10^{-7}$ and $K_{a2} = 5.6 \times 10^{-11}$.

6. If you needed a buffer solution with a pH of 6, which would you choose as the conjugate acid of the buffer: HOBr, NH_4^+, HCN, or CH_3COOH ? (K_a values: HOBr = 2.3×10^{-9}, NH_4^+ = 5.6×10^{-10} , HCN = 6.2×10^{-10} , and CH_3COOH = 1.8×10^{-5}).

ANSWERS

Practice A

1. If X = 2.0×10^{-12} , pX = ? = $-\log(2.0 \times 10^{-12}) = -(-11.70) = \boxed{11.70}$

   The prefix **p** is an abbreviation for the function **—log .**

2. If $K_a = 4.5 \times 10^{-7}$, pK_a = ? = $-\log(4.5 \times 10^{-7}) = -(-6.35) = \boxed{6.35}$

3. If pK_a = 5.50 , K_a = ? Since $\boxed{\mathbf{pH} \equiv -\log[H^+] \text{ and } [H^+] \equiv 10^{-pH}}$

   then $\boxed{pK_a \equiv -\log K_a \quad \text{and} \quad K_a \equiv 10^{-pK_a}}$ = ? = $10^{-5.50}$ = $\boxed{3.2 \times 10^{-6} = K_a}$

4. WANT: pH of a buffer. To find buffer pH directly, fill in the buffer chart, then solve the H-H equation.

   Buffer Chart: WA *formula* = **HCN** CB *formula* = CN^-

   mol or $[WA]_{mixed}$ = **0.15 M** HCN mol or $[CB]_{mixed}$ = **0.25 M** CN^-

$$pH \approx pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = -\log(6.2 \times 10^{-10}) + \log(0.25 / 0.15)$$

$$= 9.21 + \log(1.67) = 9.21 + 0.22 = \boxed{9.43 = pH}$$

Practice B

1. **Question 4**. If [WA] = [CB] , then pH = pK_a .
2. The check rule: the calculated pH and the number after the minus sign in the K_a should be within ± 2 .
   a. K_a of HF = 6.8×10^{-4} , pH should be 4 ± 2: **between 2 and 6**.
   b. K_a of HOCl = 3.5×10^{-8} , pH should be 8 ± 2: **between 6 and 10.**

3a. WANT: pH of a buffer. Fill in the buffer chart, then solve the H-H equation.

Buffer Chart: WA *formula* = **HF** CB *formula* = F^-

mol or $[WA]_{mixed}$ = **0.45 M** HF mol or $[CB]_{mixed}$ = **0.15 M** F^-

$$pH \approx pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = -\log(6.8 \times 10^{-4}) + \log(0.15 / 0.45)$$

$$= 3.17 + \log(0.33) = 3.17 - 0.48 = \boxed{2.69 = pH}$$ Between 2-6? Check.

3b. WANT: pH of a buffer. Fill in the buffer chart, then solve the H-H equation.

Since the buffer data is in moles, complete the buffer chart second line based on moles instead of mol/L.

Buffer Chart: WA *formula* = **HOCl** CB *formula* = ClO^-

mol or $[\mathbf{WA}]_{mixed}$ = **0.15 mol** HOCl mol or $[\mathbf{CB}]_{mixed}$ = **0.30 mol** ClO^{-}

pH ≈ **pK_a** **+ log (mol base /** mol **acid**) = $-\log(3.5 \times 10^{-8})$ + log (0.30 **/** 0.15)

= **7.46** + log (2.00) = 7.46 **+ 0.30** = $\boxed{\mathbf{7.76 = pH}}$ Between 6-10? Check.

4 WANT: **pH** of a buffer. Solve using the shortcut: Since [WA] = [CB] , **pH ≈ pK_a** . But in this problem, we are given the K_b of the base.

To find K_a of the acid, use the rule for conjugate pairs: $\boxed{K_a \times K_b = 1.0 \times 10^{-14}}$

$$? = K_a\ NH_4^{+} = \frac{1.0 \times 10^{-14}}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = K_a\ NH_4^{+}$$

$$pH \approx pK_a = -\log(5.6 \times 10^{-10}) = -(-9.25) = \boxed{9.25 = pH}$$

<u>Check</u>: K_a of NH_4^{+} = 5.6×10^{-10} , pH estimate is 8 -12. Check.

5. Two mixed substances with similar formulas often indicate a buffer. Try to complete the buffer chart by inspection. If needed, *REC* the salt(s).

   1. **Buffer Chart:** W**A** *formula* = $\mathbf{HCO_3^{-}}$ **CB** *formula* = $\mathbf{CO_3^{2-}}$

      mol or $[WA]_{mixed}$ = **0.40 M** HCO_3^{-} mol or $[CB]_{mixed}$ = **0.30 M** CO_3^{2-}

   2. In the Henderson-Hasselbalch equation, K_a is needed.

      In this problem, the two conjugate ions are formed by the successive ionization of the polyprotic acid H_2CO_3. The K_a value for the *acid* in this buffer, HCO_3^{-} , is the *K* of the second H_2CO_3 ionization: K_{a2} = 5.6×10^{-11} (see Lesson 28G on polyprotic acids).

$$pH \approx pK_a + \log([base]/[acid]) = -\log(5.6 \times 10^{-11}) + \log(0.30 / 0.40)$$

$$= -(-10.25) + \log(0.75) = 10.25 + (-0.12) = \boxed{10.13 = pH}$$

<u>Check</u>: K_a of $\mathbf{HCO_3^{-}}$ = 5.6×10^{-11} , pH should be between 9 and 13.

6. The pH of the buffer will be within ±2 of the after the negative sign in the K_a of the acid component. Only CH_3COOH has a K_a number that is within 2 of 6.

* * * * *

<u>SUMMARY – Buffers</u>

1. A buffer solution resists a change in pH when an acid or base is added. A buffer can be made from a weak acid or base and the conjugate of the acid or base.

2. To solve buffer calculations for $[H^{+}]$, the methodical steps are:
   1. Fill in the buffer chart. If needed, *REC* the *salt(s)*.
   2. *WRECK* the *WA* ionization, then add [CB added].
   3. At the WA ***K*** step, write the three *buffer* K_a equations.

4. Solve the buffer approximation.
5. Calculate the % dissociation. If >5%, solve the exact buffer quadratic.

3. To solve buffer calculations for $[H^+]$, the quick steps are
   1. Write the symbol WANTED.
   2. Fill in the buffer chart. If needed, *REC* the *salt(s)*.

      Buffer Chart: **WA** *formula* = ______________ **CB** *formula* = ________________

      mol *or* $[WA]_{mixed}$ = _______ mol *or* $[CB]_{mixed}$ = __________

   3. Write and solve the buffer approximation:

$$\boxed{K_a \approx \frac{[H^+]\,[CB]_{mixed}}{[WA]_{mixed}}} \quad OR \quad K_a \approx \frac{[H^+]\,(\text{base moles as mixed})}{(\text{acid moles as mixed})}$$

4. To solve buffer calculations directly for pH,
   - Complete the buffer chart in moles or mol/L, then
   - Substitute the buffer chart values into the Henderson-Hasselbalch equation:

$$\mathbf{pH} \approx \mathbf{p}K_a + \mathbf{log}\left(\frac{[\text{base}]}{[\text{acid}]}\right) \quad or \quad \text{pH} \approx \text{p}K_a + \log(\textit{mol}\ \textbf{base} / \textit{mol}\ \textbf{acid})$$

5. In a buffer, if [WA] = [CB] **or** *mol* WA = *mol* CB, then $[H^+] \approx K_a$ and $pH \approx pK_a$.
6. **In general in buffers,** the $[H^+]$ is close to the K_a of the weak acid component, and the pH is close to the pK_a of the weak acid component.
7. **Summary of acid-base check rules**
   a. In aqueous solutions, $[H^+] \times [OH^-]$ must = $K_w = \mathbf{10.0} \times 10^{-15}$ or $\mathbf{1.0} \times 10^{-14}$.

   b. In conjugate pairs, $K_b \times K_a$ must estimate to = $K_w = \mathbf{10.0} \times 10^{-15}$ or $\mathbf{1.0} \times 10^{-14}$.

   c. If the $[H^+]$ is written in scientific notation, the number after the negative sign in the exponent of the $[H^+]$ must be within ± 1 of the pH.

   d. **The Quick 5% Test** to see if an approximation equation can be used
      - Using scientific notation, compare [WA] to $[H^+] = x$ or [WB] to $[OH^-] = x$.
      - If the *exponents differ* by *3 or more*, the ionization is less than 5%.
      - If the exponents differ by *2 or less*, use the % dissociation *equation* for the 5% test.

   e. **Buffer pH check rule**: when the acid and base are in close to equal moles or concentrations (as in most buffers), *check* that
      - the exponent of the K_a and the $[H^+]$ are within ± 1 .
      - the *pH* is within **± 2** of the number after the negative sign in the K_a of the acid.

# # # # #

Module 34 — pH During Titration

Prerequisites: Complete Module 33 before starting this module.

* * * * *

Lesson 34A: pH In Mixtures

Solving for pH in Acids and Bases, Salts, and Buffers

So far, our study of acids and bases has included finding $[H^+]$ and pH for solutions of

- *One* acid or base that is strong or weak;
- Polyprotic acids;
- Salts with one ion that is acidic, basic, or amphoteric; and
- A mixture of an acid and its conjugate base (a buffer).

These types of calculations have components in common, but their steps are not the same. In calcuations involving on acids and bases, it will be necessary to identify what *type* a problem is, then to apply the steps needed to solve that problem type. A summary can helping in learning the similarities and distinctions in the problem types. Your list might include the following.

Summary: In aqueous solutions, to calculate $[H^+]$, $[OH^-]$, or pH, for

1. A strong acid or hydroxide base, use the *REC* steps based on ~100% ionization

   or quick steps: $[HCl \text{ or } HNO_3]_{mixed} = [H^+]$ *and* $[NaOH \text{ or } KOH] = [OH^-]$
2. Weak *acids*: use the *WRRECK* steps and and/or K_a approximation.
3. Weak *bases*: use the *WRRECK* steps and solve K_b approximation.
4. Conjugate pairs: use $\boxed{K_a \times K_b = 1.0 \times 10^{-14}}$
5. Polyprotic acids: use K_{a1} and the *WRRECK* steps if K_{a1} is >100 times K_{a2}.
   If not, add the contributions of the first two ionizations.
6. Salts with *one* ion that is a weak acid or base:
   - *REC* the salt, write and label the ions as A, B, or N, *WRRECK* the A or B ion.
7. Buffer solutions:
   - Treat as a weak acid with conjugate base added.
   - Complete the buffer chart.
   - Solve the buffer approximation or the H-H equation using mol or mol/L WA and CB as mixed.

Practice A

For aqueous solutions of the following,

1. NaF and HF 2. NaCN 3. NH_3 4. CH_3COOH 5. $NaHCO_3$
6. KCl 7. H_2CO_3 8. KOH 9. NH_4Cl 10. HNO_3

Pick *one* term from the following list that *best* characterizes the solution.

a. Strong acid b. Strong base c. Weak acid d. Weak base
e. Acidic salt f. pH neutral salt g. Basic salt h. Amphoteric salt
i. Polyprotic acid j. Buffer

Types of Acid-Base Solutions

So far, all of our $[H^+]$, $[OH^-]$, and pH calculations have been for solutions at equilibrium: if an acid-base reaction did occur, it is now over, and no further changes in the solution are taking place.

In addition, all of the systems we have studied have had either

- one pH-dominant component (one strong or weak acid or base), or
- have been a buffer: a mixture of one weak acid or base and its conjugate.

We now turn our attention to other *mixtures* of acids and bases. The rules for finding $[H^+]$ or pH for mixtures acids or bases include the following.

1. For mixtures of acids and bases, we will adopt the following vocabulary:
   a. The *opposite* of an acid will mean a base, and the *opposite* of a base will mean an acid.
   b. *Strong* acids and bases are those that ionize ~100% to form H^+ or OH^- ions.
   c. *Weak* acids and bases will be those with K_a or K_b values between one and 10^{-16} according to acid-strength tables (see Lesson 31B).
2. Any *strong* acid or base will react with its opposite *if* opposite is present.

   If a mixture contains a strong acid and any base, or a strong base and any acid, a *reaction* must take place. The limiting reactant will be used up quickly, and the mixture will *then* be at *equilibrium*. We will discuss these *reaction* cases in a later lesson.

   However, a strong acid can be *at equilibrium* in a mixture with other acids or pH-neutral particles. A strong base can be at equilibrium in a mixture with other bases or pH-neutral particles. In those mixtures, no further net reaction will occur.
3. In a mixture at equilibrium, the pH is largely determined by the *types* of particles present in significant concentrations (greater than ~0.001 M). To calculate the pH in a mixture of acidic, basic, and neutral particles, use these general steps.
   - Label each particle in the mixture as neutral or as a strong or weak acid or base,
   - Solve for the pH as determined by the pH-*dominant* particle.

3. Specifically, apply these steps in order to determine the $[H^+]$ or pH for a solution at equilibrium.
   a. Re-write formulas for soluble ionic compounds (salts) in their *separated*-ions format.
   b. Label each particle in the mixture as a strong acid (SA), strong base (SB), weak acid (WA), weak base (WB), or pH neutral (N), based on the definitions in point 1 above. These definitions and labels are based on *absolute* rather than comparative strength: a solution may have more than one SA, SB, WA, WB, or N particle.
   c. If all particles in a mixture are pH neutral, solution pH = 7 .
   d. Ignore pH-neutral (N) particles if mixed with acidic or basic particles.

      Particles that are pH-neutral, including Na^+, K^+, Cl^-, and NO_3^-, do *not* change the solution pH.
   e. If the mixture contains a *strong* acid or base, its concentration determines the pH.

      The logic is: if a *strong* acid or base is present, it is the dominant factor in deciding pH. Contributions by any weak components in the mixture are relatively small and with rare exception can be ignored.

      To find $[H^+]$ in solutions containing *strong* acids or bases, either write the *REC* steps for 100% ionization *or* use the quick steps:

      $[\text{HCl or } HNO_3]_{\text{mixed}} = [H^+]_{\text{in soln.}}$ *and* $[\text{NaOH or KOH}] = [OH^-]_{\text{in soln.}}$
   f. If a *weak* acid or base and its *conjugate* are present in substantial amounts, the solution is a buffer. Use the buffer chart and K_a or Henderson-Hasselbalch equations to find the pH.
   g. If the only non-pH-neutral particle present is a *weak* acid or base, its K_a or K_b determines the pH. Solve the K_a or K_b equation, then determine pH.

Summary: Steps For Calculating pH in a Mixture At Equilibrium

Apply in this order.

a. Re-write soluble salts as separated ions.
b. Label each particle in the mixture as SA, SB, WA, WB, or N.
c. Ignore pH-neutral (N) particles if mixed with acidic or basic particles.
d. If all particles are N, pH = pH of water = 7.
e. If SA or SB is present, ignore other particles. Find pH based on quick steps:

   $[\text{HCl or } HNO_3] = [H^+]$ and $[\text{NaOH or KOH}] = [OH^-]$
f. If a WA or WB *and* its conjugate is present, solve a buffer chart and the Henderson-Hasselbalch equation in moles or mol/L.
g. If only *one* WA or WB is present, solve the K_a or K_b equation, then find pH.

The logic is:

- pH-neutral particles do not change the $[H^+]$ and pH.
- If a strong acid or base is present, it determines the $[H^+]$ and pH.

Practice B: Study the steps in the summary until you can write them from memory, then apply the steps to these problems. Save a few for your next practice session.

1. For each mixture a-d below,
   - List the particles present in the solution in significant concentration.
   - Label each particle as SA, SB, WA, WB, or N.
   - Write which *step* (c, d, e, or f) in the summary for pH in mixtures above should be used to solve for the pH of the solution.

   a. A mixture of 0.40 M NH_4Cl, 0.10 M NaCl, and 0.20 M HCl.

   b. 0.50 L of solution containing 0.20 mol KCN, 0.20 mol HCN, and 0.10 mol KCl.

   c. A solution containing 0.45 M HF and 0.50 M KCl.

   d. 0.20 mol KCl and 0.35 mol KNO_3 dissolved in 75 mL of solution.

Solve these.

2. A solution contains 0.350 mol KCl in 120.0 mL of solution. Calculate the solution pH.
3. A solution contains 0.010 M KOH, 0.20 M KF , and 0.10 M KCl. Find the pH.
4. A solution contains 0.0050 moles of KCN and 0.010 mol KCl in 25.0 mL of solution. Calculate the pH. (K_b CN^- = 1.6×10^{-5}).
5. After a reaction, at equilibrium, a solution contains 0.020 mol CH_3COOH and 0.020 mol CH_3COO^-. Find the pH. (K_a CH_3COOH = 1.8×10^{-5})

ANSWERS

Practice A

1. NaF and HF **(j) buffer:** a weak acid and its conjugate.
2.. NaCN **(g) basic salt:** Na^+ is pH neutral, CN^- is the CB of the weak acid HCN.
3. NH_3 **(d) weak base:** see the acid strength table.
4. CH_3COOH **(c) weak acid**
5. $NaHCO_3$ **(h) amphoteric salt:** HCO_3^- is an amphoteric ion.
6. KCl **(f) pH neutral salt:** K^+ is pH neutral, Cl^- is the pH-neutral conjugate base of strong acid HCl.
7. H_2CO_3 **(i) polyprotic acid:** Forms HCO_3^- at 1st ionization and CO_3^{2-} 2nd. See strength table.
8. KOH **(b) strong base**
9. NH_4Cl **(e) acidic salt:** NH_4^+ is a weak acid (see table); Cl^- is pH neutral.
10. HNO_3 **(a) strong acid**

Practice B

1a. The particles present are	Na^+	NH_4^+	HCl	Cl^-	If an SA or SB is present, it decides
	N	**WA**	**SA**	**N**	the pH. Use step **e .**

1b. The particles present are K^+ CN^- HCN Cl^- Contains a weak acid and its base conjugate. Use step **f .**

K^+	CN^-	HCN	Cl^-
N	**WB**	**WA**	**N**

1c. The particles present are K^+ HF Cl^- Ignore pH-neutrals. Weak acid determines the pH. Use step **g .**

K^+	HF	Cl^-
N	**WA**	**N**

1d. The particles present are K^+ Cl^- NO_3^- All are pH-neutral. Use step **c .**

K^+	Cl^-	NO_3^-
N	**N**	**N**

2. WANTED = pH. This solution contains only KCl, a pH-neutral salt. The **pH = 7 .**

3. WANTED = **pH** The particles present are K^+ OH^- F^- and Cl^- .

K^+	OH^-	F^-	Cl^-
N	**SB**	**WB**	**N**

If one strong particle is present, it determines the pH. Use the quick steps for strong bases.

For this solution: $[SB] = [OH^-] = 0.010\ M = 1.0 \times 10^{-2}\ M$, $[H^+] = 1.0 \times 10^{-12}\ M$, **pH = 12.00**

4. WANTED = **pH**

KCN is composed of K^+ and CN^-. The K_b reflects that CN^- is a weak base.

KCl consists of K^+ and Cl^-. Both are neutral ions. The only ion that determines pH is CN^-. Use $\boldsymbol{K_b}$ **.**

See pH? Write $\boxed{\textbf{pH} \equiv -\log [H^+] \quad \text{and} \quad [H^+] \equiv 10^{-pH}}$ at least once in each problem set or quiz.

If a final mixture is a buffer, you may also use the Henderson-Hasselbalch pH approximation.

In K_b calculations, begin by solving the K_b approximation.

$$\boxed{K_b \approx \frac{x^2}{[W\mathbf{B}]_{\text{mixed}}}} \quad \text{where } \boldsymbol{x = [OH^-]}$$

To solve the approximation for $[OH^-]$, you need $[W\mathbf{B}]_{\text{mixed}} = [KCN] = [CN^-]_{\text{mixed}}$ in this problem.

$$? = [W\mathbf{B}]_{\text{mixed}} = \frac{\text{mol } CN^-}{\text{L soln.}} = \frac{0.0050 \text{ mol } CN^-}{25.0 \text{ total mL soln.}} \cdot \frac{1 \text{ mL}}{10^{-3} \text{ L}} = \mathbf{0.200\ M}\ CN^-$$

$$\boxed{\boldsymbol{K_b} \approx \frac{x^2}{[W\mathbf{B}]_{\text{mixed}}}} \quad \text{Substituting:} \quad 1.6 \times 10^{-5} \approx \frac{x^2}{\mathbf{0.200\ M}\ CN^-}$$

$$\boldsymbol{x^2} = (1.6 \times 10^{-5})(0.200) = 0.32 \times 10^{-5} = 3.2 \times 10^{-6}$$

$$\boldsymbol{x} \approx (\text{estimate } 1\text{-}2 \times 10^{-3}) \approx \boxed{\mathbf{1.79 \times 10^{-3}\ M = [OH^-]}} \quad (\text{In } K_b,\ \boldsymbol{x} = [OH^-])$$

<u>Quick 5% test</u> : $\boldsymbol{x} = 1.79 \times 10^{-3}$ M, $[\mathbf{WB}] = 0.20\ M = 2.0 \times 10^{-1}$ M

Since the difference in the exponents is 2 or less, do the 5% test:

$$5\% \text{ test} = \frac{x}{[\text{WA or WB}]_{\text{mixed}}} \bullet 100\% = \frac{1.79 \times 10^{-3}}{2.0 \times\ \times 10^{-1}} \bullet 10^2\ \%$$

= 0.90 %, which is less than 5%, so approximation is OK -- but pH was wanted.

* * * * *

p**OH** = — log [OH$^-$] = — log(1.79 x 10^{-3}) = **2.75 = pOH**   pH = 14.00 — pOH = $\boxed{\textbf{11.25 = pH}}$

It's a good idea to carry an extra sf until the last step, but the last digit in calculations is doubtful and will often vary $\pm$1 due to rounding.

The solution of an ion that is a weak base should have a basic pH, and this solution does.

5. WANTED = pH. This solution contains a weak acid and its conjugate: a buffer. Buffer pH problems can be solved using the buffer chart and the Henderson-Hasselbalch equation. Since the acid and base data is in moles, solve the buffer chart and H-H fraction in moles (see Lesson 32H).

Buffer Chart:	**WA** *formula* = CH_3COOH	**CB** *formula* = CH_3COO^-
	mol WA = **0.020 mol**	mol CB = **0.020 mol**

Since mol WA **=** mol CB , the H-H equation: $\boxed{\text{pH} \approx \text{p}K_a + \log(\textbf{mol base/mol acid})}$ simplifies to

pH ≈ pK_a + log (**1**) ≈ pK_a + 0 **≈ pK_a** ≈ **—log** (1.8 x 10^{-5}) ≈ **— (— 4.74)** = $\boxed{\textbf{4.74 = pH}}$

* * * * *

Lesson 34B: pH After Neutralization

Finding pH After A Reaction From Amounts Before the Reaction

Calculations to find pH can be divided into two types:

- Those in which the moles or mol/L of acidic or basic particles are known for a stable solution: one that is at equilibrium and therefore *not* changing (our pH calculations so far have been this type), and
- Those in which you are *given* amounts of acid and base in the initial *reactants*, and you must find the pH of the mixture *after* the acid-base reaction stops.

Let's turn our attention to the second type: calculating the *pH* of a solution *after* a reaction from known amounts of acid and base *before* the reaction.

In *neutralization* reactions, acid and base reactants are used up (react) if the reactants are a *stronger* acid and base than the products.

To find the pH after the reaction, we need to know the amounts of *all* of the particles present in the mixture after the reaction: which is when the reaction stops, which is when the reaction reaches equilibrium. The simplest way to calculate *all* of the amounts present *after* a reaction is to use our "chemistry accounting system:" a *rice moles* table.

Once we know the composition of a mixture after neutralization, we can solve using the rules for *mixture* pH.

In first-year chemistry courses, our interest is limited to finding the pH of a mixture after neutralization when *at least one* of the components, either the acid or base, is *strong*. An acid or base that is *strong* is **highly reactive**: *if* opposite is present, it will react with its opposite until the limiting reactant is ~100% used up.

This allows us to use a key rule that simplifies neutralization reactions and *rice* tables:

When an acid and base are reacted, IF one of the components is *strong*, the reaction will go until the limiting component, either the acid or the base, is 100% used up.

Another way to state this rule is

At the end of a neutralization, if one of the reactants is strong, the *moles* of one of the *reactants* must be *zero*.

Using this rule, we can complete a *rice moles* table for neutralization, using the same steps that were used in Lessons 10H to find the mixture present at the end of a reaction that goes to completion. Then, by applying the rules for mixtures to the particles in the End/Equilibrium row, pH can be calculated.

Steps For Calculating pH *After* Reaction From Amounts *Before* Reaction

1. Convert the initial amounts of acid and base to *moles* (or prefix-*moles*).
2. Enter those moles in the ***I***nitial row of a *rice moles* table.
3. In the **C**hange row, use the rule: when acid and base are mixed, if *one* or both are strong, one reactant is 100% used up.
4. Calculate the pH of the mixture at the ***E***nd of the reaction (in the *bottom* ric***e*** row).

The steps can be summarized as

To find pH *after* reaction from acid and base amounts *before* reaction:

Reactants **> reactant moles >** ***rice*** **moles > equilibrium mixture pH** .

Lets apply these steps to an example.

Q. A solution containing 0.100 moles of HCl is combined 0.080 moles of NaOH. After mixing, the total volume is 120. mL. What is the pH of the solution after mixing?

Solve using the steps above and table below.

Reaction				
Initial				
Change (use **+** , **—**)				
End**/E**quilibrium				

* * * * *

a. The initial moles of acid and base are known.

b. From Lesson 14B: acids reacted with hydroxide bases form water as one product.

The balanced equation is: $1\ \text{HCl} + 1\ \text{NaOH} \rightarrow 1\ \text{H}_2\text{O} + 1\ \text{NaCl}$ (goes ~100%)

* * * * *

- If a reaction starts with all reactants, the sign in the **C**hange row for the reactants must be negative, since reactant must be *used up* if there is a reaction.
- In the **C**hange row, the *signs* of the reactants and products must be opposites.
- The *ratios* in the **C**hange row and the Row 1 coefficients must be the same.

(For a *rice* review for reactions that go to completion, see Lesson 10H.)

* * * * *

Reaction	1 HCl	**1** NaOH	**1** H_2O	**1 NaCl**
Initial	**0.100 mol**	**0.080 mol**	**solvent**	**0 mol**
Change	**— 0.080 mol**	**— 0.080 mol**	**+ 0.080 mol**	**+ 0.080 mol**
At **E**nd/**E**quilibrium	**+ 0.020 mol**	**0 mol**	**solvent**	**+ 0.080 mol**

In this mixture, NaOH moles are *limiting*: when the NaOH is used up, the reaction stops. The limiting reactant determines how much of the products form.

The amount of water initially present can be said to be zero from the reaction, or large because water is the solvent for the reaction. In either case, the amount of water will not affect this type of calculation.

Calculate the pH of the solution mixture above present at the ***E***nd of the reaction.

* * * * *

To begin, label the particles present in the bottom row as SA, SB, WA, WB, or N.

* * * * *

Water and NaCl ions are pH neutral (N). HCl is a strong acid (SA). If a strong acid or base is in a mixture, it determines the pH. Use the quick SA rule to find $[H^+]$, then pH.

* * * * *

$$[H^+]_{\text{in solution}} = [\text{HCl or HNO}_3]_{\text{mixed}}$$

Calculate the [HCl] in the solution at the end of the reaction, then check your answer below.

* * * * *

$$? = [\text{HCl}] = \frac{\text{mol H}^+}{\text{L soln}} = \frac{\mathbf{0.020\ mol}\ \text{HCl}}{\mathbf{120.}\ \text{mL soln.}} \bullet \frac{1\ \mathbf{mL}}{10^{-3}\ \text{L}} = \mathbf{0.167\ M\ HCl}$$

(carrying an extra *sf*)

To finish, find the pH.

* * * * *

$$[\mathbf{H^+}]_{\text{in solution}} = [\text{HCl or HNO}_3]_{\text{as mixed}} = \mathbf{0.167\ M}$$

$$\mathbf{?} = \text{pH} = -\log[\mathbf{H^+}] = -\log(0.167) = -(-0.78) = \boxed{\mathbf{0.78 = pH}}$$

Practice A: Learn the rules and steps above, *then* try these problems.

1. To 0.0250 mol HCl is added 0.0300 mol NaOH. The final volume of the mixture after the reaction is 40.0 mL. What is the pH in the solution after the reaction?

Strong-Weak Neutralization

Let's try a second calculation of pH *after* the reaction, starting from amounts measured *before* the reaction. This time we will react a strong and a weak component. For any acid-base reaction with one or more strong components, we use the same steps as above.

When dealing with moles/liter and *milli*liters, it is often convenient (but not required) to solve the *rice moles* table in *milli*moles. As long as all of the units in the table are the same, our *rice moles* "accounting system" works in

- Moles *or prefix*-moles, or
- Mol/L (M) *if* all of the particles are contained in the same volume.

Let's add that step to this problem.

Q. A solution of 50.0 mL of 0.100 M HCl is mixed with 20.0 mL of 0.150 M KF.

a. Calculate the millimoles of each reactant.

b. Write the balanced equation for the reaction.

c. Complete the *rice moles* table in millimoles.

d. Find the pH in the mixture after the reaction.

Start by completing steps *a* and *b*.

* * * * *

a. For the HCl calculation, use HCl data.

$$\textbf{? mmol HCl = 50.0 mL HCl} \bullet \frac{10^{-3}\text{ L}}{1\text{ mL}} \bullet \frac{0.100\text{ mol HCl}}{1\text{ L HCl}} \bullet \frac{1\text{ mmol}}{10^{-3}\textbf{ mol}} = \textbf{5.00 mmol HCl}$$

A way to calculate millimoles more quickly is to use the rule

> If you WANT a *prefix*-unit, and are *given* the *same-prefix* unit, cancel the *given unit*, but don't cancel the *given* prefix.

For example, to find the mmol KF in this problem:

$$\textbf{? }\underset{\uparrow}{\textbf{m}}\textbf{mol KF =}\quad 20.0\ \underset{\uparrow}{\textbf{m}}\cancel{\textbf{L}}\ \textbf{KF} \bullet 0.150\ \frac{\textbf{mol}}{\cancel{\textbf{L}}} \quad = \quad \textbf{3.00 }\underset{\uparrow}{\textbf{m}}\textbf{mol KF}$$

This form of unit cancellation works because *milli-* is simply an abbreviation for " times 10^{-3} ." When doing the math, an exponential term can be separated from the unit after it, so a prefix may also be treated as separate from the unit after it.

An alternative rule for solution millimoles is to memorize $\boxed{\textbf{mmol = mL x (mol/L)}}$.

The logic is the same: a prefix can be separated from its unit: $\mathbf{m}\cancel{\mathbf{L}} \bullet \frac{\text{mol}}{\cancel{\text{L}}} = \mathbf{m}\text{mol}$

b. The reactants are $HCl + KF \rightarrow$

Write the products using molecular formulas, then balance the equation.

* * * * *

You may be able to solve by inspection. If not, to determine the products, first separate the reactant *salt* into ions: $HCl + \mathbf{KF} = HCl + \mathbf{K^+} + \mathbf{F^-} \rightarrow$

The *products* of the reaction are the conjugates of the acid and base.

$$\underset{\text{SA}}{HCl} + KF = HCl + \underset{\text{N}}{K^+} + \underset{\text{B}}{F^-} \rightarrow \underset{\mathbf{B}}{\mathbf{Cl^-}} + \underset{\mathbf{N}}{K^+} + \underset{\mathbf{A}}{\mathbf{HF}}$$

The acid-strength table supplies the formulas for the conjugates if needed.

Will this reaction go to the right? Why or why not?

* * * * *

The reaction will go to the right. One reason is

- Any time a strong acid (HCl) is mixed with a base of any kind (F^-), the reaction will go until one of the reactants is completely used up.

Using molecular formulas, the balanced ***R***eaction equation is:

$$1\,HCl + 1\,KF \rightarrow 1\,HF + 1\,KCl$$

c. If you have not already done so, complete the *rice moles* table using millimoles.

* * * * *

Reaction	<u>1</u> HCl	**1** KF	**1** HF	**1 KCl**
Initial	**5.00 mmol**	**3.00 mmol**	**0 mol** formed	**0 mol**
Change (use **+** , **—**)	**— 3.00 mmol**	**— 3.00 mmol**	**+ 3.00 mmol**	**+3.00 mmol**
At **E**nd/**E**quilibrium	**+ 2.00 mmol**	**0 mmol**	**+ 3.00 mmol**	**+ 3.00 mmol**

d. At the end of the reaction, the bottom row indicates the mixture present. Analyze the mixture and find the pH.

* * * * *

The mixture contains the strong acid HCl, the weak acid HF, and the salt KCl that contains two pH-neutral ions. What determines the pH?

* * * * *

The [HCl] determines the pH. If a strong component is present, it's contribution to the $[H^+]$ nearly always overwhelms the others. Find pH based on [HCl].

* * * * *

First find the [HCl]. How many moles of HCl are in the solution?

* * * * *

? mol HCl = 2.00 mmol HCl = **2.00 x 10^{-3} mol** HCl (*milli-* means " **x 10^{-3}** ")

Those moles of HCl are in how many liters of solution?

* * * * *

Hint: How much is the *total* volume of solution at this point?

* * * * *

Though the KF has been entirely used up, and part of the HCl was used up, the *water* in which the KF and HCl particles were originally dissolved has *not* been used up.

For reactions that take place in a solution, the number of *reacting* particles is always very small compared to the number of *solvent* particles. A relatively large amount of solvent is used so that the reacting particles can dissolve completely, move about, collide, and react. The large amount of *solvent* present determines almost entirely the *volume* of a solution.

When solutions are combined, *reacting* substances are used up or formed, but the *volume* of the combined solution is determined by the volumes of solvent combined, and those simply *add*.

Even for reactions run in aqueous solutions in which water is a reactant or product, the volume of water used up or formed is nearly always small compared to the volume of the water present as a solvent, and any change in the volume of water present due to the reaction can nearly always be *ignored* in calculations.

The rule is: | When *solutions* with liquid solvents are combined, their *volumes* simply *add*. |

If needed, complete the calculation of [HCl].

* * * * *

We combined the original 50.0 mL of HCl solution with 20.0 mL of KCl solution. All reactants and products present after the reaction are therefore dissolved in a total solution volume of **70.0 mL**. [HCl] = ?

* * * * *

Moles HCl were found above.

$$? = [\text{HCl}] = \frac{\text{mol H}^+}{\text{L soln}} = \frac{\mathbf{2.00 \times 10^{-3}\ mol}\ \text{HCl}}{\mathbf{70.0\ mL}\ \text{soln.}} = \frac{2.00 \times 1\cancel{0^{-3}}\ \cancel{\textbf{mol}}\ \text{HCl}}{70.0\ \mathbf{\times\ 1\cancel{0^{-3}}}\ \text{L soln.}} = \mathbf{0.02857\ M\ HCl}$$

For *part d*, find the WANTED pH.

* * * * *

Using the quick rule: $[\mathbf{H^+}]_{\text{in solution}}$ = $[\text{HCl or HNO}_3]_{\text{mixed}}$ = **0.02857 M**

? = pH = $-$ log [$\mathbf{H^+}$] = $-$ log(0.02857) = $-$ ($-$1.54) = $\boxed{\mathbf{1.54 = pH}}$

* * * * *

Let's summarize.

Rules in this lesson include

1. In a *reaction* between an acid and a base, IF one of the components is strong, the reaction will go until one component, either the acid or the base, is 100% used up.
2. When *solutions* are combined, their *volumes add*.
3. The millimoles shortcut for *rice moles* tables: millimoles = $\boxed{\textbf{mmol = mL x (mol/L)}}$.
4. To find the **[H$^+$]** or **pH** in a solution,
   a. Ask: Is the problem about a stable solution at equilibrium, or does it supply amounts of reactants *before* reaction and ask for [H$^+$] or pH *after* reaction?
   b. If about a stable solution, apply the steps for finding **mixture pH**.
   c. IF about "reactants *before* and pH *after*" reaction, the steps are

      Reactants **> reactant mol > *rice* moles > *then* pH of mixture at equilibrium**.
5. Once the amounts in a mixture at equilibrium are solved or known, use the

Steps For Finding Mixture pH

Apply in this order.

a. Re-write soluble salts as separated ions.
b. Label the particles in the mixture as SA, SB, WA, WB, or N.
c. In pH calculations, ignore pH-neutral (N) particles.
d. If all particles are N, pH = 7.
e. If SA or SB is present, ignore other particles. Find pH with

   the quick steps: [HCl or HNO_3] = [H$^+$] and [NaOH or KOH] = [OH$^-$]
f. If a WA or WB *and* its conjugate is present, solve a buffer chart and Henderson-Hasselbalch equation in moles or mol/L.
g. If only *one* WA or WB is present, solve the K_a or K_b equation.

Practice B: Commit the rules summary above to memory, then try these problems.

1. Complete the following *rice moles* table.

Reaction	1 HCl	**1** NaCN	**1** HCN	**1 NaCl**
Initial	**4.50 mmol**	**3.00 mmol**	**0 mol**	**0 mol**
Change				
At **E**nd/**E**quilibrium				

2. Find the pH for the reaction in Problem 1 if the mixture at equilibrium is in 200. mL of solution.

3. If 50.0 mL of 0.100 M KF is combined with 20.0 mL of 0.150 M HCl, find the pH after the reaction. Solve in millimoles. (K_a HF = 6.8×10^{-4})
4. To a solution containing 200. mmol HOBr (hypobromous acid) and 50. mmol NaOBr is added 150. mmol NaOH. What is the pH of the solution after the reaction? (K_a of HOBr = 2.8×10^{-9}).

ANSWERS

Practice A

1. WANTED: **pH**

Begin by asking: what type of problem is this? A stable solution or reactants before and pH after?

This is about pH *after* reaction from amounts *before*. The steps are

Reactants **> reactant mol > *rice* moles > mixture pH**

Reaction	1 HCl	**1** NaOH	**1** H_2O	**1 NaCl**
Initial	**0.0250 mol**	**0.0300 mol**	**solvent**	**0 mol**
Change (use **+** , **—**)	**— 0.0250 mol**	**— 0.0250 mol**	**+ 0.0250 mol**	**+ 0.0250 mol**
At **E**nd/**E**quilibrium	**0 mol**	**0.0050 mol**	**lots**	**0.0250 mol**

In acid-base reactions, if one component is strong, one reactant must be totally used up.

At equilibrium, the mixture contains the strong base NaOH and a pH-neutral salt. Find pH.

* * * * *

For strong bases, the quick rule is: [NaOH or KOH] = $[OH^-]$. Find [NaOH] first.

* * * * *

DATA: 0.0050 mol NaOH in 40.0 mL total volume

$$? = [NaOH] = \frac{\text{mol NaOH}}{\text{L soln}} = \frac{\textbf{0.0050 mol HCl}}{\textbf{40.0}\text{ mL soln.}} \bullet \frac{1\text{ mL}}{10^{-3}\text{ L}} = \textbf{0.125 M NaOH} = [OH^-]$$

pH ≡ — log $[H^+]$ and $[H^+] \equiv 10^{-pH}$ and pH + **pOH** = 14.00

pOH = — log $[OH^-]$ = — log (**0.125**) = 0.90 ; **pH** = 14.00 — 0.90 = **13.10 = pH**

Practice B

1.

Reaction	1 HCl	**1** NaCN	**1** HCN	**1 NaCl**
Initial	**4.50 mmol**	**3.00 mmol**	**0 mol**	**0 mol**
Change (use **+** , **—**)	**— 3.00 mmol**	**— 3.00 mmol**	**+ 3.00 mmol**	**+ 3.00 mmol**
At **E**nd/**E**quilibrium	**1.50 mmol**	**0 mmol**	**3.00 mmol**	**3.00 mmol**

In acid-base reactions, if one component is strong, one reactant must be totally used up.

2. WANTED = pH

Begin by asking: what type of problem is this: a stable solution or a reaction?

In this part, the mixture is at equilibrium. No net change is occurring. Any reaction is over.

Apply the rules for acid-base *mixture* pH. What type of solution is this?

* * * * *

At equilibrium, the mixture contains a strong acid, a weak acid, and a salt. What determines the pH?

* * * * *

The ionization of the strong acid is the largest contributor to the $[H^+]$, so [SA] determines pH. Find pH.

* * * * *

For strong acids, the quick rule is: $[HCl \text{ or } HNO_3] = [H^+]$. Find [HCl] first.

* * * * *

DATA: 1.50 mmol HCl in 200. mL soln.

$$? = [HCl] = \frac{\text{mol HCl}}{\text{L soln}} = \frac{\mathbf{1.50}\ \cancel{\text{m}}\textbf{mol}\ \text{HCl}}{\mathbf{200.}\ \cancel{\text{m}}\text{L soln.}} = \mathbf{0.00750\ M\ HCl}$$

A prefix can be treated as independent of the number before and unit after it. Like-prefixes cancel.

$\boxed{\mathbf{pH} \equiv -\log [H^+] \quad \text{and} \quad [H^+] \equiv 10^{-pH}}$ $\mathbf{pH =} -\log [H^+] = -\log (\mathbf{0.00750}) = \boxed{\mathbf{2.12 = pH}}$

3. WANTED: **pH after reaction**

Begin by asking: what type of problem is this? Stable solution or reaction? This is about a *reaction*.

For pH *after* reaction from amounts *before*, the steps are

$\boxed{\text{Reactants} > \textbf{reactant mol or } \textit{prefix}\textbf{-moles} > \textbf{\textit{rice} moles} > \textbf{mixture pH}}$

? **m**mol KF = 50.0 **m**L KF x 0.100 mol/L KF = 5.00 **m**mol KF

? **m**mol HCl = 20.0 **m**~~L~~ HCl x 0.150 mol/~~L~~ HCl = 3.00 **m**mol HCl

Reaction	1 HCl	**1** KF	**1** HF	**1 KCl**
Initial	**3.00 mmol**	**5.00 mmol**	**0 mol**	**0 mol**
Change (use **+** , **–**)	**– 3.00 mmol**	**– 3.00 mmol**	**+ 3.00 mmol**	**+3.00 mmol**
At **E**nd/**E**quilibrium	**+0 mmol**	**2.00 mmol**	**+ 3.00 mmol**	**+ 3.00 mmol**

At equilibrium, what type of solution is this? What steps do you follow to find the pH?

* * * * *

This mixture contains substantial amounts of both the weak acid HF and its conjugate base F^-, which makes the solution a buffer. The solution also contains the pH-neutral ions K^+ and Cl^-, but pH-neutral ions do not affect pH. Solve for pH using the buffer steps.

* * * * *

To find buffer pH,

- for the two "at end" substances that are not pH-neutral, fill in a buffer chart, and
- find the pH using the K_a or Henderson-Hasselbalch equations.

Buffer Chart: **WA** *formula* = HF **CB** *formula* = F^{-}

moles WA = **3.00 mmol** HF ***moles*** CB = **2.00 mmol** F^{-}

Henderson-Hasselbalch: **pH** ≈ pK_a + log (**mol base/mol acid**)

≈ **—log** (6.8 x 10^{-4}) + log (**2.00** mmol /**3.00** mmol)

≈ **—(—3.17**) + log (**0.667**) ≈ 3.17 **— 0.17** = $\boxed{\textbf{3.00 = pH}}$

The units in the base/acid ratio of the Henderson-Hasselbalch equation can be M, mol, or **m**mol, as long as the top and bottom units are consistent.

4 WANTED: **pH**

Begin by asking: what type of problem is this: a stable solution or reactants before and pH after?

This is about reactants before and pH after reaction. The base NaOH will react with the acid HOBr.

For pH *after* reaction from amounts *before*, the steps are

Reactants **> reactant mol > *rice* moles > mixture pH**

When an acid reacts with a hydroxide base, one product is always water.

Reaction	**1** HOBr	**1** NaOH	**1 H_2O**	**1 NaOBr**
Initial	**200. mmol**	**150. mmol**	**solvent**	**50 mmol**
Change (use **+ , —**)	**– 150. mmol**	**– 150. mmol**	**+150. mmol**	**+ 150. mmol**
At **E**nd/**E**quilibrium	**50. mmol**	**0 mmol**	**lots**	**200. mmol**

In acid-base reactions, if one component is strong, one reactant must be totally used up.

Apply the rules for acid-base *mixture* pH. What type of solution is this?

* * * * *

This mixture contains substantial amounts of the weak acid HOBr (weak based on its K_a value) and its conjugate base OBr^{-}, which makes the solution a buffer. The solution also contains the pH-neutral ions Na^{+} ions that do not affect pH. Solve for pH using the buffer steps.

* * * * *

To find buffer pH,

- for the two "at end" substances that are not pH-neutral, fill in a buffer chart, and
- find the pH using the Henderson-Hasselbalch equation.

Buffer Chart: **WA** *formula* = HOBr **CB** *formula* = OBr^{-}

moles WA = **50. mmol** HOBr ***moles*** CB = **200. mmol** OBr^{-}

Henderson-Hasselbalch: **pH** ≈ pK_a + log (**mol base/mol acid**)

≈ **—log** (2.8 x 10^{-9}) + log (**200. mmol / 50. mmol**)

≈ **— (— 8.552**) + log (**4.0**) ≈ 8.552 **+ 0.602** ≈ $\boxed{\textbf{9.15 = pH}}$

* * * * *

Lesson 34C: pH Behavior During Titration

Timing: Calculations of *how much* acid and base are required to reach the endpoint of a titration are neutralization stoichiometry, and they were covered in Module 14. Begin this lesson when you are asked to calculate the *pH* at points *during* an acid-base titration.

* * * * *

Terminology of Acid-Base Titration

Redox, precipitation, and other types of reactions can be studied by titration, but in this module the term *titration* will refer to *acid-base neutralization* titration. For purposes of discussing acid-base titration, as with other acid-base mixtures,

- The *opposite* of an acid will mean a base, and the *opposite* of a base will mean an acid.
- *Strong* acids and bases will be defined as those that ionize ~100% to form H^+ or OH^- ions. *Weak* acids and bases will be those with K_a or K_b values between one and 10^{-16} according to acid-strength tables (see Lesson 31B).

The substance gradually added to a sample during a titration is termed the **titrant**.

The Equivalence Point

Acid-base titration was discussed in Lesson 14C. To briefly review:

- An acid-base *titration* is a gradual neutralization. Using burets, volumes of acid and base that have been combined in a reaction vessel are carefully measured when the **endpoint** of the titration is reached. To detect the endpoint, a small amount of pH-sensitive dye called an **indicator** is added to the reaction mixture. At the endpoint, the indicator changes color.
- The endpoint signaled by an indicator is ideally a sharp color change at the precise **equivalence point** at which the *moles* of acid and base that have been combined are *equal* (or, for compounds with more than one acidic or basic group, the moles are in a simple whole-number ratio).

Types of Titration Calculations

In acid-base titration, we are most often concerned with two questions:

1. How much of one reactant (acid or base) is needed to exactly use up the other?
2. What happens to the pH during the titration?

The first question we have answered previously. In an acid-base reaction, if one component is strong, the reaction will go to completion. The point at which the H^+ ions of the acid reactant are equal to the moles of the basic reactant is the equivalence point and are solved by conversion stoichiometry. If the amount of one component at the equivalence point is known, the amount of the other can be calculated by the *stoichiometry* steps:

WDBB, units → moles → moles → units

Practice A: If additional review of equivalence point calculations is needed, see Lessons 12C and 14C.

1. To 50.0 mL of 0.0500 M KOH is added 0.100 M HNO_3.
   a. Will this reaction go to completion?
   b. How many mL of acid must be added to neutralize all of the KOH?

Indicating the Endpoint

Let's turn our attention to the second question above: What happens to the pH during an acid-base titration?

This question is important because during neutralization, different acids and bases have different pH behaviors. In addition, different substances can be used as acid-base indicators, and each indicator changes color in a limited pH range. In order to choose the correct indicator to accurately signal an equivalence point, the pH of the acid-base mixture *during* a titration must be determined.

If a *sharp* change in the pH of the reaction mixture occurs at the equivalence point, *and if* the indicator is chosen carefully, allowing for small experimental error, the endpoint shown by the indicator and the equivalence point for the neutralization will be the *same*. If the equivalence point can be determined, many unknown characteristics of an acid or base can then be determined.

pH Behavior During Titration

During titration, the following rules apply.

1. The indicator in a titration will accurately identify an equivalence point only if there is a *sharp* pH change (large and occurring with just a *drop* or two of titrant) at the equivalence point.
2. For a sharp pH change to occur, at least one reactant must be *strong*. In most titrations, one reactant is usually an aqueous solution of HCl, HNO_3, NaOH, or KOH.
3. Acid-base indicators work best when *strong* or *moderately weak* acids and bases (K_a *or* $K_b > 10^{-7}$) are combined with *strong opposites*. The weaker the acid or base being neutralized, the less sharp the pH change at the endpoint will be. If the *K* for the weaker component is below 10^{-7}, the pH change may not sharp enough for an indicator to accurately signal an equivalence point (though an unwieldy pH meter *may* do so).

   Similarly, if a *weak* acid and a *weak* base are combined by titration, the pH change at the endpoint is often too small for an indicator dye to accurately detect.
4. Substances with *two or more* acidic or basic groups will titrate to an equivalence point for each group. The calculation of pH is treated as successive titrations: the conjugate product at the first endpoint is the starting acid or base for the titration to the second endpoint, etc. Some of the endpoints may be sharp while others are not.

5. A titration of substances with single acidic or basic groups can be separated into *four* stages.

   a. *Before* the titration begins, the sample to be titrated is a solution of a strong or moderately weak acid or base.

   b. When the *first drop* of strong opposite is added, it *reacts* with the original acid or base. Since one of the particles is strong, the reaction will go until the reactant with the lowest moles (normally the titrant being added) is completely used up, and products, including conjugates of the acid and base, form.

      Between the beginning and endpoint, as opposite continues to be added, all of the titrant is used up, the number of particles of the original acid or base goes *down*, and the particles of products go *up*. The reaction continues as long as particles of the original acid or base remain to react with the titrant.

      But *between* the beginning of the titration and the equivalence point, in the reaction flask is a *mixture* of the original acid or base, products that include both conjugates, and no titrant.

   c. At the *equivalence point*,

      - there is *no* original acid or base and *no* titrant.
      - The last added titrant has reacted with the last particles of original acid or base, and both reactants have been exactly and completely used up.
      - In the solution are only the *products* of the reaction.

   d. If titrant continues to be added *after* the endpoint, there is no reaction. There is no opposite left for the titrant to react with. Titrant added after the endpoint simply mixes with the particles of products that were present at the endpoint.

Summary: The four *stages* of an acid-base titration are

Stage	**The solution contains**
Before titrant is added	original acid or base
Between the beginning and endpoint	original acid or base plus products
At the endpoint	Products only
After the endpoint	products plus titrant added *after* endpoint

---

Practice B. Check your answers after each part.

1. Write the products using molecular (solid) formulas, then balance these equations for reactions in aqueous solution.

   a. $KOH + HNO_3 \rightarrow$

   b. $HCN + RbOH \rightarrow$

c. NH_3 + HCl →

d. $NaHCO_3$ + NaOH →

2. Which compounds among the 7 *products* above are not pH-neutral?
3. Assuming for the reactions in problem 1 that the 2nd reactant listed is gradually titrated into the first, write molecular formulas for the substances that will be present in the reaction mixture
   a. In problem 1a before the titration begins.
   b. In problem 1b just before the endpoint of a titration.
   c. In problem 1c at the endpoint.
   d. In problem 1d three drops after the endpoint.
4. In which answer to *question 3* is the solution a buffer?
5. Label each substance formula in the answers to *question 3* as a strong acid (SA), strong base (SB), weak acid (WA), weak base (WB), or pH-neutral (N).

ANSWERS

Practice A

1a. If an acid and base are mixed, and one or both components is strong, the reaction will go to completion.

1b. **W**ANTED: ? mL HNO_3 solution

DATA: 50.0 mL KOH
0.0500 mol KOH = 1 L KOH soln.
0.100 mol HNO_3 = 1 L HNO_3 soln.

Strategy: This is stoichiometry: how much of one substance is needed to exactly use up another.
If you need a review of solution stoichiometry, see Lessons 12C and 14C.
When solving for a single unit, the *stoichiometry* steps are

WDBB, units → moles → moles → units

Balance: **1** HNO_3 + **1** KOH → **1** H_2O + **1** KNO_3

Bridge: **1** mol HNO_3 = **1** mol KOH

SOLVE:
$$\underset{\uparrow}{?\text{ mL }HNO_3} = \underset{\uparrow}{50.0\text{ m}}\mathbf{L\ KOH} \cdot \frac{0.0500\text{ mol KOH}}{1\ \mathbf{L\ KOH}} \cdot \frac{\mathbf{1\ mol\ HNO_3}}{\mathbf{1\ mol\ KOH}} \cdot \frac{1\text{ L }\mathbf{HNO_3}}{0.100\text{ mol }HNO_3} =$$

$$= \boxed{\mathbf{25.0\ mL\ HNO_3}}$$ The conversions above use the optional rule:

> If you WANT a *prefix*-unit and are *given* the *same-prefix* unit, cancel the *given unit*, but don't cancel the *given* prefix.

Practice B

1. All coefficients are one.

   a. $KOH + HNO_3 \rightarrow H\text{-}OH + KNO_3$　　b. $HCN + RbOH \rightarrow H\text{-}OH + RbCN$

   c. $NH_3 + HCl \rightarrow NH_4Cl$　　d. $NaHCO_3 + NaOH \rightarrow H_2O + Na_2CO_3$

2. RbCN is a salt that is a weak base: it contains the weak conjugate base CN^- and pH-neutral Rb^+.

   NH_4Cl is a weakly acidic salt containing the weak acid ion NH_4^+ and pH-neutral Cl^-.

   Na_2CO_3 is a basic salt containing the moderately weak base CO_3^{2-} and pH-neutral Na^+.

   All of the other products are pH neutral.

3. a. In 1a, before the reaction begins, is **KOH.** Neutral water is also present in aqueous solutions.

   b. In 1b, just before the endpoint of a titration is **HCN, H-OH,** and **RbCN.** Before the endpoint, as the strong base RbOH is added, it is 100% used up.

   c. In 1c, at the endpoint are only products: **NH_4Cl** dissolved in water.

   d. In 1d, three drops after the endpoint are the products **H-OH** and **Na_2CO_3**, plus the **NaOH** added after the endpoint. After the endpoint, the original acid has been all used up, and the added base has nothing to react with.

4. In which answer to question 3 is the solution a buffer? **3b** is the only part in which a weak acid (HF) or base is mixed with its conjugate.

5. a. KOH (**SB**) (All aqueous solution also have H-OH (**N**)).

   b. HCN **(WA),** H-OH (**N)** , and RbCN (**WB**). RbCN is a salt composed of the alkali metal ion Rb^+ that is pH neutral and CN^- which is the conjugate of the weak acid HCN. Conjugates of mildly weak acids are mildly weak bases. Salts that combine neutral ions and weak basic ions are weak bases.

   c. NH_4Cl **(WA)** is a salt composed of NH_4^+ that is a weak acid and Cl^- which is pH neutral. Salts composed of pH neutral ions and ions that are weak acids behave as weak acids.

   d. Na_2CO_3 (**WB**) is a salt containing the moderately weak carbonate ion ($K_b = 1.9 \times 10^{-4}$); NaOH (**SB**)

* * * * *

Lesson 34D: pH During Strong-Strong Titration

Calculating pH During a Titration

At all points during a titration, in the reaction flask is a *mixture* of substances. The pH is determined by the types of particles in the mixture. To calculate the solution pH, apply the rules that solve for the pH of a mixture.

In the case of titration, we have a special interest in

- Tracking what happens to the pH during the four stages of a titration; and
- Developing rules that will simplify calculations.

We will develop these rules as we solve examples. Let's begin with

Finding pH During A Strong Acid-Strong Base Titration

Q1. A solution of 50.0 mL of 0.100 M HCl is titrated by 0.250 M NaOH.

a. What is the pH of the solution before any base is added?
b. Write the balanced reaction equation.
c. What is the pH at the equivalence point of the titration?
d. How many mL NaOH must be added to reach the equivalence point?
e. What is the pH after 10.0 mL of base has been added? (Solve in mmol.)

Try *part a*, then check your answer below.

* * * * *

a. See pH? Write $\boxed{\mathbf{pH} \equiv -\log[H^+] \quad \text{and} \quad [H^+] \equiv 10^{-pH}}$

The initial solution is a strong acid. Use the strong acid rules to find pH.

* * * * *

For any ~100% ionization, *REC:* $HCl \rightarrow H^+ + Cl^-$ (goes 100%)

$\cancel{0.100\ M}$ **0 M** **0.100 M** 0.100 M

or by the quick rule: $[H^+]_{\text{in solution}} = [HCl \text{ or } HNO_3]_{\text{mixed}} =$ **0.100 M = $[H^+]$** ;

$$\mathbf{pH} = -\log[H^+] = -\log(0.100) = -\log(1.00 \times 10^{-1}) = -\log(10^{-1}) = -(-1) = \mathbf{1.00}$$

Try *part b*, then check your answer below.

* * * * *

b. When acid reacts with a hydroxide base, one of the products is always….?

* * * * *

Water. This reaction is: $1\ HCl + 1\ NaOH \rightarrow\rightarrow 1\ \mathbf{H_2O} + 1\ NaCl$ (goes ~100%)

* * * * *

c. In any neutralization reaction with one strong component, the rules are

At an equivalence point in the neutralization,

- the moles acid reacted are equivalent to (the same as) the moles base reacted.
- The acid and base reactants are exactly neutralized: both are 100% used up.
- Since no reactants remain, only products are present.

In this reaction flask is salt water: dissolved NaCl. NaCl is a combination of two pH-neutral ions; the solution has a neutral pH of 7 .

In a titration of *a strong* acid and *strong* base, at the equivalence point: pH = **7**

d. *Part d* is what *kind* of problem?

* * * * *

At the *endpoint*, *all* of the acid or base in the original sample is used up, so *Part d* asks what amount of *one* reactant is needed to use up all of another reactant. What kind of problem is that?

* * * * *

Stoichiometry. We apply stoichiometry steps to reactions which

- go essentially to completion (rather than to equilibrium), and
- ask how much of *one* substance is needed or formed when one other substance is completely used up (and is therefore a limiting reactant).

In acid-base reactions, if *one* or both reactants is strong, the reaction goes to completion.

Apply the stoichiometry steps, then check below.

* * * * *

In stoichiometry, the first four steps are WDBB. Then, if a *single* unit is WANTED, chain conversions to solve.

* * * * *

1. **W**ANTED: **?** mL NaOH (a single unit)
2. **D**ATA: 50.0 mL HCl (the single-unit *given*)

   0.100 mol HCl = 1 L HCl (M prompt)

   0.250 mol NaOH = 1 L NaOH (M prompt)

   (If *two* substances are involved, each unit must include its substance formula.)
3. **B**alance. **1** NaOH + **1** HCl → 1 HOH + 1 NaCl
4. **B**ridge**.** **1** mol NaOH = **1** mol HCl
5. SOLVE.

$$\underset{\uparrow}{\textbf{? mL NaOH}} = 50.0\ \underset{\uparrow}{\text{m}\mathbf{L}}\ \text{HCl} \bullet \frac{0.100\ \text{mol HCl}}{1\ \mathbf{L}\ \text{HCl}} \bullet \frac{\textbf{1 mol NaOH}}{\textbf{1 mol HCl}} \bullet \frac{1\ \text{L NaOH}}{0.250\ \text{mol NaOH}} =$$

$$= \boxed{\textbf{20.0 mL NaOH}}$$

(It is optional but saves steps to use the rule: if you WANT a *prefix*-unit, and are *given* the *same prefix*-unit, cancel the *given unit*, but don't cancel its prefix.)

This titration will reach its endpoint when **20.0 mL** of the NaOH solution is added to the original acid solution.

e. What kind of problem is *part e?* What steps will you use to solve?

* * * * *

Amounts of acid and base *before* the reaction are supplied, and pH *after* the reaction at a point in the titration that is not necessarily the endpoint, is WANTED. The result of the reaction will be a mixture.

To find pH *after* a reaction, given reactant amounts *before* the reaction, use
Reactants **> reactant mol or** *prefix*-**mol >** ***rice*** **moles > pH of mixture** at equilibrium.

In most titration calculations, it is easier to solve *rice* tables in millimoles.

* * * * *

Find **m**mol HCl using HCl DATA: Want a single unit? Start with a single unit.

$$\text{WANTED} = \textbf{? m}\text{mol } \textbf{HCl} = 50.0\ \textbf{m}\text{L HCl} \bullet \frac{0.100\ \text{mol HCl}}{1\ \text{L HCl soln.}} = \textbf{5.00 m}\text{mol } \textbf{HCl}$$

* * * * *

For NaOH calculations, use NaOH DATA:

$$?\ \textbf{mmol}\ \text{Na}\textbf{OH} = 10.0\ \text{mL NaOH} \bullet \frac{0.250\ \text{mol NaOH}}{1\ \text{L NaOH soln.}} = \textbf{2.50 mmol NaOH}$$

Now complete the *rice* table below for the reaction.

* * * * *

Reaction	1 HCl	**1** NaOH	**1** H_2O	**1 NaCl**
Initial	**5.00 mmol**	**2.50 mmol**	**0 mol** *formed*	**0 mol**
Change (use **+** , **—**)	**— 2.50 mmol**	**— 2.50 mmol**	**+ 2.50 mmol**	**+2.50 mmol**
At **E**nd/**E**quilibrium	**+ 2.50 mmol**	**0 mmol**	**+ 2.50 mmol**	**+ 2.50 mmol**

At this point in the reaction, the reaction must stop when the NaOH is used up. The limiting NaOH also determines how much of the products form.

Calculate the pH of the solution present for the mixture in the ***E***nd row above.

* * * * *

The HCl at the end determines the pH. Use the quick SA rule to find $[H^+]$, then pH.

* * * * *

$$[H^+]_{\text{in solution}} = [\text{HCl or } HNO_3]_{\text{mixed}}$$

Calculate the $[\text{HCl}]_{\text{mixed}}$ into the solution, then check your answer below.

* * * * *

Hint: How much is the *total* volume of solution at this point?

* * * * *

In *part e*, we mix the original 50.0 mL of acid solution with 10.0 mL of added base solution. All reactants and products present are therefore dissolved in a total solution volume of 60.0 mL. [HCl] = ?

* * * * *

$$? = [\text{HCl}] = \frac{\text{mol } H^+}{\text{L soln}} = \frac{\mathbf{2.50\ \cancel{m}mol}\ \text{HCl}}{\mathbf{60.0\ \cancel{m}}\text{L soln.}} = \mathbf{0.04167\ M\ HCl}$$

Since *milli* is simply an abbreviation for " x 10^{-3} " it can cancel. If needed, finish *part e*.

* * * * *

Using the quick rule: $[\text{HCl or } HNO_3]_{\text{mixed}} = \mathbf{[H^+]}_{\text{in solution}} = \mathbf{0.04167\ M}$

$$\mathbf{? = pH} = -\log\,\mathbf{[H^+]} = -\log(0.04167) = -(-1.38) = \boxed{\mathbf{1.38 = pH}}$$

In these calculations, we carried an extra significant figure, but because pH is very temperature dependent, in the lab predictions are rarely accurate to more than two places past the decimal.

* * * * *

One of our goals in these calculations is to track what happens to *pH* during a titration.

<u>Let's summarize</u> what we have calculated so far. For the strong acid-strong base titration in this problem,

- in the initial acid solution, the pH was **1.00**
- After adding **10.0 mL** of this particular base solution, pH = **1.38**
- After adding **20.0 mL** of this particular base solution, we reached the endpoint/equivalence point, where pH = **7.0**

Somewhere during the titration, the pH drops substantially, but these numbers indicate that it hasn't dropped much by *half-way* to the endpoint.

For this same titration, let's try a pH calculation much *closer* to the endpoint. Since the endpoint is at 20.0 mL, let's try

Q2. For the same solutions (50.0 mL of 0.100 M HCl is titrated by 0.250 M NaOH), what is the pH after **19.8 mL** of base has been added? (Solve in millimoles)

* * * * *

The mmol HCl *being* titrated is the same, but the mmol NaOH added have increased.

$$? \text{ mmol Na}\mathbf{OH} = 19.8 \text{ mL NaOH} \bullet \frac{0.250 \text{ mol NaOH}}{1 \text{ L NaOH soln.}} = \mathbf{4.95\ mmol\ NaOH}$$

* * * * *

Reaction	<u>1</u> HCl	**1** NaOH	**1** H_2O	**1** NaCl
Initial	**5.00 mmol**	**4.95 mmol**	**0 mmol**	**0 mmol**
Change	**— 4.95 mmol**	**— 4.95 mmol**	**+ 4.95 mmol**	**+ 4.95 mmol**
At **E**nd/**E**quilibrium	**+ 0.05 mmol**	**0 mmol**	**+ 4.95 mmol**	**+ 4.95 mmol**

Calculate the pH in the mixture after the reaction, at equilibrium.

* * * * *

The only substance present that is not pH neutral is HCl. The strong acid will determine the pH. Find [HCl], then $[H^+]$, then pH.

* * * * *

To 50.0 mL original acid solution has been added 19.8 mL base = 69.8 mL total volume.

* * * * *

$$? \text{ [HCl]} = \frac{\text{mol HCl}}{\text{L soln}} = \frac{0.05 \text{ }\cancel{\text{m}}\text{mol HCl}}{69.8 \text{ total }\cancel{\text{m}}\text{L soln.}} = \mathbf{0.0007\ mol/L\ HCl} \qquad \mathbf{pH = ?}$$

* * * * *

? = pH = $-\log[H^+]$ Since HCl is a strong acid, $[H^+]$ **=** [HCl] = **0.0007 M**

? = pH = $-\log[H^+] = -\log 0.0007 = -(-3.1) = \boxed{\textbf{3.1 = pH}}$

Between **0** mL and **19.8** mL base added, the pH has fallen from 1.00 to **3.1** . By **20.0 mL** base added at the endpoint, the pH must fall to **7** – a comparatively large change for 0.2 mL of additional added NaOH.

Titration Past the Equivalence Point

In the titration above, the equivalence point is at 20.0 mL NaOH added. What happens to the pH if we go just two drops past the equivalence point? Each drop contains about 0.05 mL, so two drops past would take us to 20.0 + 0.10 = 20.1 mL NaOH added, so the question is

Q3. For the same solutions (50.0 mL of 0.100 M HCl titrated by 0.250 M NaOH), what is the pH after **20.1 mL** of base has been added?

* * * * *

The mmol HCl *being* titrated is the same, but the mmol NaOH added has increased.

$$? \text{ mmol Na}\mathbf{OH} = 20.1 \text{ mL NaOH} \bullet \frac{0.250 \text{ mol NaOH}}{1 \text{ L NaOH soln.}} = \mathbf{5.02 \text{ mmol NaOH}}$$

Complete the *rice* table using the increased initial millimoles of NaOH.

* * * * *

Reaction	**1** HCl	**1** NaOH	**1** H_2O	**1** NaCl
Initial	**5.00 mmol**	**5.02 mmol**	**0 mmol**	**0 mmol**
Change	**— 5.00 mmol**	**— 5.00 mmol**	**+ 5.00 mmol**	**+ 5.00 mmol**
At **E**nd/**E**quilibrium	**+ 0 mmol**	**+ 0.02 mmol**	**+ 5.00 mmol**	**+ 5.00 mmol**

Calculate the pH at equilibrium in this mixture.

* * * * *

The only substance present that is not pH neutral is the strong base. Find [NaOH], then $[OH^-]$, then pH.

* * * * *

To 50.0 mL original acid solution has been added 20.1 mL base = 70.1 mL total volume.

* * * * *

$$? \,[\text{NaOH}] = \frac{\text{mol NaOH}}{\text{L soln}} = \frac{0.02\ \textbf{m}\text{mol NaOH}}{70.1\ \text{total } \textbf{m}\text{L soln.}} = \mathbf{0.0003\ mol/L}\ \text{NaOH} \qquad \mathbf{pH = ?}$$

* * * * *

Since NaOH is a strong base, [NaOH] = $[OH^-]$ = **0.0003 M**

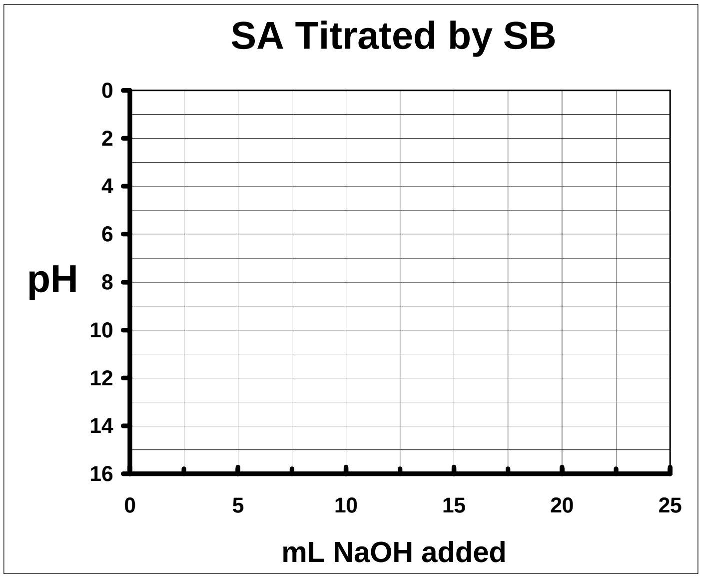
p**OH** = − log $[OH^-]$ = − log(3×10^{-4}) = **3.5** **pH** = 14.00 − pOH = $\boxed{\mathbf{10.5 = pH}}$

Graphing pH During Titration

Q4. In pencil, on the grid at the right, plot the data calculated for the titration above at 0, 10.0, 19.8, 20.0, and 20.1 mL NaOH added.

Check your answer at the end of the **ANSWER** section below.

* * * * *



The graph reflects an important fact of acid-base neutralization:

> If a strong or moderately weak acid or base is titrated by a strong opposite, the pH changes sharply during the titration, but not until *very* close to the endpoint.

Practice: Do problem 1. You may want to save problem 2 for later review.

1. For the titration in the lesson above, calculate the pH after 25.0 mL NaOH has been added. Add this value to the graph above.
2. 50.0 mL of 0.0500 M KOH is titrated by 0.150 M HNO_3.
   a. What is the pH before any acid is added?
   b. What is the pH at the endpoint?
   c. Calculate the pH after 18.0 mL of HNO_3 has been added.

ANSWERS

1. The mmol HCl *being* titrated is the same, but the mmol NaOH added have increased.

$$? \text{ mmol Na}\mathbf{OH} = 25.0 \text{ mL NaOH} \bullet \frac{0.250 \text{ mol NaOH}}{1 \text{ L NaOH soln.}} = \mathbf{6.25 \text{ mmol NaOH}}$$

Reaction	<u>1</u> HCl	**1** NaOH	**1** H_2O	**1** NaCl
Initial	**5.00 mmol**	**6.25 mmol**	**0 mmol**	**0 mmol**
Change	**— 5.00 mmol**	**— 5.00 mmol**	**+ 5.00 mmol**	**+ 5.00 mmol**
At **E**nd/**E**quilibrium	**+ 0 mmol**	**+ 1.25 mmol**	**+ 5.00 mmol**	**+ 5.00 mmol**

The NaOH determines the pH. Find [NaOH], then $[OH^-]$, then pH.

* * * * *

To 50.0 mL original acid solution has been added 25.0 mL base = 75.0 mL total volume.

* * * * *

$$? [\text{NaOH}] = \frac{\text{mol NaOH}}{\text{L soln}} = \frac{\mathbf{1.25\ m}\text{mol NaOH}}{75.0 \text{ total } \mathbf{m}\text{L soln.}} = \mathbf{0.0167\ mol/L} \text{ NaOH} \qquad \mathbf{pH = ?}$$

* * * * *

Since NaOH is a strong base, [NaOH] = $[OH^-]$ **= 0.0167 M**

p**OH** = — log $[OH^-]$ = — log(1.67×10^{-2}) = **1.78** **pH** = 14.00 — pOH = $\boxed{\mathbf{12.22 = pH}}$

Once you are a few drops past the end point, the pH graph again plateaus: the pH again changes slowly.

2a. WANTED: pH

The initial solution contains the strong base KOH that ionize 100% in water.

To find the ion concentrations in strong acid or base, either use the *REC* steps,

Or recall the quick rule: $[\text{NaOH or KOH}]_{\text{mixed}} = [OH^-]_{\text{in solution}}$ (see Lesson 27E)

Since $[OH^-]$ = 0.0500 M; pOH = — log $[OH^-]$ = — log(0.0500) = **1.30 = pOH**

pH = 14.00 — pOH = $\boxed{\mathbf{12.70 = pH}}$

2b. In this reaction: $KOH + HNO_3 \rightarrow\rightarrow H_2O + KNO_3$ (goes ~100%)

At the equivalence point of any neutralization titration, only products are in the mixture. In the reaction flask is KNO_3, composed of two pH-neutral ions, K^+ and NO_3^-, so the solution has a neutral pH of 7.

2c. WANTED: **pH after reaction**

Begin by asking: what type of problem is this: a stable solution or "before and after" reaction?

This is a *reaction*. For pH after reaction from amounts before, the steps are

Reactants **> reactant mol or mmol > *rice* moles > mixture pH**

1) Convert all amounts of reactants to *moles*, (or, in titration, *milli*moles).
2) Enter the initial millimoles in a *rice* initial row.
3) Complete the *rice moles* table with one reactant used up.
4) Solve for pH based on the substances present after the reaction (in the bottom *rice* row).

The millimoles of base being titrated in the sample are

$$\textbf{? mmol KOH} = 50.0\ \textbf{mL KOH} \cdot \frac{0.0500\ \text{mol KOH}}{1\ \textbf{L KOH}} = \textbf{2.50 mmol KOH}$$

The millimoles of acid added so far are

$$\textbf{? mmol HNO}_3 = 18.0\ \text{mL HNO}_3 \cdot \frac{0.150\ \text{mol HNO}_3}{1\ \text{L HCl soln.}} = \textbf{2.70 mmol HNO}_3$$

Reaction	**1** HNO_3	**1** KOH	**1** H_2O	**1** KNO_3
Initial	**2.70 mmol**	**2.50 mmol**	**0 mmol**	**0 mmol**
Change	**— 2.50 mmol**	**— 2.50 mmol**	**+ 2.50 mmol**	**+ 2.50 mmol**
At **E**nd/**E**quilibrium	**0.20 mmol**	**0 mmol**	**2.50 mmol**	**2.50 mmol**

Label the particles present at the end as SA, SB, WA, WB, or N.

* * * * *

In the mixture at this point, we have "overshot the endpoint" by adding more moles of titrant acid than base. Only the HNO_3 (**SA**) titrant is not pH neutral. It will therefore determine the pH.

To find the pH, $[H^+]$ is needed. To find $[H^+]$, [SA] is needed: its moles and its liters.

The total volume in the flask is 50.0 mL original base + 18.0 mL acid solution added = 68.0 mL total.

$$? = [HNO_3] = \frac{\textbf{mol}\ HNO_3}{\text{L soln}} = \frac{\textbf{0.20 m}\text{mol}\ HNO_3}{\textbf{68.0}\ \text{total}\ \textbf{m}\text{L soln.}} = \textbf{0.00294 M}\ HNO_3$$

Since HNO_3 is a strong acid,

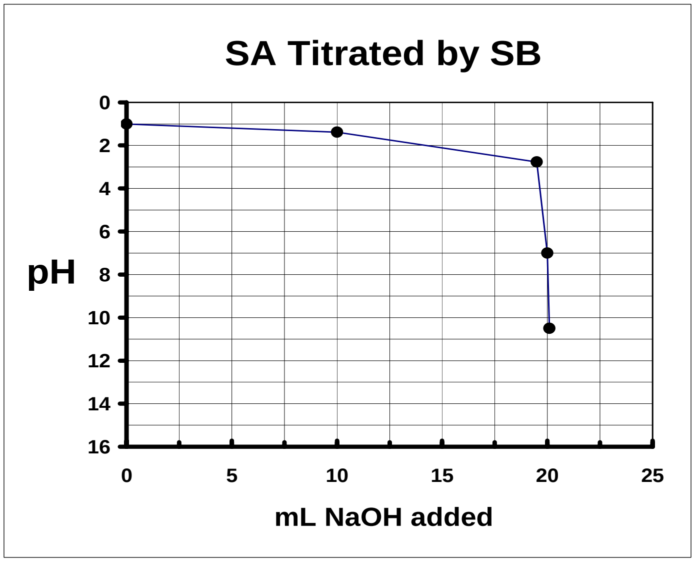
$[H^+]$ **=** $[HNO_3]$ = **0.00294 M** H^+

p**H** = $-\log[H^+] = -\log(0.00294)$

$$= \boxed{\textbf{2.53 = pH}}$$

The graph at the right is the answer to **Q4** in the lesson.

* * * * *



Lesson 34E: pH During Strong-Weak Titration

Using Mol/L After Reaction As the *Rice* Unit

Our *rice* table "accounting system" for reactions can be solved in units of

- Moles *or prefix*-moles, or
- Mol/L (M) *if* all of the particles are dissolved in the same volume;

as long as all of the *units* in the *rice* table are consistent (the same).

So far, we have solved all of our *rice* tables for acid-base reactions in moles or millimoles, and not mol/L. Combining solutions of two substances does not change the moles of each in the new solution before they react, but it does decrease their concentrations because the *volume* in which each substance is dissolved increases.

When solutions of two different substances are combined, but before they react, the moles of each substance does not change, but the mol/L of *both* are *diluted*.

Rice moles tables *can* be solved in moles/liter IF you know the concentrations of the acid and base reactants *after* they are combined, but *before* they react. Why?

After two solutions of reactants are mixed together, all of the moles present, whether before, during, or after the reaction, are in *same* volume of solution. The volume in dilute aqueous solutions is determined ~100% by how much of the *solvent* (water) is present. Once the solutions are combined, the volume of water does not substantially change if an acid-base reaction takes place, even if water is a reactant or product.

Rice tables are based on mole *ratios*: the coefficients of the balanced equation. If all of the moles are divided by the same constant liters, the mole *ratios* of the *rice* table remain the same, so that "mol/L *after* combining" may be used as a consistent unit in a *rice* table.

For solution reactions, IF you enter into a *rice* table the ***i***nitial [reactants] *after* they are combined, but *before* they react, you can find all mol/L *after* the reaction.

For acid-base reactions, if we know the concentrations of all of the substances after the reaction, we can find the $[H^+]$ and the pH.

Let's apply that rule on this example.

Q. Complete the following table, then find the pH after the reaction.

Reaction	**1** HCl	**1** KOH		
Initial (after combining, but before reacting)	**0.025 M**	**0.035 M**	**0 mol**	**0 mol**
Change				
At **E**nd**/E**quilibrium				

* * * * *

Since the table shows the ***i***nitial concentrations *after* the reactants have been combined, the solution volume is the same at all points during the reaction, and the *rice moles* table can be solved in moles/liter (M).

Reaction	**1** HCl	**1** KOH	**1 H_2O**	**1 KCl**
Initial (after combining, but before reacting)	0.025 M	0.035 M	**0 mol**	**0 mol**
Change	**–0.025 M**	**–0.025 M**	**+ 0.025 M**	**+ 0.025 M**
At **E**nd**/E**quilibrium	**0 M**	**+ 0.010 M**	**+ 0.025 M**	**+ 0.025 M**

After the reaction, the [KOH] at equilibrium determines the pH.

$[KOH] = \mathbf{[OH^-]} = \mathbf{0.010\ M} = 1.0 \times 10^{-2}\ M$; p**OH** = 2.00 ; **pH = 12.00**

Using Mol/L *Before* Reaction With A *Rice* Table

The question above was solved relatively quickly. Why haven't we solved all neutralization calculations this way?

The reason is that in most problems, we are not *given* the acid and base concentrations *after* they are combined. What we usually given the acid and base concentrations *before* they are combined. Those concentrations *before* combining cannot be put directly into a *rice* table. The acid and base are *diluted* as they are mixed together. How much they are diluted varies with how much of each solution is mixed together.

We *can* solve *rice* tables in *mol/L* if we use this rule:

For *solution* reactions: *rice* calculations can be solved in mol/L IF all supplied mol/L *before* combining are converted to mol/L *after* combining but before reacting, using dilution rules.

This gives us two ways to find pH after reaction from amounts before reaction.

To find pH *after* reaction, given amounts of reactants *before* the reaction, the steps are

Reactants **> reactant mol or** *prefix***-mol > *rice* moles > mixture pH steps**, *OR*

Reactant M before **> reactant M combined > *rice* M > mixture pH steps**.

In general, for *rice* tables, use this rule.

The values that go into the ***i***nitial row of a *r**i**ce* table can be moles, or prefix-moles, or mol/L after combining but before reacting (as long as all units are consistent).

Before we use mol/L to solve a *rice* table, let's refresh our memory on dilution calculations (from Lesson 12A).

Dilution Review

The dilution equation is written in symbols as

$\boxed{V_C \times M_C = V_D \times M_D}$ in which **C** means concentrated and **D** diluted.

The dilution equation is memorized by recitation:

"In dilution, volume times molarity equals volume times molarity."

To find concentrations *after* two solutions are combined, you are always solving for the *diluted molarity*. That equation is always

$$M_{\text{Diluted – after combining}} = \frac{V_{\text{Conc – before combining}} \times M_{\text{Conc – before combining}}}{V_{\text{Diluted-}\mathbf{Total}\text{ after combining}}}$$

In some problems, [reactant after combining] can be solved by inspection using the rule:

In dilution, if **V** or **M** changes by an easy multiple , multiply the other by 1/multiple.

For example, if equal volumes of solutions of two different substances are combined, the volume containing the particles of each substance is doubled, so the concentration of both substances is *cut in half.*

Practice A: For additional review, see Lesson 12A.

1. If 20.0 mL of 0.100 M NaOH is combined with 20.0 mL of 0.200 M HCl, after mixing but before reacting,

   [HCl] = [NaOH] = ?

2. If 10.0 mL of 0.45 KOH is combined with 20.0 mL of 0.300 M HCN, after combining, but before reacting,

   [HCN] = [KOH] = ?

3. If 25.0 mL of 0.150 M HF is combined with 21.5 mL of 0.120 M KOH,
   a. [HF] after combining, before reacting = ?
   b. [KOH] after combining, before reacting = ?

As the **practice** above shows, finding mol/L after dilution is relatively easy when dilution can be done by inspection, but it takes time when the numbers are complex.

In acid-base *rice* tables, which units *should* be used: moles, millimoles, or mol/L? All three methods work, but a rule that may save time is

- If [acid] and [base] after combining but before reacting can be solved by inspection, solve in mol/L;
- If the dilutions are time-consuming, or if calculations must be done at several points of the same titration, solve in moles or millimoles.

If it's a tossup, solve in moles or millimoles. In chemistry, the unit that best makes sense of most processes is the unit that *counts* the particles: moles or *prefix*-moles.

pH During Weak-Strong Titration

During the titration of a moderately *weak* acid or base by a strong opposite, most rules are the same as for strong-strong titration.

- The moles or mol/L present at any point can be tracked by a *rice* table.
- At the equivalence point, the solution contains only products.

The differences include

1. *Before* the titration begins, the solution contains a *weak* acid or base. The solution pH is calculated using K_a or K_b .
2. *Between* the beginning and equivalence point of a weak-strong titration, both the original weak acid and base and its conjugate are present, so the reaction mixture is a *buffer*. The pH is determined using *buffer* methods: write the buffer chart and then the K_a or Henderson-Hasselbalch equation.
3. *At* the *equivalence point*, only one non-pH-neutral product is present: the conjugate of the original weak acid or base. That conjugate is also a weak acid or base, and the pH is calculated based on its K_a or K_b.
4. Past the endpoint, the solution contains strong titrant and the weak conjugate. The [strong titrant] added after the endpoint will nearly always determine the pH.

You should be aware of the points above, but you should not need to memorize them. The bottom row of the *rice* table identifies the mixture present at each step of a titration. To find pH, simply apply the rules for mixture pH to the <u>e</u>nd row of the ric<u>e</u> table.

To find pH *after* reaction, given amounts of reactants *before* the reaction, the steps are

Reactants **> reactant mol or** *prefix***-mol > *rice* moles > mixture pH steps**, *OR*

Reactant **M** *before* **> reactant M *after combining* > *rice* M at end > mixture pH**.

Let's apply those steps to a weak-strong example.

Q. A 20.0 mL sample of a 0.200 M HF is titrated with 0.120 M KOH. Calculate the pH after 20.0 mL of KOH solution has been added (K_a of HF = 6.8 x 10^{-4}). Solve the *rice* table in mol/L.

* * * * *

When any acid is reacted with any hydroxide (OH^-) base, one product is H-OH.

* * * * *

In the *rice* table, [initial] must be after mixing, but before reacting. When equal volumes of solutions of two different substances are combined, the concentration of both substances is cut in half. After mixing, by inspection, [HF] = 0.100 M and [KOH] = 0.0600 M .

* * * * *

Reaction	**1 HF**	**1** KOH	**1** H_2O	**1 KF**
Initial	**0.10$\underline{0}$ M**	**0.0600 M**	**0 M**	**0 M**
Change	**— 0.0600 M**	**— 0.0600 M**	**+ 0.0600 M**	**+ 0.0600 M**
At **E**nd**/E**quilibrium	**+ 0.04$\underline{0}$ M**	**0 M**	**+ 0.0600 M**	**+ 0.0600 M**

What type of solution is this?

* * * * *

A buffer. Solve for buffer pH.

* * * * *

Buffer Chart: **WA** *formula* = HF — **CB** *formula* = F^-

moles or [WA] = **0.040 M** HF — *moles* or [CB] = **0.0600 M F^-**

* * * * *

H-H equation: $\boxed{\text{pH} \approx \text{p}K_a + \log(\mathbf{[base]/[acid]})}$

$$\approx \ -\log(6.8 \times 10^{-4}) + \log(\mathbf{0.0600\ M / 0.040\ M})$$

$$\approx \ -(-\mathbf{3.17}) + \log(\mathbf{1.5}) \approx 3.17 + 0.18 = \boxed{\mathbf{3.35 = pH}}$$

Buffer check: $K_\mathbf{a}$ = 6.8 x 10^{-4} , buffer pH estimate is **4±2** = 2 to 6. Check.

A Special Case: The Half-Way Point

When a weak acid or base is titrated by a strong opposite, between the initial solution and the endpoint, the solution is a buffer.

By definition, when the titration is *half-way* to the endpoint, *half* of the *moles* of the initial weak acid or base have been neutralized and converted to its conjugate, and half of the moles of the original substance remain. If the moles of the original weak acid or base and its conjugate are both half the original concentration, the moles of both are *equal*.

We know that

> In buffer solutions, *if* either [WA] **=** [CB] *or* moles WA **=** moles CB, then
> **$[H^+] \approx K_a$** and **$pH \approx pK_a$**.

At the half-way point, this rule can solve some weak acid or base titration calculations by inspection:

> *Half-way* to the endpoint in the neutralization of a *weak* acid or base, a buffer exists in which moles WA = moles CB, and **$[H^+] \approx K_a$** and **$pH \approx pK_a$**.

Limitations

The Henderson-Hasselbalch equation is an approximation because it is derived from the buffer approximation. Buffer approximations generally supply answers within the range of experimental error for *K* and pH except

- for relatively strong weak acids and bases, and
- very close to the beginning of the titration, and very close to the endpoint, when [WA or WB] is not large compared to ionization (x).

In those cases, if more accurate predictions are needed, use the exact buffer quadratic to find $[H^+]$, then pH definitions to find pH.

Summary: Strong-Strong vs. Weak Strong Titration

Stage	**$[H^+]$ and pH Determined By**	
	If Strong by Strong	**If Weak Titrated by Strong**
Before start	[Initial SA or SB]	[Weak Acid or Base] & *K*
Between start & endpoint	[SA or SB remaining]	*Buffer*
***Half**way to endpoint*	**1/2** [Initial SA or SB]	$[H^+] \approx K_a$ and $pH \approx pK_a$
At endpoint	pH = 7	[Conjugate] and its *K*
After endpoint	[titrant]	[titrant]

Strong-strong and weak-strong titration calculations differ due to the differences between the substances being titrated. Strong acids and bases hydrolyze 100% and form pH-neutral conjugates. Weak acids and bases hydrolyze slightly and form *non*-pH-neutral conjugates.

In *some* titration calculations, the summary chart above may allow solving by inspection. In *all* cases, a *rice* table and mixture rules will solve for pH.

Practice B: Apply the rules above from memory. Solve problems 1 and 2. Save Problem 3 for your next practice session. Problem 4 is more challenging.

1. 25.0 mL of 0.0700 M HCl is combined with 25.0 mL of 0.100 M NaCN. Find the pH after the reaction. (K_a of HCN = 6.2×10^{-10}). (Solve the *rice* table using molarity).
2. What is the [H^+] half-way to the equivalence point.
   a. When a strong acid is titrated by a strong base?
   b. When a weak acid is titrated by a strong base?
   c. When a weak base is titrated by a strong acid?
3. 20.0 mL of 0.200 M CH_3COOH (K_a = 1.8×10^{-5}) is titrated by 0.200 M NaOH.
   a. How many mL of NaOH is required to reach the endpoint?
   b. When pH = pK_a , how many mL of NaOH have been added?
   c. Calculate the pH in the solution after 19.0 mL NaOH is added (solve in millimoles).
   d. Calculate the pH at the endpoint of the titration.
4. To determine the K_a of a water soluble weak acid with one acidic hydrogen (call it HCb), 20.0 mL of a 0.150 M HCb solution is combined with 10.0 mL of 0.200 M KOH. The solution pH of this "before the endpoint" mixture is found to be 5.25. What is the new acid's K_a value?

ANSWERS

Practice A

1. When equal volumes are combined, the concentrations of both substances are cut in half.

   [HCl] = 0.100 M ; [NaOH] = 0.0500 M

2. The total volume after mixing is 30.0 mL. The volume of the KOH is tripled, so its concentration is 1/3 the original. **[KOH] = 0.45 M x 1/3 = 0.15 M after mixing.**

   If needed, for [HCN], you can use $\boxed{V_C \times M_C = V_D \times M_D}$

   $$? \, M_D \text{ HCN} = \frac{V_C \times M_C}{V_D} = \frac{20.0 \, \cancel{\text{mL}} \times 0.300 \text{ M HCN}}{30. \, \cancel{\text{mL}} \text{ total}} = \textbf{0.200 M HCN diluted = [HCN] after mixing.}$$

   Using the dilution equation with M, the units and substances will cancel properly, but the labels C and D often will not.

3a. To use the dilution equation, $\boxed{V_C \text{ x } M_C = V_D \text{ x } M_D}$, set up a data table with

DATA: V_C = 25.0 mL HF (C before mixing)

M_C = 0.150 M (in wording, goes with 25.0 mL)

V_D = 25.0 + 21.5 = 46.5 mL soln. = Total, diluted volume

M_D = **?** = WANTED

SOLVE:

$$\textbf{? } \mathbf{M_D} = \frac{V_C \text{ x } M_C}{V_D} = \frac{25.0\ \cancel{\text{mL}} \text{ x } 0.150\text{ M HF}}{46.5.\ \cancel{\text{mL}}\ \textbf{total}} = \textbf{0.806 M HF diluted}$$

Using the dilution equation with M, the units will cancel properly, but the C and D labels often will not.

Check: from 25 mL to 46.5 mL nearly doubles the volume; [HF] should be about cut in half, and is.

3b. To use the dilution equation, $\boxed{V_C \text{ x } M_C = V_D \text{ x } M_D}$, set up a data table with

DATA: V_C = 21.5 mL KOH (C before mixing)

M_C = 0.120 M KOH

V_D = 25.0 + 21.5 = 46.5 mL soln. = Total, diluted volume

M_D = **?** = WANTED

SOLVE:

$$\textbf{? } \mathbf{M_D} = \frac{V_C \text{ x } M_C}{V_D} = \frac{21.5\ \cancel{\text{mL}} \text{ x } 0.120\text{ M KOH}}{46.5.\ \cancel{\text{mL}}} = \textbf{0.0555 M KOH diluted}$$

Check: 21.5 mL to 46.5 mL about doubles the volume; [KOH] should be about cut in half and is.

Practice B

1. The *rice* table needs initial concentrations after mixing, but before reacting. Since equal volumes of the acid and base are combined, the initial mol/L of each is *cut in half* as they are mixed together.

Reaction	1 HCl	**1** NaCN	**1 HCN**	**1 NaCl**
Initial	**0.0350 M**	**0.0500 M**	**0 mol**	**0 mol**
Change	**— 0.0350 M**	**—0.0350 M**	**+ 0.0350 M**	**+ 0.0350 M**
At **E**nd/**E**quilibrium	**0 M**	**+ 0.0150 M**	**+ 0.0350 M**	**+ 0.0350 M**

The solution mixes CN^- and HCN. It is a buffer.

Buffer Chart: **WA** *formula* = HCN **CB** *formula* = CN^-

moles or [WA] = **0.0350 M HCN** *moles* or [CB] = **0.0150 M CN^-**

* * * * *

H-H equation: $\boxed{\text{pH} \approx \text{p}K_a + \log(\textbf{[base] / [acid]})}$

$$\approx \mathbf{-\log}\,(6.2 \text{ x } 10^{-10}) + \log(\mathbf{0.0150\ M} / \mathbf{0.0350\ M})$$

$$\approx -(-\mathbf{9.21}) + \log(\mathbf{0.429}) \approx 9.21 - 0.37 = \boxed{\mathbf{8.84 = pH}}$$

<u>Check</u>: K_a = 5.6 x 10^{-10} , buffer pH estimate 10 ± 2 = 8 -12. Check.

2a. Half way, half of the acid is neutralized, and all products of an SA+SB titration are pH neutral.
$[H^+]$ = 1/2 [SA initial]

2b. Between the beginning and end of WA or WB titration by strong opposite, the solution is a buffer.
Half way to the equivalence point, **$[H^+] \approx K_a$**

2c. Between the beginning and end of WA or WB titration by strong opposite, the solution is a buffer.
Half way to the equivalence point, you have the same mixture as in the titration of a weak acid by a strong base: What exists is half weak acid and half its conjugate base. As in part 2c, **$[H^+] \approx K_a$** of the conjugate of the weak base. All buffers can be treated as a weak acid mixed with its conjugate base.

3. WANTED: mL NaOH to neutralize the acetic acid.

In this reaction, one mole of base neutralizes one mole of acid:

$1\ CH_3COOH + 1\ NaOH \rightarrow\rightarrow 1\ H_2O + 1\ CH_3COONa$

Since both acid and base have the same concentration, the moles of acid and base particles will be the same when their volumes are the same.

mL of **0.200 M** NaOH to neutralize this 20.0 mL of **0.200 M** acid = **20.0 mL NaOH**

3b. pH = pK_a half-way to the end point. so pH = pK_a at **10.0 mL** NaOH added, based on *part a*.

3c. The K_a conveys that acetic acid is a weak acid.

To find pH *after* reaction, given amounts of reactants *before* the reaction, the steps are
Reactants **> reactant mol or** *prefix***-mol > *rice* moles > mixture pH steps**, OR
Reactant **M** *before* **> reactant M *after* mixing > *rice* M > mixture pH steps**.

If we solve in mmol, the moles of acid and base before reacting are

? mmol CH_3COOH = $20.0\text{ mL } CH_3COOH \cdot \frac{0.200\text{ mol } CH_3COOH}{1\text{ L } CH_3COOH\text{ soln.}}$ = **4.00 mmol CH_3COOH**

? mmol NaOH = $19.0\text{ mL NaOH} \cdot \frac{0.200\text{ mol NaOH}}{1\text{ L NaOH soln.}}$ = **3.80 mmol NaOH**

Reaction	**1** CH_3COOH	**1** NaOH	**1** H_2O	**1** CH_3COONa
Initial	**4.00 mmol**	**3.80 mmol**	**-**	**-**
Change	**−3.80 mmol**	**−3.80 mmol**	**+ 3.80 mmol**	**+ 3.80 mmol**
At **E**nd/**E**quilibrium	**+ 0.20 mmol**	**0 mmol**	**+ 3.80 mmol**	**+ 3.80 mmol**

Label the particles at the end as SA, SB, WA, WB, or N.

* * * * *

The pH-not-neutrals are CH_3COOH and its conjugate CH_3COO^-. This is a buffer.

* * * * *

Buffer Chart: **WA** *formula* = CH_3COOH **CB** *formula* = CH_3COO^-

moles WA = **0.20 mmol** CH_3COOH ***moles*** CB = **3.80 mmol** CH_3COO^-

Henderson-Hasselbalch: $\mathbf{pH} \approx pK_a + \log(\textbf{mol base/mol acid})$

$\approx \mathbf{-\log}(1.8 \times 10^{-5}) + \log(\textbf{3.80 mmol /0.20 mmol})$

$\approx \mathbf{-(-4.74)} + \log(\mathbf{19}) \approx 4.74 + 1.28 = \boxed{\mathbf{6.02 = pH}}$

<u>Buffer check</u>: $K_\mathbf{a} = 1.8 \times 10^{-5}$, buffer pH estimate is 5 ± 2 = 3 -7. Check.

3d. At the endpoint, the acid and base have neutralized each other: their moles are zero. The mixture contains water and a dissolved salt (CH_3COONa). Recall the rules for pH of salt solutions?

* * * * *

The salt is composed of two ions. If one ion is not pH neutral, find pH based on its reaction as a weak acid or weak base. CH_3COO^- is the conjugate of the weak acetic acid, and is therefore a weak base. *WRRECK* it, and\or solve the K_b approximation.

* * * * *

WANT: pH of CH_3COO^- solution

R+***E***: specific $\mathbf{CH_3COO^- + H_2O \leftarrow\leftarrow\rightarrow OH^- + CH_3COOH}$ (goes slightly)

R+***E***: general WB + H_2O $\leftarrow\leftarrow\rightarrow$ $\mathbf{OH^-}$ + conjugate acid (goes slightly)

^ ^ ^

Conc. at Eq:	$[WB]_{mixed} - x$	x	x

(*rice* bottom row)

<u>*K*</u>$\underline{K_\mathbf{b}}$: $K_b = \dfrac{[OH^-][\text{conjugate}]}{[WB]_{mixed} - x} \approx \boxed{\dfrac{x^2}{[WB]_{mixed}} \approx K_b}$

Solve the K_b approximation for x.

* * * * *

To solve the approximation, you need K_b and $[WB]_{mixed}$. Find K_b first.

* * * * *

You don't know K_b, but you know that K_a of conjugate acid = 1.8×10^{-5}

For conjugate acid-base pairs: $K_w = \boxed{\mathbf{K_a \times K_b = 1.0 \times 10^{-14}}}$

$$\mathbf{K_b} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{\mathbf{1.8 \times 10^{-5}}} = 0.556 \times 10^{-9} = \boxed{\mathbf{5.56 \times 10^{-10} = K_b}}$$

Now find $[WB]_{mixed}$.

* * * * *

$[WB]_{mixed} = [CH_3COO^-]_{\text{at the endpoint}}$. At and after the endpoint,

? = mol salt ion formed = mol of initial weak acid used up = 0.00400 mol $\mathbf{CH_3COO^-}$

In how much aqueous solution is the salt ion dissolved at the endpoint?

* * * * *

20.0 mL initial acid + 20.0 added of base (see part a) = 40.0 mL total soln.

$$? [CH_3COO^-] = \frac{\text{mol } CH_3COO^-}{\text{L soln}} = \frac{0.00400 \text{ mol } CH_3COO^-}{\mathbf{40.0} \text{ total mL soln.}} \cdot \frac{1 \text{ mL}}{10^{-3} \text{ L}} = 0.100 \text{ M } CH_3COO^-$$

Solve the approximation.

* * * * *

$$\boxed{K_b \approx \frac{x^2}{[W\mathbf{B}]_{\text{mixed}}}} \qquad \text{Substituting:} \quad 5.6 \times 10^{-10} \approx \frac{x^2}{0.100 \text{ M}}$$

$$\mathbf{x^2} = (5.6 \times 10^{-10}) (0.100) = 5.56 \times 10^{-11} = 55.6 \times 10^{-12}$$

$$\mathbf{x} \approx (\text{estimate } 7\text{-}8 \times 10^{-6}) \approx \boxed{\mathbf{7.46 \times 10^{-6} \text{ M} = [OH^-]}}$$

Since the approximation was used, do the:

Quick 5% test : $x = 7.46 \times 10^{-6}$ M, [**WB**] = 0.10 M = 1.0×10^{-1} M

Since the exponent difference is 3 or more, the ionization passes the 5% test, and the approximation may be used.

But pH was WANTED.

* * * * *

p**OH** = — log [OH$^-$] = — log(7.46 x 10^{-6}) = **5.13 = pOH** pH = 14.00 — pOH = $\boxed{\mathbf{8.87 = pH}}$

4. WANTED = K_a of HCb

You know the pH. You want K_a . You are titrating a weak acid with a strong base, before the endpoint.

What equation involves these variables and conditions?

* * * * *

Before the endpoint, a titrated weak acid or base produces a buffer solution.

The buffer equation that includes pH and K_a is the Henderson-Hasselbalch, which can be solved in moles or mol/L. If you choose moles, **pH** ≈ p$\mathbf{K_a}$ + log (**mol base/mol acid**)

To solve for p$\mathbf{K_a}$ then $\mathbf{K_a}$, you need to find the moles of acid and base at the point where the pH = 5.25

You can solve in moles, but if volumes are given in milliliters, you may want to solve in millimoles.

To find moles of acid and base in the solution at a stated point in a titration, use a *rice moles* table.

* * * * *

For the balanced equation, you can write either

$HCb + KOH \rightarrow H_2O + KCb$ *or* $HCb + OH^- \rightarrow H_2O + Cb^-$

Both give the same results. Find the initial mmol, before the reactants react.

* * * * *

$$\textbf{? m}\text{mol } \mathbf{KOH} = 10.0 \text{ } \mathbf{m}\text{L KOH} \cdot \frac{0.200 \text{ mol KOH}}{1 \text{ L KOH soln.}} = 2.00 \text{ } \mathbf{m}\text{mol KOH} = \mathbf{2.00 \text{ } m}\text{mol } \mathbf{OH^-}$$

The millimoles of acid mixed is

$$\textbf{? m}\text{mol } \mathbf{HCb} = 20.0 \text{ } \mathbf{m}\text{L HCb} \cdot \frac{0.150 \text{ mol HCb}}{1 \text{ L HCb soln.}} = \mathbf{3.00 \text{ } m}\text{mol } \mathbf{HCb}$$

Reaction	1 HCb	**1** OH^-	**1** H_2O	**1** Cb^-
Initial	**3.00 mmol**	**2.00 mmol**	**0 mmol**	**0 mmol**
Change	**– 2.00 mmol**	**–2.00 mmol**	**+ 2.00 mmol**	**+ 2.00 mmol**
At **E**nd/**E**quilibrium	**+ 1.00 mmol**	**0 mmol**	**+ 2.00 mmol**	**+ 2.00 mmol**

Label the end particles at this point as SA, SB, WA, WB, or N.

* * * * *

This is a buffer. The pH-not-neutral components are HCb (WA) and its conjugate Cb^-. Solve H-H.

Buffer Chart: **WA** *formula* = HCb **CB** *formula* = Cb^-

moles or [WA] = **1.00 mmol** HCb ***moles*** or [CB] = **2.00 mmol** Cb^-

H-H: pH ≈ $\mathbf{p}K_a$ + log (**mol base/mol acid**)

You want K_a. Solve for $\mathbf{p}K_a$ first. From the above equation,

$$\mathrm{p}K_a \approx \mathrm{pH} - \log(\textbf{mol base/mol acid})$$

$$\approx \mathbf{5.25} - \log(\mathbf{2.00}\text{ mmol}/\mathbf{1.00}\text{ mmol}) \approx 5.25 - \log(2.00) \approx$$

$$\approx 5.25 - 0.30 \approx \boxed{\mathbf{4.95} = \mathrm{p}K_a}$$

But we WANT K_a · Since $\boxed{\mathbf{pH} \equiv -\log[H^+] \quad \text{and} \quad [H^+] \equiv 10^{-pH}}$

$\boxed{\mathrm{p}K_a \equiv -\log K_a \quad \text{and} \quad K_a \equiv 10^{-\mathrm{p}K_a}}$ Finish from here.

* * * * *

$? = K_a \equiv 10^{-\mathrm{p}K_a} = 10^{-4.95} = ?? \times 10^{-5} = \boxed{1.1 \times 10^{-5} = K_a \text{ of HCb}}$

<u>Check</u>: Buffer pH and $-K_a$ exponent should be ± 2. pH is 5.25. K_a estimate = ? x $10^{-3 \text{ to } 7}$. Check.

* * * * *

SUMMARY – pH During Neutralization and Titration

1. When an acid and base are reacted, IF one of the components is *strong*, the reaction will go until one component, either the acid or the base, is 100% used up.

   Another way to express this rule:

   > At the end of a neutralization reaction, if one of the reactants is strong, the *moles* of one of the *reactants* must be *zero*.

2. **Steps For Finding Mixture pH**

   Apply in this order.

   a. Re-write soluble salts as separated ions.

   b. Label the particles in the mixture as SA, SB, WA, WB, or N, based on K_a or K_b.

   c. In pH calculations, ignore pH-neutral (N) particles.

   d. If all particles are N, pH = 7.

   e. If SA or SB is present, ignore other particles. Find pH based on 100% ionization:

   $$[\text{HCl or HNO}_3] = [\text{H}^+] \quad \text{and} \quad [\text{NaOH or KOH}] = [\text{OH}^-]$$

   f. If a WA or WB a*nd* its conjugate is present, solve a buffer chart and the Henderson-Hasselbalch equation in moles or mol/L.

   g. If only *one* WA or WB is present, use K_a or K_b approximation, then the 5% test.

3. *Rice* tables must have consistent units. The values that go into the ***i***nitial row of a *r**i**ce* table can be *moles,* or *prefix*-moles, or *mol/L* after combining but before reacting.

4. To Calculate pH *After* Reaction From Amounts *Before* Reaction

   a. Convert the initial amounts of acid and base to *moles,* or *prefix*-moles, or mol/L after combining but before reacting.

   b. Enter those values in the ***i***nitial row of a *r**i**ce moles* table.

   c. In the ***c***hange row, use the rule: when acid and base are combined, if *one* or both are strong, the one reactant is 100% used up.

   d. Calculate pH based on the mixture at the ***e***nd of the reaction (in *bottom* ric***e*** row).

   Those four steps can be summarized as:

> To find pH a*fter* reaction, given amounts of reactants *before* the reaction,
>
> Reactants **> reactant mol or** *prefix*-**mol > *rice* moles > mixture pH steps**, OR
>
> Reactant **M** *before* **> reactant M *after* mixing > *rice* M > mixture pH steps**.

5. To solve calculations for [**H**$^+$] or **pH,**
   a. Ask: Is the problem about a stable solution at equilibrium, or reactants reacting that then become a stable solution?
   b. If about a stable solution, apply the steps for finding **mixture pH**.
   c. IF about a reaction use the steps for pH *after* from amounts *before* combining.
6. The millimoles shortcut for *rice moles* tables: millimoles = $\boxed{\textbf{mmol = mL x (mol/L)}}$.
7. When solvent solutions are combined, their volumes add.
8. For reactions, to choose between using stoichiometry steps or the *rice moles* table:
   a. For *any* calculation involving amounts involved in chemical reactions, if you know the amount of *one* reactant that is 100% used up (the limiting reactant), and you want to know how much of *one* other reactant will react or *one* other product will form, use the *stoichiometry* steps:

      WDBB, units → moles → moles → units

      Amounts needed for exact neutralization at the equivalence point can be solved by stoichiometry IF one or both of the acid-base reactants is strong.
   b. For all other types of reaction calculations, a *rice moles* table (or, for simple reactions, the abbreviated version of the *rice* table used in the *WRECK* steps) is needed to determine amounts used up, formed, and present in the final mixture at equilibrium. These cases include:
      - IF you know the amounts for *two* reactants present before the reaction, but you do not know which is limiting, or
      - the reaction does not go essentially to completion, or
      - you need the amounts of *all* of the particles in the mixture after the reaction stops.
9. Special rules for titration calculations
   a. At the equivalence point in any titration,
      - the moles of acid added to the reaction mixture are equivalent to (the same as) the moles base added.
      - The acid and base reactants are exactly neutralized: both are 100% used up.
      - Since there are no reactants left, there are only products present.
   b. If a strong or moderately weak acid or base is titrated by a strong opposite, the pH changes sharply during the titration, but not until *very* close to the endpoint.
   c. For the titration of *any* strong acid and strong base, at the endpoint: pH = 7 .
   d. Half-way to the endpoint in the titration of a *weak* acid or base, a buffer solution exists in which moles WA = moles CB, and $[\mathbf{H^+}] \approx K_\mathbf{a}$ and $\mathbf{pH} \approx \mathbf{p}K_\mathbf{a}$.

10. Summary: Strong-Strong vs. Weak Strong Titration

Stage	**[H$^+$] and pH Determined By**	
	If Strong By Strong	**If Weak By Strong**
Before start	[Strong Acid or Base]	[Weak Acid or Base] & K
Between start & endpoint	[Strong Acid or Base]	*Buffer*
Half-*way to endpoint*	**1/2** [Initial SA or SB]	$[H^+] \approx K_a$ and $pH \approx pK_a$
At endpoint	pH = 7	[Conjugate] and its K
After endpoint	[strong titrant]	[strong titrant]

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