

Modules 30 to 36 are *beta* versions. They are being posted in *draft* form to provide help on as many topics as possible during this semester. If you have need for help in this topic now, they will be useful, but they will have a higher than usual rate of typos and errors. Check back for updated versions at www.ChemReview.Net if you have time.

Calculations In Chemistry



Module 30: pH of Salts

Module 31: Buffers

Module 32: pH During Titration

Module 30 – pH of Salts	879
Lesson 30A: The Acid-Base Behavior of Salts.....	879
Lesson 30B: Will A Salt Acid-Base React?	886
Lesson 30C: Calculating the pH of a Salt Solution	890
Lesson 30D: Salts That Contain Amphoteric Ions.....	896
Module 31 – Buffers	901
Lesson 31A: Acid-Base Common Ions, Buffers	901
Lesson 31B: Buffer Example	904
Lesson 31C: Buffer Components	910
Lesson 31D: Methodical Buffer Calculations.....	914
Lesson 31E: Buffer Quick Steps.....	919
Lesson 31F: The Henderson-Hasselbalch Equation.....	925
Module 32 – pH During Titration	932
Lesson 32A: pH In Mixtures.....	932
Lesson 32B: pH After Neutralization	937
Lesson 32C: Distinguishing Types of Acid-Base Calculations.....	946
Lesson 32D: pH During Strong-Strong Titration	952
Lesson 32E: Titration pH: Weak by Strong	965

Table of Contents

How to Use These Lessons	1
Module 1 - Scientific Notation	2
Lesson 1A: Moving the Decimal	2
Lesson 1B: Calculations Using Exponential Notation	8
Lesson 1C: Tips for Complex Calculations	16
Module 2 - The Metric System	23
Lesson 2A: Metric Fundamentals	23
Lesson 2B: Metric Prefix Formats	29
Lesson 2C: Cognitive Science -- and Flashcards	33
Lesson 2D: Calculations With Units	39
Module 3 - Significant Figures	43
Lesson 3A: Rules for Significant Figures	43
Lesson 3B: Sig Figs -- Special Cases	46
Lesson 3C: Sig Fig Summary and Practice	49
Module 4 - Conversion Factors	52
Lesson 4A: Conversion Factor Basics	52
Lesson 4B: Single Step Conversions	56
Lesson 4C: Multi-Step Conversions	59
Lesson 4D: English/Metric Conversions	61
Lesson 4E: Ratio Unit Conversions	65
Lesson 4F: <i>Review Quiz For Modules 1-4</i>	69
Module 5 - Word Problems	72
Lesson 5A: Answer Units -- Single Or Ratio?	72
Lesson 5B: Mining The DATA	74
Lesson 5C: Solving For Single Units	81
Lesson 5D: Finding the <i>Given</i>	82
Lesson 5E: Some Chemistry Practice	85
Lesson 5F: Area and Volume Conversions	87
Lesson 5G: Densities of Solids: Solving Equations	92
Module 6 - Atoms, Ions, and Periodicity	99
Lesson 6A: Atoms	99
Lesson 6B: The Nucleus, Isotopes, and Atomic Mass	104
Lesson 6C: Elements, Compounds, and Formulas	111
Lesson 6D: The Periodic Table	116
Lesson 6E: A Flashcard Review System	120
Module 7 - Writing Names and Formulas	123
Lesson 7A: Naming Elements and Covalent Compounds	123
Lesson 7B: Naming Ions	128
Lesson 7C: Names and Formulas for Ionic Compounds	138
Lesson 7D: <i>Review Quiz For Modules 5-7</i>	150
Module 8 - Grams and Moles	154
Lesson 8A: The Mole	154
Lesson 8B: Grams Per Mole (Molar Mass)	156
Lesson 8C: Converting Between Grams and Moles	158
Lesson 8D: Converting Particles, Moles, and Grams	163

Module 9 – Mole Applications	168
Lesson 9A: Fractions and Percentages.....	168
Lesson 9B: Empirical Formulas.....	170
Lesson 9C: Empirical Formulas from Mass or % Mass.....	171
Lesson 9D: Mass Fraction, Mass Percent, Percent Composition.....	174
Module 10 – Balanced Equations and Stoichiometry.....	185
Lesson 10A: Chemical Reactions and Equations.....	185
Lesson 10B: Balancing Equations.....	188
Lesson 10C: Using Coefficients -- Molecules to Molecules	193
Lesson 10D: Mole to Mole Conversions	195
Lesson 10E: Conversion Stoichiometry.....	199
Lesson 10F: Limiting Reactants and RICE Tables	205
Lesson 10G: Limiting Reactants and Non-Mole Units	212
Lesson 10H: <i>Review Quiz For Modules 8-10</i>	221
Module 11 – Molarity	224
Lesson 11A: Ratio Unit Review	224
Lesson 11B: Word Problems with Ratio Answers	225
Lesson 11C: Molarity	231
Lesson 11D: Conversions and Careers	237
Lesson 11E: Units and Dimensions	241
Lesson 11F: Ratios versus Two Related Amounts	246
Lesson 11G: Solving Problems With Parts	253
Module 12 – Molarity Applications.....	263
Lesson 12A: Dilution	263
Lesson 12B: Ion Concentrations	272
Lesson 12C: Solution Stoichiometry	279
Lesson 12D: Reaction Stoichiometry For Ratio Units	286
Lesson 12E: <i>Review Quiz For Modules 11-12</i>	293
Module 13 – Ionic Equations and Precipitates	295
Lesson 13A: Predicting Solubility for Ionic Compounds	295
Lesson 13B: Total and Net Ionic Equations	299
Lesson 13C: Predicting Precipitation.....	303
Lesson 13D: Precipitate and Gravimetric Calculations	310
Module 14 – Acid-Base Neutralization	317
Lesson 14A: Ions in Acid-Base Neutralization	317
Lesson 14B: Balancing Hydroxide Neutralization	321
Lesson 14C: Acid-Hydroxide Neutralization Calculations	328
Lesson 14D: Neutralization Calculations in Parts.....	334
Lesson 14E: Carbonate Neutralization.....	341
Module 15 – Redox Reactions	349
Lesson 15A: Oxidation Numbers	349
Lesson 15B: Balancing Charge.....	354
Lesson 15C: Balancing Redox Using Oxidation Numbers	358
Lesson 15D: Oxidizing and Reducing Agents	360
Lesson 15E: Redox Stoichiometry	364
Module 16 – Half-Reaction Balancing.....	368
Lesson 16A: Constructing Half-Reactions – The CA-WHe! Method.....	368

Lesson 16B:	Balancing By Adding Half-Reactions.....	374
Lesson 16C:	Separating Redox Into Half-Reactions.....	377
Lesson 16D:	Balancing Redox With Spectators Present.....	380
Lesson 16E:	<i>Review Quiz For Modules 13-16</i>	384
Module 17 - Ideal Gases	387	
Lesson 17A:	Gas Fundamentals.....	387
Lesson 17B:	Gases at STP.....	391
Lesson 17C:	Complex Unit Cancellation.....	396
Lesson 17D:	The Ideal Gas Law and Solving Equations.....	401
Lesson 17E:	Density, Molar Mass, and Choosing Equations.....	405
Lesson 17F:	Using the Combined Equation.....	412
Lesson 17G:	Gas Law Summary and Practice.....	418
Module 18 - Gas Labs, Gas Reactions	422	
Lesson 18A:	Charles' Law; Graphing Direct Proportions.....	422
Lesson 18B:	Boyle's Law; Graphs of Inverse Proportions.....	429
Lesson 18C:	Avogadro's Hypothesis; Gas Stoichiometry.....	433
Lesson 18D:	Dalton's Law of Partial Pressures.....	440
Module 19 - Graphing.....	447	
Lesson 19A:	Graphing Fundamentals.....	447
Lesson 19B:	The Specific Equation for a Line.....	458
Lesson 19C:	Graphing Experimental Data.....	465
Lesson 19D:	Deriving Equations From Linear Data.....	475
Lesson 19E:	Linear Equations Not Directly Proportional.....	486
Lesson 19F:	Graphing Inverse Proportions.....	493
Module 20 - Phases Changes and Energy.....	502	
Lesson 20A:	Phases and Phase Changes.....	502
Lesson 20B:	Specific Heat Capacity and Equations.....	515
Lesson 20C:	Water, Energy, and Consistent Units.....	522
Lesson 20D:	Calculating Joules Using Unit Cancellation.....	526
Lesson 20E:	Calorimetry.....	532
Module 21 - Heats Of Reaction (ΔH)	540	
Lesson 21A:	Energy, Heat, and Work.....	540
Lesson 21B:	Exo- And Endothermic Reactions.....	547
Lesson 21C:	Adding ΔH Equations (Hess's Law).....	552
Lesson 21D:	Heats of Formation and Element Formulas.....	558
Module 22 - Light and Spectra	570	
Lesson 22A:	Waves.....	570
Lesson 22B:	Planck's Constant.....	575
Lesson 22C:	DeBroglie's Wavelength.....	583
Lesson 22D:	The Hydrogen Atom Spectrum.....	588
Lesson 22E:	Quantum Mechanics.....	594
Module 23 - Electron Configuration.....	599	
Lesson 23A:	The Multi-Electron Atom.....	599
Lesson 23B:	Abbreviated Electron Configurations.....	603
Lesson 23C:	The Periodic Table and Electron Configuration.....	609
Lesson 23D:	Electron Configurations: Exceptions and Ions.....	613

Module 24 – Bonding	618
Lesson 24A: Covalent Bonds.....	618
Lesson 24B: Molecular Shapes and Bond Angles	623
Lesson 24C: Electronegativity.....	631
Lesson 24D: Molecular Polarity.....	636
Lesson 24E: Solubility.....	641
Lesson 24F: Double and Triple Bonds	645
Lesson 24G: Ion Dot Diagrams	651
Lesson 24H: Orbital Models for Bonding.....	653
Module 25 – Kinetics	657
Lesson 25A: Kinetics Fundamentals	657
Lesson 25B: Rate Laws	661
Lesson 25C: Integrated Rate Law --Zero Order	671
Lesson 25D: Logarithms	679
Lesson 25E: Integrated Rate Law -- First Order.....	694
Lesson 25F: Reciprocal Math.....	704
Lesson 25G: Integrated Rate Law -- Second Order.....	709
Lesson 25H: Half-Life.....	716
Module 26 – Equilibrium	725
Lesson 26A: Le Châtelier’s Principle.....	726
Lesson 26B: Powers and Roots of Exponential Notation.....	738
Lesson 26C: Equilibrium Constants.....	748
Lesson 26D: K Values	754
Lesson 26E: K_p Calculations	758
Lesson 26F: The Rice Moles Table	764
Lesson 26G: K Calculations From Initial Concentrations	772
Lesson 26H: Q: The Reaction Quotient	778
Lesson 26I: Calculations Using K and Q.....	781
Lesson 26J: Solving Quadratic Equations.....	787
Module 27 – Acid-Base Fundamentals	798
Lesson 27A: Acid-Base Math Review	798
Lesson 27B: K_w Calculations: H^+ and OH^-	801
Lesson 27C: Strong Acid Solutions	805
Lesson 27D: The $[OH^-]$ in Strong Acid Solutions	810
Lesson 27E: Strong Base Solutions.....	813
Lesson 27F: The pH System.....	816
Module 28 – Weak Acids and Bases	826
Lesson 28A: K_a Math and Approximation Equations	826
Lesson 28B: Weak Acids and K_a Expressions	830
Lesson 28C: K_a Calculations	834
Lesson 28D: Percent Dissociation.....	842
Lesson 28E: Solving K_a Using the Quadratic Formula	845
Lesson 28F: Weak Bases and K_b Calculations.....	850
Lesson 28G: Polyprotic Acids	859
Module 29 – Brønsted-Lowry Definitions	866
Lesson 29A: Brønsted-Lowry Acids and Bases	866

Lesson 29B: Which Acid-Base Reactions Go?	870
Module 30 – pH of Salts	879
Lesson 30A: The Acid-Base Behavior of Salts.....	879
Lesson 30B: Will A Salt Acid-Base React?	886
Lesson 30C: Calculating the pH of a Salt Solution	890
Lesson 30D: Salts That Contain Amphoteric Ions	896
Module 31 – Buffers	901
Lesson 31A: Acid-Base Common Ions, Buffers	901
Lesson 31B: Buffer Example	904
Lesson 31C: Buffer Components.....	910
Lesson 31D: Methodical Buffer Calculations.....	914
Lesson 31E: Buffer Quick Steps	919
Lesson 31F: The Henderson-Hasselbalch Equation.....	925
Module 32 – pH During Titration	932
Lesson 32A: pH In Mixtures	932
Lesson 32B: pH After Neutralization.....	937
Lesson 32C: Distinguishing Types of Acid-Base Calculations	946
Lesson 32D: pH During Strong-Strong Titration.....	952
Lesson 32E: Titration pH: Weak by Strong	965
Module 33 – Solubility Equilibrium.....	978
Lesson 33A: Slightly Soluble Ionic Compounds	978
Lesson 33B: K_{sp} Calculations	984
Lesson 33C: Solubility and Common Ions.....	989
Lesson 33D: pH and Solubility	996
Lesson 33E: Quantitative Precipitation Prediction.....	1000
Module 34 – Thermodynamics.....	1012
Lesson 34A: Energy, Heat, and Work.....	1012
Lesson 34B: Entropy and Spontaneity	1021
Lesson 34C: Free Energy	1027
Lesson 34D: Standard State Values.....	1033
Lesson 34E: Adding ΔG° Equations.....	1038
Lesson 34F: Free Energy at Non-Standard Conditions	1041
Lesson 34G: Free Energy and K	1048
Module 35 – Electrochemistry	1053
Lesson 35A: Redox Fundamentals	1053
Lesson 35B: Charges and Electrical Work	1060
Lesson 35C: Standard Reduction Potentials.....	1064
Lesson 35D: Non-Standard Potentials: The Nernst Equation	1067
Lesson 35E: Predicting Which Redox Reactions Go	1073
Lesson 35F: Calculating Cell Potential	1080
Module 36 – Electrochemical Cells	1090
Lesson 36A: Cells and Batteries.....	1090
Lesson 36B: Anodes and Cathodes	1099
Lesson 36C: Depleted Batteries and Concentration Cells.....	1118
Lesson 36D: Electrolysis	1115
Lesson 36E: Amperes and Electrochemical Calculations.....	1119

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Module 30 — pH of Salts

Prerequisites: Complete Modules 28 and 29 before starting this module.

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Lesson 30A: 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.

* * * * *

Salts

Historically in chemistry, **salt** has been a term 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 may not be clear.

Soluble Salts

Some ionic compounds are soluble in water, but others are not. 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 concentrations of 0.10 M or less.

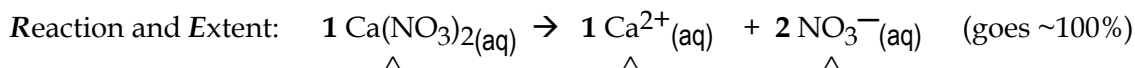
When a soluble ionic compound dissolves, if the moles of solid dissolved per liter of solution is known, the concentration of the ions in solution can be found by the *REC* steps (Lessons 7C and 12B). To briefly review, try this problem.

Q. Write the chemical formula and concentration for each particle formed when 0.10 M $\text{Ca}(\text{NO}_3)_2$ dissolves in water.

* * * * *

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.



Concentrations: 0.10 M \rightarrow 0 M 0.10 M and 0.20 M formed

In this solution are *no* $\text{Ca}(\text{NO}_3)_2$ 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.)

- In dilute solutions, will these dissolve $\sim 100\%$ *and* dissociate $\sim 100\%$ into ions? State your reasoning.

a. KCl	b. CH_4	c. $\text{Ra}(\text{NO}_3)_2$	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		
- Which compound above is

a. A strong base?	b. An element?	c. Radioactive?
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- 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 \rightarrow
b. 0.50 M $\text{Ba}(\text{NO}_3)_2$ \rightarrow
c. 0.25 M potassium cyanide \rightarrow
d. 0.10 M sodium sulfate \rightarrow

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 ions 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 29B), the rules include:

- Each line in the table includes an acid-base conjugate 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 $\sim 10^{-16}$), 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 \rightarrow
- which are those with a K_a larger than $\sim 10^{-16}$.

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

\equiv	\equiv	$K_a = \text{Large}$
\equiv	\equiv	
H_2O	\equiv	$K_a = \sim 10^{-16}$

- b. Another type of *acidic* ion is the highly charged ion of small-radius metal atoms, 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 base conjugates of acids that have a K_a below 1.0. \rightarrow
- which are also bases with K_b larger than $\sim 10^{-16}$.

\equiv	\equiv	$K_a = \text{Large}$
H_3O^+	H_2O	$K_a = 1.0$
\equiv	\equiv	$K_a = \# \times 10^{-x}$
\equiv	\equiv	

Basic ions include F^- , CN^- , CH_3COO^- , and $\text{C}_6\text{H}_5\text{COO}^-$.

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

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

- Using the acid-strength table in Lesson 29B, but applying the *rules* in this lesson from memory, label these ions as acidic (A), basic (B), or pH-neutral (N).
 - CH_3COO^-
 - K^+
 - NH_4^+
 - Al^{3+}
 - F^-
 - Cl^-
 - Ca^{2+}
- Which of the ions in Problem 1, if present in a compound, will always result in the compound to be soluble?
- In this problem, do *not* consult the acid-strength table.

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

- Fill in the blanks with the conjugate formulas.
- After the conjugate formula, label it as an acid (A) or base (B).
- What is the formula for the table *ion* (other than H^+) that is the strongest acid?

HCl	\rightarrow	H^+	+	_____ ()
_____ ()	\rightarrow	H^+	+	SO_4^{2-}
_____ ()	\rightarrow	H^+	+	F^-
$\text{C}_6\text{H}_5\text{COOH}$	\rightarrow	H^+	+	_____ ()
HCN	\rightarrow	H^+	+	_____ ()
_____ ()	\rightarrow	H^+	+	NH_3
H_2O	\rightarrow	H^+	+	_____ ()
NH_3	\rightarrow	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: $\text{HBr} > \text{HF} > \text{HCO}_3^- > \text{H}_2\text{O} > \text{CH}_3\text{CH}_2\text{OH}$
 Arrange these bases strongest to weakest: $\text{CO}_3^{2-}, \text{CH}_3\text{CH}_2\text{O}^-, \text{F}^-, \text{Br}^-, \text{OH}^-$
-

Salt Solutions: Acidic or Basic?

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

- 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?

* * * * *

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 dissolves in water to form an *acidic* solution.

Practice C: Consult the acid-strength table in Lesson 29B 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**

- KCl** **YES**. Compounds with alkali metals dissolve and ionize ~100% in dilute aqueous solutions.
 - CH₄** **NO**. Two non-metals form a covalent, not ionic, compound.
 - Ra(NO₃)₂** **YES**. It is ionic (Ra is metal atom) and it is soluble (NO₃[−] compounds).
 - Sodium acetate** **YES**. Is ionic (sodium is metal atom). Is soluble (Na⁺ = soluble).
 - Cl₂** **NO**. May dissolve, but two non-metal atoms form a covalent, not ionic, compound.
 - Calcium phosphate** **NO**. It is ionic, but by solubility rules for phosphate ions, it is insoluble. It will dissolve only slightly in water.
 - Ammonium bromide** **YES**. All ammonium (NH₄⁺) compounds are soluble.
 - HCl** **YES**. HCl is a strong acid. Strong acids dissolve and ionize ~100% in water.
 - RbOH** **YES**. All compounds with alkali metal atoms dissolve and ionize ~100%.
 - Silver chloride** **NO**. AgCl is a well-known precipitate: if it precipitates in water, it is insoluble.
 - PbCl₂** **NO**. By solubility rules is insoluble. **1. Lead nitrate** **YES**. Nitrates are ionic and soluble.
- A strong base? **RbOH** Alkali metal compounds ionize ~100%, hydroxide ion is formed.
 - An element? **Cl₂** Only one kind of atom.
 - Radioactive? **Ra(NO₃)₂** Ra is radium; all atoms with more than 83 protons are radioactive.
- 0.20 M NH₄Cl **1 NH₄Cl → 1 NH₄⁺ + 1 Cl[−] ; 0.20 M NH₄⁺ and 0.20 M Cl[−]**
 - 0.50 M Ba(NO₃)₂ **1 Ba(NO₃)₂ → 1 Ba²⁺ + 2 NO₃[−] ; 0.50 M Ba²⁺ and 1.0 M NO₃[−]**
 - 0.25 M potassium cyanide **1 KCN → 1 K⁺ + 1 CN[−] ; 0.25 M K⁺ and 0.25 M CN[−]**
 - 0.10 M sodium sulfate **1 Na₂SO₄ → 2 Na⁺ + 1 SO₄^{2−} ; 0.20 M Na⁺ and 0.10 M SO₄^{2−}**

Practice B

- CH₃COO[−]** **B** Appears in table on right, in the base column. The conjugate of an acid is a base.
 - K⁺** **N** Ions of alkali metals in rows 3-7 are pH neutral.
 - NH₄⁺** **A** Appears in the acid column as a weak acid.
 - Al³⁺** **A** Metals ions with a 3+ or 4+ charge form acidic solutions in water.
 - F[−]** **B** Appears in table on right side: the base column.
 - 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.
 - Ca²⁺** **N** Ions of column 2 metals in rows 3-7 are pH neutral.
- Compounds containing row 3-7 alkali metals (including **b. K⁺**) and compounds containing ammonium ion (**c. NH₄⁺**) always dissolve more than 0.1 mol/L in water, which is the general definition for “soluble.” *Except* for silver acetate, acetate compounds (**a. CH₃COO[−]**) are also always soluble.

3. a, b.

HCl	→	H ⁺ + Cl ⁻ (B)
HSO ₄ ⁻ (A)	→	H ⁺ + SO ₄ ²⁻
HF (A)	→	H ⁺ + F ⁻
C ₆ H ₅ COOH	→	H ⁺ + C ₆ H ₅ COO ⁻ (B)
HCN	→	H ⁺ + CN ⁻ (B)
NH ₄ ⁺ (A)	→	H ⁺ + NH ₃
H ₂ O	→	H ⁺ + OH ⁻ (B)
NH ₃	→	H ⁺ + NH ₂ ⁻ (B)

- c. Strongest acid ion? **HSO₄⁻** is the ion closest to top left. Ions are *charged* particles.
- d. Weakest acid ion? **NH₄⁺** Ion closest to the bottom left.
- e. Strongest basic ion? **NH₂⁻** 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: **CH₃CH₂O⁻ > OH⁻ > CO₃²⁻ > F⁻ > Br⁻**

Practice C

1. a. NaCl Both are neutral ions = **Neutral**
- b. NH₄NO₃ NH₄⁺ is acidic in the acid-strength table, NO₃⁻ is pH-neutral, combined: **Acidic**
- c. KCN pH-neutral K⁺, basic CN⁻ in table = **Basic**
- d. Sodium acetate Neutral Na⁺, basic CH₃COO⁻ = **Basic**
- e. Barium Chloride Both are neutral ions = **Neutral**
- f. Cesium fluoride Neutral Cs⁺, basic F⁻ = **Basic**
- g. Ferric Nitrate Acidic Fe³⁺ (highly charged metal ion), neutral NO₃⁻ = **Acidic**
- h. Ammonium Fluoride Acidic NH₄⁺, basic F⁻; must **compare** K_a and K_b

NH₄⁺, from the acid-strength table, has **K_a = 5.6 × 10⁻¹⁰**

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

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

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

- i. Ammonium Cyanide NH₄⁺ is acidic and CN⁻ is basic, so we must *compare* K_a and K_b

NH₄⁺, from the acid-strength table, has a **K_a = 5.6 × 10⁻¹⁰ = 0.000 000 000 56 = K_a**

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

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

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

* * * * *

Lesson 30B: Will A Salt Acid-Base React?

Brønsted-Lowry With Spectators Present

In Lesson 29B, 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 stronger 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 *sA* to label the *stronger* acid when comparing two acids, and use *SA* 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:

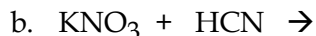
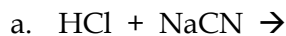
13. When predicting whether acid-base reactions with salt formulas will go, take out the pH-neutral spectators, apply the Brønsted-Lowry rules, put the spectators back in.

These rules are consistent with our general rule:

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

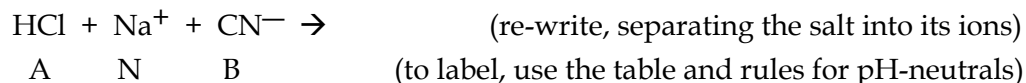
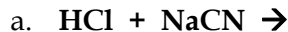
Try Rule 13 on this example.

Q. Will these reactions go? If so, write the products using molecular/ionic solid formulas. Use the acid-strength table in Lesson 29B.

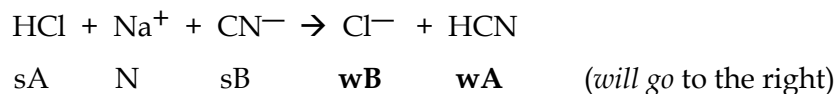


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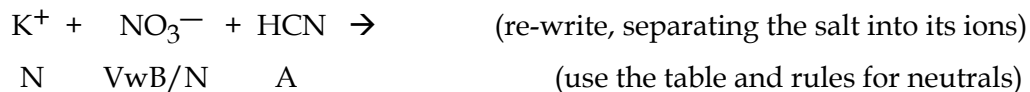
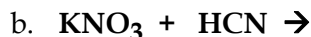
Answers



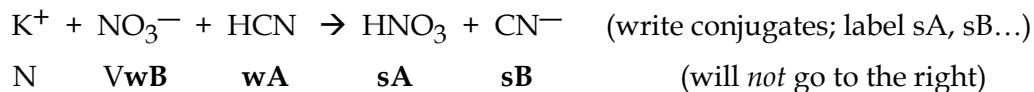
Use the table to write the conjugates, then label sA, sB, wA, wB, and go or no.



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



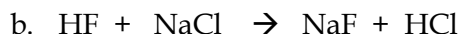
Nitrate ion is a *very* weak base (VwB): essentially pH neutral. Using the table:

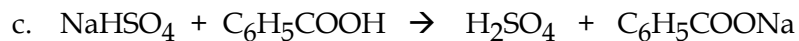


If NO_3^- is labeled as neutral, the combination of N, N, and A is also predicted to *not* react.

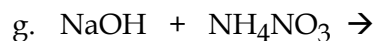
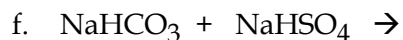
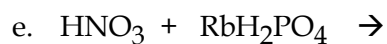
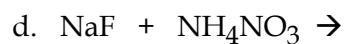
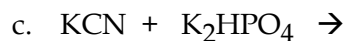
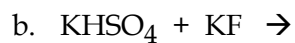
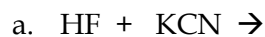
Practice: Put a check by and do every other letter. Save the rest for your next practice session. Use the table of acid strengths in Lesson 29B as needed. Check answers as you go.

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).





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*.



* * * * *

ANSWERS

- 1,2 a. $\text{CH}_3\text{COOH} + \text{Na}^+ + \text{CN}^- \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+ + \text{HCN}$
 sA N sB wB N wA (Will go)
- b. $\text{HF} + \text{Na}^+ + \text{Cl}^- \rightarrow \text{Na}^+ + \text{F}^- + \text{HCl}$
 wA N wB N sB sA (Will NOT go)
- c. $\text{Na}^+ + \text{HSO}_4^- + \text{C}_6\text{H}_5\text{COOH} \rightarrow \text{H}_2\text{SO}_4 + \text{C}_6\text{H}_5\text{COO}^- + \text{Na}^+$
 N wB wA sA sB N (Will NOT go)
3. a. $\text{HF} + \text{KCN} = \text{HF} + \text{K}^+ + \text{CN}^- \rightarrow \text{K}^+ + \text{F}^- + \text{HCN} = \text{KF} + \text{HCN}$
 sA N sB N wB wA (Will go)
- b. $= \text{K}^+ + \text{HSO}_4^- + \text{K}^+ + \text{F}^- \rightarrow \text{SO}_4^{2-} + 2\text{K}^+ + \text{HF} = \text{K}_2\text{SO}_4 + \text{HF}$
 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. $= \text{K}^+ + \text{CN}^- + 2\text{K}^+ + \text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-} + 3\text{K}^+ + \text{HCN} = \text{K}_3\text{PO}_4 + \text{HCN}$
 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. $= \text{Na}^+ + \text{F}^- + \text{NH}_4^+ + \text{NO}_3^- \rightarrow \text{HF} + \text{NH}_3 + \text{Na}^+ + \text{NO}_3^- = \text{HF} + \text{NH}_3 + \text{NaNO}_3$
 N wB wA N sA sB N N (Will NOT go)
- e. $= \text{HNO}_3 + \text{Rb}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4 + \text{Rb}^+ + \text{NO}_3^- = \text{H}_3\text{PO}_4 + \text{RbNO}_3$
 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.
 * * * * *
- f. $= \text{Na}^+ + \text{HCO}_3^- + \text{Na}^+ + \text{HSO}_4^- \rightarrow [\text{H}_2\text{CO}_3] + 2\text{Na}^+ + \text{SO}_4^{2-} = \text{H}_2\text{O} + \text{CO}_2\uparrow + \text{Na}_2\text{SO}_4$
 N sB N sA wA N wB (Will go)
 (HSO_4^- as A and HCO_3^- as B are \ . H_2CO_3 decomposes to $\text{H}_2\text{O} + \text{CO}_2$ (see Lesson 14E).)
- g. $= \text{Na}^+ + \text{OH}^- + \text{NH}_4^+ + \text{NO}_3^- \rightarrow \text{H}_2\text{O} + \text{NH}_3 + \text{Na}^+ + \text{NO}_3^- = \text{H}_2\text{O} + \text{NH}_3 + \text{NaNO}_3$
 N sB sA N wA wB N N (Will go)

Note in the table the conjugate of NH_4^+ .

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Lesson 30C: 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 30A), but do not assign calculations of the *pH* of salt solutions. Do this lesson if you are asked to calculate the $[H^+]$ or pH of a salt solution.

* * * * *

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.

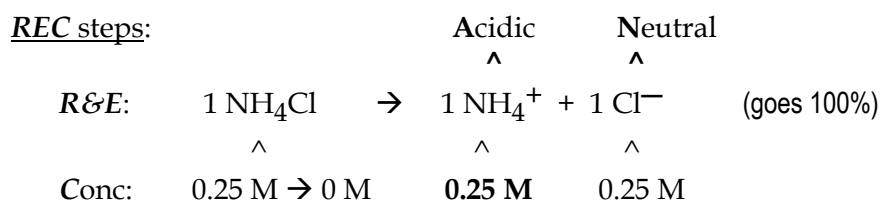
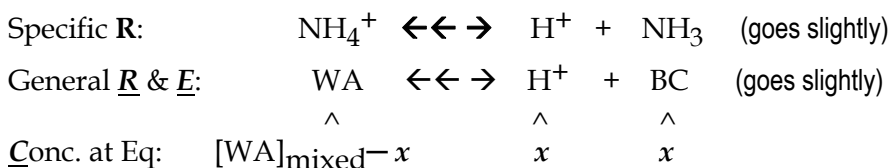
Using the above rule, try this calculation.

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

* * * * *

AnswerWANT: pH. Find $[H^+]$ first.DATA: $[NH_4Cl]_{\text{as mixed}} = 0.25 \text{ M}$ pH prompt: $\boxed{pH \equiv -\log [H^+] \text{ and } [H^+] \equiv 10^{-pH}}$

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.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.WRRECK: To find $[H^+]$, apply the **WRRECK** steps to the *non*-pH-neutral ion.WANT $[H^+] = x$ Since the non-pH-neutral ion is *acidic*, write its **R**eaction as an acid and its **K** as a K_a .

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

^ Definition ^ Exact ^ Approximate

SOLVE the K_a approximation for the WANTED symbol.

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

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

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

$$\begin{aligned} \% \text{ Dissociation} &= \frac{x}{[\text{WA or WB}]_{\text{mixed}}} \bullet 100\% = \frac{1.2 \times 10^{-5}}{0.25} \bullet 10^2 \% = \\ &= 4.8 \times 10^{-3} \% = 0.0048\% = \text{less than } 5\%, \text{ so the approximation is OK.} \end{aligned}$$

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

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

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

Quick 5% Test

Here's a quick way to apply the 5% test to see if a K_a or K_b approximation may be used.

- Using *scientific* notation, compare [WA] to the calculated $[\text{H}^+]$ or [WB] to $[\text{OH}^-]$.
- If the *exponents differ by 3 or more*, the ionization must be *less than 5%* and the approximation is acceptable to use.
- If the exponents differ by *2 or less*, solve the % dissociation equation for the 5% test.

Let's test this rule.

Q. For a weak acid solution, $[\text{H}^+]$ is calculated using the K_a approximation to be 9.9×10^{-4} M at $[\text{WA}] = 0.10$ M. Does this calculation pass the 5% test?

* * * * *

$$[\text{WA}] = 0.10 \text{ M} = 1.0 \times 10^{-1} \text{ M}, [\text{H}^+] = x = 9.9 \times 10^{-4} \text{ M}.$$

Since the difference between -1 and -4 is **3** or greater, this ionization must be less than 5%, so the approximation gives acceptable results, but let's calculate to be sure.

$$\% \text{ Dissoc.} = \frac{x}{[\text{WA or WB}]_{\text{mixed}}} \bullet 100\% = \frac{9.9 \times 10^{-4} \text{ M}}{1.0 \times 10^{-1} \text{ M}} \bullet 10^2 \% = 0.99 \%$$

This example is contrived to show the highest percent dissociation possible when the exponents differ by 3 or more, and it passes the 5% test, so the *quick* rule works.

Practice: Problem 3 is more challenging.

- Which of these solutions passes the 5% test by the quick rule?
 - For a weak base solution, $[\text{WB}] = 0.020$ M and $[\text{OH}^-] = 5.0 \times 10^{-5}$ M
 - For a weak acid solution, $[\text{WA}] = 0.0010$ M and $[\text{H}^+] = 4.0 \times 10^{-5}$ M
- Calculate the pH in a 0.10 M $\text{C}_6\text{H}_5\text{COOK}$ solution (K_b of $\text{C}_6\text{H}_5\text{COO}^- = 1.6 \times 10^{-10}$).
- Calculate the $[\text{OH}^-]$ in a 0.20 M calcium acetate solution.

DATA: $x = [\text{OH}^-] = ?$

$$K_b \text{ of } \text{C}_6\text{H}_5\text{COO}^- = 1.6 \times 10^{-10}$$

$[\text{WB}]_{\text{mixed}} = [\text{C}_6\text{H}_5\text{COO}^-] = 0.10 \text{ M}$ based on the *REC* steps above,

SOLVE: WANT: $[\text{OH}^-] = x = ?$ Solving the K_b approximation:

$$x^2 = K_b \cdot [\text{WB}] = K_b \cdot [\text{C}_6\text{H}_5\text{COO}^-] = (1.6 \times 10^{-10}) (0.10) = 1.6 \times 10^{-11}$$

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

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

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 $[\text{OH}^-]$, one option is to find pOH then use $\text{pH} + \text{pOH} = 14.00$ at 25°C

$$\text{pOH} = -\log [\text{OH}^-] = -\log(4.0 \times 10^{-6}) = 5.4 = 5.40 \quad (\text{estimate, then calculate.})$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.40 = 8.60, \text{ which is a mildly basic pH, as expected.}$$

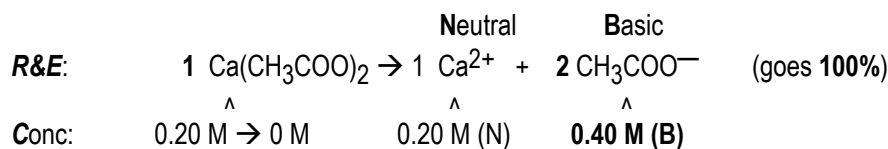
3. WANT: $[\text{OH}^-]$

DATA: 0.20 M calcium acetate = 0.20 M $\text{Ca}(\text{CH}_3\text{COO})_2$

Analysis: $\text{Ca}(\text{CH}_3\text{COO})_2$ is a salt. Acetates (except silver acetate) are soluble in water.

To find pH (or $[\text{H}^+]$ or $[\text{OH}^-]$) 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.



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: $[\text{OH}^-]$

R and E specific: $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$ (goes slightly)
 (K_b reactions have base on left and OH^- + acid conjugate on right.)

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

Conc. at Eq: $[\text{WB}]_{\text{mixed}} - x$ x x

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

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

DATA: $x = [\text{OH}^-] = ? = [\text{CH}_3\text{COOH}]$

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

$$\boxed{K_w = K_b \times K_a}, K_b = \frac{K_w}{K_a \text{ of } \text{CH}_3\text{COOH}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$K_b \text{ for } \text{CH}_3\text{COO}^- = 5.6 \times 10^{-10}$$

$$[\text{WB}]_{\text{mixed}} = \text{from the REC steps: } \boxed{[\text{CH}_3\text{COO}^-] = 0.40 \text{ M}}$$

SOLVE: WANT: $[\text{OH}^-] = x = ?$

Solving the K_b approximation for the WANTED symbol:

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

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

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

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

* * * * *

Lesson 30D: 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 28G 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 29B: HPO_4^{2-} HSO_4^- 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.

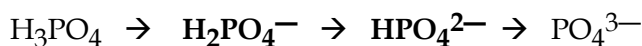
Examples: Sulfuric acid forms one amphoteric ion: the hydrogen sulfate ion.



The HSO_4^- ion can react as an acid with a base, or as a base with an acid:



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



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 acid conjugate using $K_w = K_a \times K_b$

Use those rules and the acid-strength table in Lesson 29B on the following problem.

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

- What is the K_a value for HCO_3^- ?
- What is the K_b value for HCO_3^- ?
- 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. $K_a = 5.6 \times 10^{-11}$

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

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

$$K_b = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 0.23 \times 10^{-7} = 2.3 \times 10^{-8} = K_b$$

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 29B or a textbook to answer these.

- Which of these are amphoteric particles?
 - HSO_3^-
 - NH_4^+
 - H_2PO_4^-
 - H_2SO_4
 - PO_4^{3-}
 - H_2O
- 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^- ?
- 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).
- Will a solution of K_2HPO_4 be acidic (A), basic (B), or neutral (N)?
- For citric acid, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$, $K_{a1} = 7.1 \times 10^{-4}$, $K_{a2} = 1.7 \times 10^{-5}$, and $K_{a3} = 4.0 \times 10^{-7}$. Will a solution of $\text{NaH}_2\text{C}_6\text{H}_5\text{O}_7$ be acidic or basic?

ANSWERS

- 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 base conjugate. Its base conjugate is SO_3^{2-} , with $K_b = 6.0 \times 10^{-8}$.

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

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

Quick check: $K_b \times K_a$ must estimate to $= K_w = 10.0 \times 10^{-15}$ 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 $\boxed{6.3 \times 10^{-8}}$

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

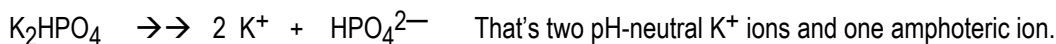
Find the K_a of that acid conjugate in the acid-strength table: 7.2×10^{-3}

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

$$\text{SOLVE: } K_b = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-3}} = \boxed{1.4 \times 10^{-12} = K_b \text{ for } \text{H}_2\text{PO}_4^-}$$

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.



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 $\boxed{4.2 \times 10^{-13}}$

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

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

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

$$\text{SOLVE: } K_b = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-8}} = \boxed{1.6 \times 10^{-7} = K_b \text{ for } \text{HPO}_4^{2-}}$$

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

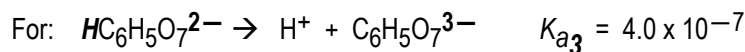
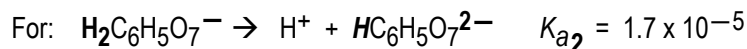
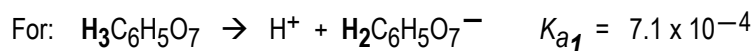
5. For ionic compounds dissolving in water, write the reaction for the ions separating.



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 $\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$ 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 $\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$ acting as an acid, $K_a = 1.7 \times 10^{-5}$

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 acid conjugate and $K_a \times K_b = 1.0 \times 10^{-14}$

The acid conjugate of $\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$ is $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ with a $K_{a1} = 7.1 \times 10^{-4}$

$$\text{SOLVE: } K_b = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{7.1 \times 10^{-4}} = 1.3 \times 10^{-11} = K_b \text{ for } \text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$$

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

* * * * *

SUMMARY – pH of Salts

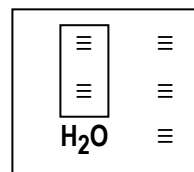
1. In salt solutions, for ions that are *not* amphoteric:

Neutral ions 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^- .

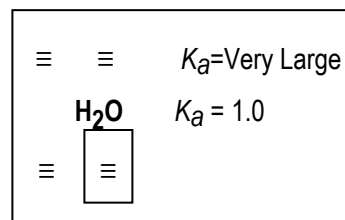
Acidic ions are

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



Basic ions are

- Base conjugates of acids *below* $K_a = 1.0$; bases below H_2O as base OR with a K_b larger than 1.0×10^{-14} .
- include F^- , CN^- , CH_3COO^- , $\text{C}_6\text{H}_5\text{COO}^-$.



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, $\text{pH} \approx 7$.
 - One ion is *acidic*, and the other is *neutral*, solution will be *acidic* ($\text{pH} < 7$).
 - One is *basic*, and the other is *neutral*, solution will be *basic* ($\text{pH} > 7$).
 - 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.
7. **The Quick 5% Test** to see if an approximation equation provides acceptable results.
 - Using *scientific notation*, compare $[\text{WA}]$ to $[\text{H}^+] = x$ or $[\text{WB}]$ to $[\text{OH}^-] = x$.
 - 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.

#

Module 31 — Buffers

Prerequisites: Complete Modules 27, 28, and 30 before starting this module.

Lesson 31A: 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.

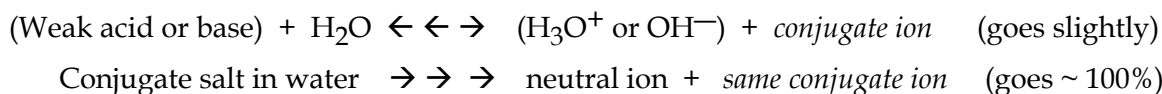
Common-Ion Buffers

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 ion* 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:



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

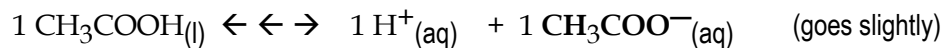
How Buffers Differ From Weak Acid or Weak Base Solutions

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.



In 0.10 M acetic acid, $[\text{CH}_3\text{COOH}] \approx 0.10 \text{ M}$ and $[\text{CH}_3\text{COO}^-] = 0.0013 \text{ M}$

In a *buffer* solution that contains 0.10 M acetic acid *and* 0.10 M acetate ions, $[\text{CH}_3\text{COOH}] \approx 0.10 \text{ M}$ and $[\text{CH}_3\text{COO}^-] \approx 0.10 \text{ M}$

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.

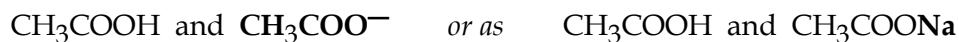
For example, in the conjugate pair HSO_4^- and SO_4^{2-} , both particles are ions.

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



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 29B).
- 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 acid-base conjugate pair.

Using the acid-strength table in Lesson 29B if needed, apply those rules to this problem.

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

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Answer: The base conjugate 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 29B as needed.

- Write the formula for the conjugates of
 - NH_4^+
 - HNO_3
 - F^-
 - HCO_3^- acting as a base
 - HCO_3^- acting as an acid
- Write the formula for an *ion* that would buffer solutions of these particles.
 - C_6H_5COOH
 - HCN
- Write the formula for a *compound* that would buffer solutions of these particles.
 - $C_6H_5COO^-$
 - CH_3COOH
- Answer the following questions using these letters. Each question may have multiple letters for its answer.
 - KF
 - NH_4NO_3
 - NH_3
 - NaCN
 - NH_4Cl
 - Which compound(s) above will serve as a common-ion buffer for an HF solution?
 - Which compound(s) above will serve as a common-ion buffer for NH_3 solution?
 - Which compound(s) will form a buffer if mixed into an NH_4Cl solution?

ANSWERS

- 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-} .
- a. $\text{C}_6\text{H}_5\text{COO}^-$ is an ion. Since it is also the base conjugate of the acid, it will buffer the solution.
b. CN^- is the base conjugate of the acid HCN ; it buffers an HCN solution.
- a. The acid-strength table shows that $\text{C}_6\text{H}_5\text{COO}^-$ is the base conjugate of $\text{C}_6\text{H}_5\text{COOH}$. A buffer is a mixture of an acid-base conjugate pair, so $\text{C}_6\text{H}_5\text{COOH}$ buffers $\text{C}_6\text{H}_5\text{COO}^-$.
b. The acid-strength table shows that for CH_3COOH , CH_3COO^- is the base conjugate 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 $(\text{CH}_3\text{COO})_2\text{Mg}$. (Except for silver acetate, metal-acetate combinations are soluble).
- i. (a). KF is a soluble salt with pH-neutral ion K^+ and basic F^- . F^- is the base conjugate 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 31B: 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 *base conjugate* 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.

- 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.

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

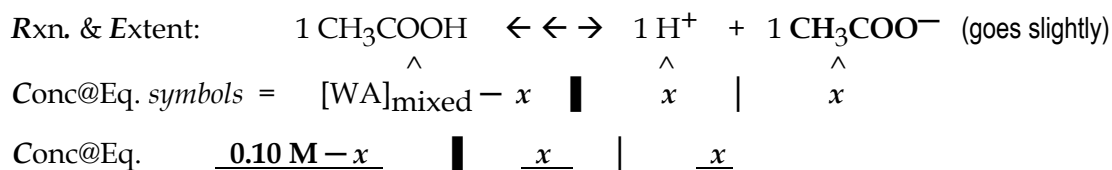
$$[\text{CH}_3\text{COOH}]_{\text{as mixed}} = \mathbf{0.10\ M} \quad \text{and} \quad [\text{CH}_3\text{COONa}]_{\text{as mixed}} = \mathbf{0.20\ mol/L}$$

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.

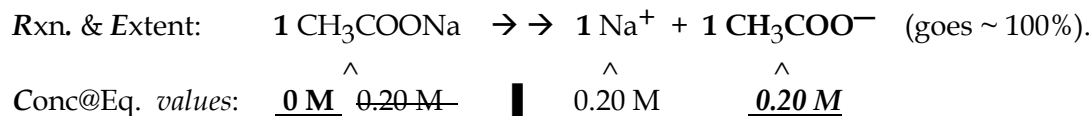
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For the weak acid:



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

For the salt:



The actual $[\text{CH}_3\text{COONa}] = 0\ \text{M}$, 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 base conjugate of the weak acid CH_3COOH . This solution is a buffer because it combines substantial amounts of both a weak acid and its base conjugate. CH_3COO^- is a *common ion* because it is formed in both reactions above that occur in the solution.

Ion Concentrations In Buffers

Adding the *numbers* and *x*'s underlined in the two “concentration 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>
$[\text{CH}_3\text{COOH}]_{\text{at eq.}} = [\text{WA}]_{\text{eq.}}$	= _____	≈ _____
$[\text{H}^+]_{\text{at equilibrium}}$	= _____	≈ _____
$[\text{CH}_3\text{COO}^-]_{\text{at eq.}} = [\text{BC}]_{\text{eq.}}$	= _____	≈ _____

* * * * *

Totals in the buffer solution are	Exact	Approx.	Approx. Symbol
$[\text{CH}_3\text{COOH}]_{\text{at eq.}} = [\text{WA}]_{\text{eq.}}$	$= 0.10 \text{ M} - x$	$\approx 0.10 \text{ M}$	$=$ _____
$[\text{H}^+]_{\text{at equilibrium}}$	$= x$	$\approx x$	
$[\text{CH}_3\text{COO}^-]_{\text{at eq.}} = [\text{BC}]_{\text{eq.}}$	$= x + 0.20 \text{ M}$	$\approx 0.20 \text{ M}$	$=$ _____

The [BC] 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 BC concentrations used in point 2 above, in the two *blanks* above, write what you think is an appropriate symbol for each approximate concentration.

* * * * *

$$[\text{CH}_3\text{COOH}]_{\text{at eq.}} = [\text{WA}]_{\text{eq.}} = 0.10 \text{ M} - x \approx 0.10 \text{ M} = [\text{WA}]_{\text{as mixed}}$$

$$[\text{CH}_3\text{COO}^-]_{\text{at eq.}} = [\text{BC}]_{\text{eq.}} = 0.20 \text{ M} + x \approx 0.20 \text{ M} = [\text{BC}]_{\text{as mixed}}$$

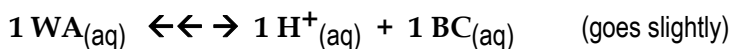
To summarize:

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

The Buffer Equations

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

For a weak acid alone, the reaction that occurs is



and the K equation that governs the reaction is:

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

\wedge Definition \wedge Exact \wedge Approximation

After base conjugate 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 $[\text{H}^+]$ 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

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

\wedge Definition \wedge Exact \wedge 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 *Conc@Eq. approximate* data in the totals table above, plus the K_a for $CH_3COOH = 1.8 \times 10^{-5}$.

* * * * *

$$K_a \approx \frac{x \cdot [BC]_{\text{mixed}}}{[WA]_{\text{mixed}}}$$

DATA: $K_a = 1.8 \times 10^{-5}$
 $x = [H^+] = ?$
 $[BC]_{\text{mixed}} = 0.20 \text{ M}$
 $[WA]_{\text{mixed}} = 0.10 \text{ M}$

SOLVE:

* * * * *

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

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: $x = [H^+] = 9.0 \times 10^{-6} \text{ M}$, $[WA] = 0.10 \text{ M} = 1.0 \times 10^{-1} \text{ M}$

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 an acid-base conjugate *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 base conjugate added, with reactions governed by K_a , or
 - A weak base with acid conjugate added, with reactions governed by K_b .

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

3. For a buffer, the K_a ratios are

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

\wedge Definition \wedge Exact \wedge Approximate

In the buffer equations, $x = [\text{H}^+] = \text{small}$, but $[\text{WA}]$ and $[\text{BC}]$ are large and often differ.

4. In a buffer solution,

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

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

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

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

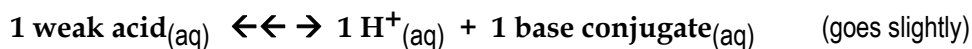
$$[\text{BC}]_{\text{at eq.}} \approx [\text{BC}]_{\text{mixed}} \text{ or } [\text{BC}]_{\text{added}} \text{ or } [\text{BC}] \text{ or } [\text{base}]$$

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

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

Practice

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



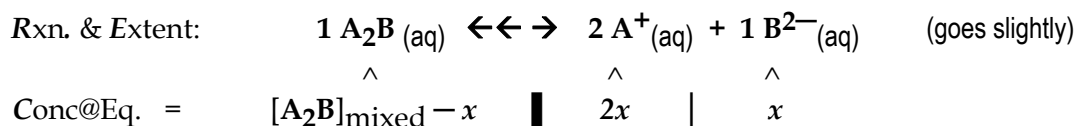
The K definition and exact equations for that reaction are

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

\wedge Definition \wedge Exact \wedge Approximation

- a. Modify the *exact* equation above to reflect the changes when base conjugate 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.



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

ANSWERS

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

^Definition ^ Exact ^ Approximation

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

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

3. In the weak acid approximation equation, $[\text{H}^+] = [\text{BC}]$

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

$$4. \quad K \equiv \frac{[\text{A}^+]_{\text{eq.}}^2 [\text{B}^{2-}]_{\text{eq.}}}{[\text{A}_2\text{B}]_{\text{eq.}}} \equiv \frac{(2x)^2 \bullet x}{[\text{A}_2\text{B}]_{\text{mixed}} - x} \quad \text{or} \quad \frac{4x^2 \bullet x}{[\text{A}_2\text{B}]_{\text{mixed}} - x}$$

^Definition ^ Exact

$$5. \quad K \equiv \frac{[\text{A}^+]_{\text{eq.}}^2 [\text{B}^{2-}]_{\text{eq.}}}{[\text{A}_2\text{B}]_{\text{eq.}}} \equiv \frac{(2x)^2 \bullet (x + [\text{B}^{2-}] \text{ as mixed})}{[\text{A}_2\text{B}]_{\text{mixed}} - x} \approx \frac{4x^2 \bullet [\text{B}^{2-} \text{ mixed}]}{[\text{A}_2\text{B}]_{\text{mixed}}}$$

^Definition ^ Exact ^ Approximate

* * * * *

Lesson 31C: 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** = _____ **BC formula** = _____
 mol or $[WA]_{mixed}$ = _____ mol or $[BC]_{mixed}$ = _____

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

The two formulas, WA and BC, 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** = _____ **BC formula** = _____
 mol or $[WA]_{mixed}$ = _____ mol or $[BC]_{mixed}$ = _____

* * * * *

Buffer Chart: **WA formula** = **HF** **BC formula** = **F^-**
 mol or $[WA]_{mixed}$ = **0.10 M HF** mol or $[BC]_{mixed}$ = **0.20 M F^-**

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

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 NO₃ NH₄**

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.

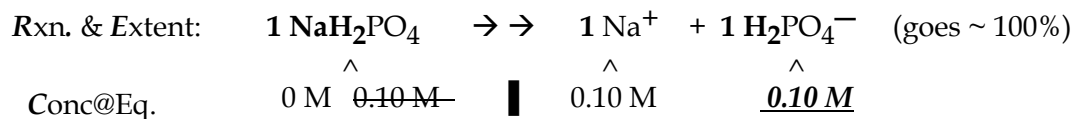
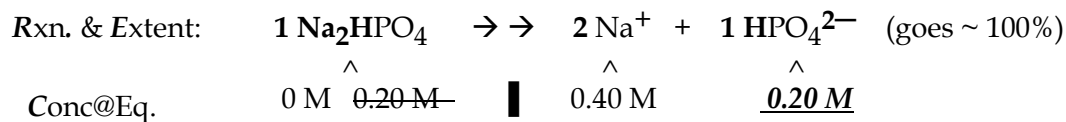
The rule is: If you cannot fill in a buffer chart by inspection, *REC* the salt(s).

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 *two* reactions are



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,



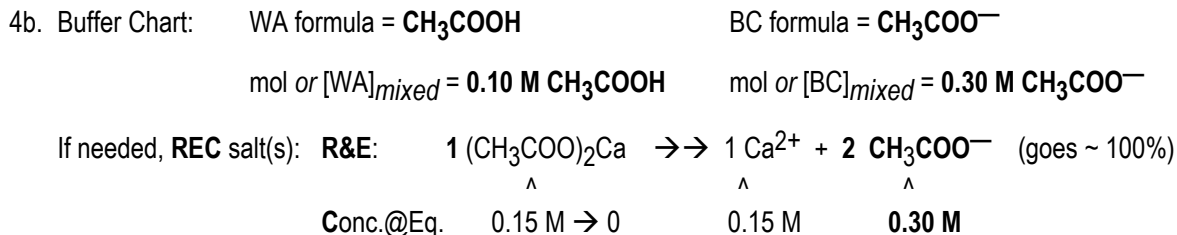
Practice: Try to solve these by inspection first, but if you are not certain of your answer, REC the salt(s) and/or consult the acid-strength table in Lesson 29B.

- From the list of ions below, write the formula(s) for the ions that are
 - pH-neutral
 - Acidic
 - Always result in a compound containing the ion to be soluble.

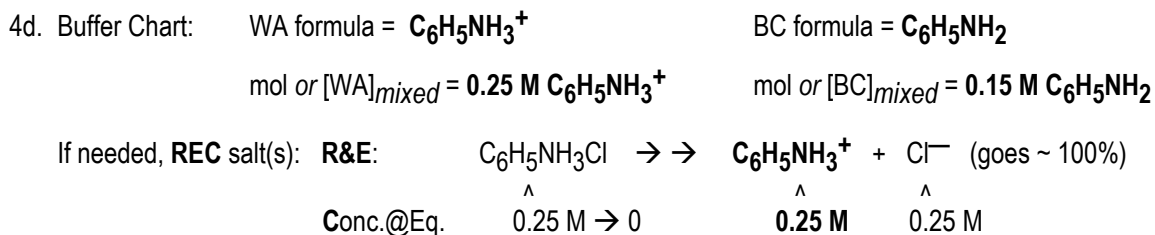
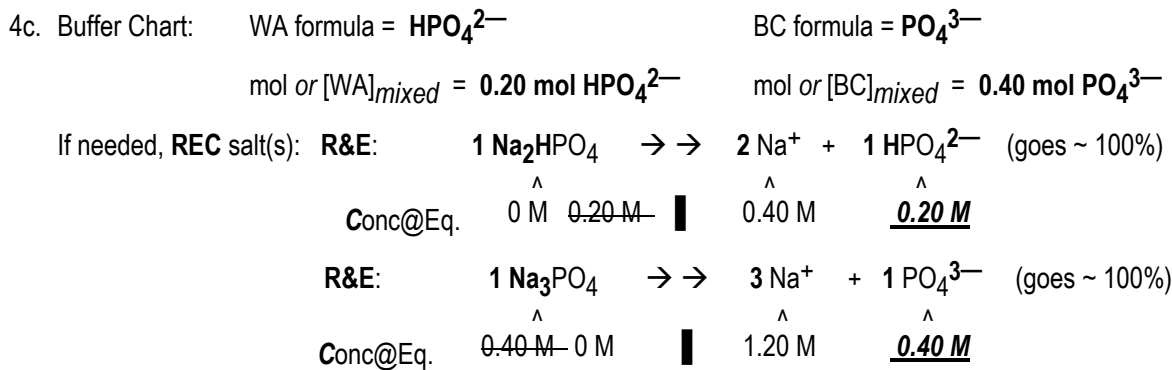
(1) Na^+ (2) NO_3^- (3) NH_4^+ (4) Cl^- (5) K^+
- The following pairs of compounds can be mixed to make aqueous buffer solutions. Circle the compounds that are soluble salts.
 - NaF and HF
 - HCN and KCN
 - NH_3 and NH_4Br
 - $\text{C}_6\text{H}_5\text{COOH}$ and $\text{C}_6\text{H}_5\text{COOK}$
 - NaHCO_3 and Na_2CO_3
- For each of the following buffer solutions, write and fill in this *first line* of the buffer chart.

Weak acid (WA) formula = _____ Base conjugate (BC) formula = _____

 - 0.20 M CN^- and 0.40 M HCN
 - 0.10 M NaHCO_3 and 0.20 M Na_2CO_3
- For each of the following buffer solutions, write and fill in a complete *buffer chart*.
 - 0.25 M NH_3 and 0.30 M NH_4Cl



$(\text{CH}_3\text{COO})_2\text{Ca}$ 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.



* * * * *

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

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

\wedge Definition \wedge Exact \wedge Approximation

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

WANT: $[\text{H}^+] = x$

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

5. % Dissociation quick check: $x = [\text{H}^+] = 3.4 \times 10^{-8} \text{ M}$, $[\text{WA}] = 0.10 \text{ M} = 1.0 \times 10^{-1} \text{ M}$
 The exponent difference is 3 or greater; so dissociation is < 5% and the approximation may be used.

Practice B

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

* * * * *

Lesson 31E: 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* $K_a \approx \frac{[\text{H}^+][\text{BC}]_{\text{mixed}}}{[\text{WA}]_{\text{mixed}}}$ 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 $[\text{H}^+]$.
(K_a of HCN = 6.2×10^{-10}).

* * * * *

Answer

1. WANT: $[\text{H}^+]$
2. **Buffer Chart:** WA formula = HCN BC formula = CN^-
mol or $[\text{WA}]_{\text{mixed}} = 0.50 \text{ M HCN}$ mol or $[\text{BC}]_{\text{mixed}} = 0.25 \text{ M CN}^-$
3. SOLVE: $K_a \approx \frac{[\text{H}^+][\text{BC}]_{\text{mixed}}}{[\text{WA}]_{\text{mixed}}} \approx 6.2 \times 10^{-10} \approx \frac{[\text{H}^+](0.25 \text{ M})}{0.50 \text{ M}};$
$$[\text{H}^+] = \frac{6.2 \times 10^{-10} (0.50)}{0.25} = 1.2 \times 10^{-9} \text{ M} = [\text{H}^+]$$

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 $C_6H_5COOH = 6.3 \times 10^{-5}$).
2. Find $[H^+]$ in a mixture of 0.10 M $NaOCN$ and 0.20 M $HOCN$ (K_a $HOCN = 3.5 \times 10^{-4}$)

Buffer Calculations Based On Moles

The buffer approximation equation can be written as

$$K_a \approx [H^+] \cdot \frac{[BC]_{\text{as mixed}}}{[WA]_{\text{mixed}}}$$

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.

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

This converts the buffer approximation to the form

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

For most buffer calculations, the data for WA and BC is supplied in moles/liter, but the buffer approximation can be solved if the WA and BC 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 $[WA_{\text{mixed}}]$ and $[BC_{\text{mixed}}]$: one is no more than 10 times the other. In the buffer approximation equation, this means that the fraction $[BC]/[WA]$ has a value of between 1/10 and 10.

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

This result means that

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

For example, in the previous calculation, $K_a = 6.2 \times 10^{-5}$; $[H^+] = 1.2 \times 10^{-9}$ M

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

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 $[\text{CH}_3\text{COONa}]$? (K_a for CH_3COOH = 1.8×10^{-5})

ANSWERS

Practice A

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

2. **Buffer Chart:** WA formula = $\text{C}_6\text{H}_5\text{COOH}$

BC formula = $\text{C}_6\text{H}_5\text{COO}^-$

mol or $[\text{WA}]_{\text{mixed}} = 0.60 \text{ M } \text{C}_6\text{H}_5\text{COOH}$ mol or $[\text{BC}]_{\text{mixed}} = 0.40 \text{ M } \text{C}_6\text{H}_5\text{COO}^-$

3. Solve the buffer approximation:

$$K_a \approx \frac{[\text{H}^+][\text{BC}]_{\text{mixed}}}{[\text{WA}]_{\text{mixed}}}$$

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

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

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

2. **Buffer Chart:** WA formula = HOCN

BC formula = OCN^-

mol or $[\text{WA}]_{\text{mixed}} = 0.20 \text{ M HOCN}$ mol or $[\text{BC}]_{\text{mixed}} = 0.10 \text{ M } \text{OCN}^-$

3. Solve the buffer approximation:

$$K_a \approx \frac{[\text{H}^+][\text{BC}]_{\text{mixed}}}{[\text{WA}]_{\text{mixed}}}$$

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

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

Practice B

1a. In problem 2, $K_a = 6.8 \times 10^{-4}$, so $[\text{H}^+]$ must end in "x $10^{-3,4,\text{or } 5}$ " by the check rule.

1b. In problem 3, $K_a = 2.3 \times 10^{-9}$, so $[\text{H}^+]$ must end in "x $10^{-8,9,\text{or } 10}$ " by the check rule.

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

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

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

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

2. **Buffer Chart:** **WA formula** = HOBr **BC formula** = OBr⁻
 mol or $[WA]_{mixed}$ = **0.50 M** HOBr mol or $[BC]_{mixed}$ = **0.25 M** OBr⁻

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

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

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

4. 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^+ **BC formula** = NH_3
 mol or $[WA]_{mixed}$ = **0.75 M** NH_4^+ mol or $[BC]_{mixed}$ = **0.25 M** NH_3

If needed, REC the salt:
$$\begin{array}{ccccccc} 1 \text{ NH}_4\text{Cl} & \rightarrow \rightarrow & 1 \text{ NH}_4^+ & + & 1 \text{ Cl}^- & & (\text{separates } \sim 100\%). \\ \text{0 M} & \text{0.75 M} & \text{0.75 M} & & \text{0.75 M} & & \end{array}$$

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

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

$$? = K_a \text{ NH}_4^+ = \frac{1.0 \times 10^{-14}}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = K_a \text{ of NH}_4^+$$

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

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

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

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

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

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

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

1. WANT: $[H^+]$

2. Buffer Chart:

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

3. Solve the buffer approximation that uses moles:

$$K_a \approx \frac{[H^+] \text{ (moles of base)}}{\text{moles of acid}}$$

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

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 $[BC]$ may no longer be true.

6. 1. WANTED: $[CH_3COONa] = [BC]_{mixed}$ (write specific and general *symbols* WANTED)

DATA: pH = 5.00

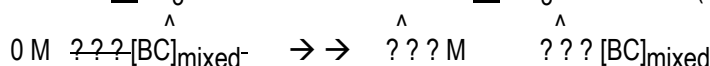
$$\boxed{\text{pH prompt: } pH \equiv -\log [H^+] \text{ and } [H^+] = 10^{-pH}}$$

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

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

Strategy: A weak acid (CH_3COOH) and a salt with its conjugate ion = buffer solution.To find the original salt concentration, find the $[BC]$ as mixed into the solution.To find $[BC \text{ mixed}]$, use the buffer steps .

2. Buffer Chart:

WA formula = CH_3COOH **BC formula** = CH_3COO^- $[WA]_{mixed}$ = **0.10 M CH_3COOH** $[BC]_{mixed}$ = **?? M $C_6H_5COO^-$** **REC** the salt: $\frac{1}{0} CH_3COONa \rightarrow \rightarrow 1 Na^+ + \frac{1}{??} CH_3COO^-$ (separates ~100%).

* * * * *

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

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

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

REC the salt: $\frac{1}{0} CH_3COONa \rightarrow \rightarrow 1 Na^+ + \frac{1}{0.18} CH_3COO^-$ (separates ~100%).

$$0 \text{ M } \overset{\wedge}{0.18 \text{ M}} \rightarrow \rightarrow 0.18 \text{ M } \overset{\wedge}{0.18 \text{ M}}$$

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

Lesson 31F: 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

$$K_a \approx [H^+] \cdot \frac{[BC]_{\text{as mixed}}}{[WA]_{\text{mixed}}}$$

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

$$-\log(K_a) \approx -\log[H^+] - \log\left(\frac{[BC]_{\text{mixed}}}{[WA]_{\text{mixed}}}\right)$$

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

$$\text{p}K_a \approx \text{pH} - \log\left(\frac{[BC]_{\text{mixed}}}{[WA]_{\text{mixed}}}\right)$$

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

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

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

since $[BC] = [\text{base}]$
and $[WA] = [\text{acid}]$ 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.
($K_a \text{ CH}_3\text{COOH} = 1.8 \times 10^{-5}$)

★ ★ ★ ★ ★

Answer

1. WANTED = pH of a buffer.
2. **Buffer Chart:** WA formula = CH₃COOH BC formula = CH₃COO⁻
 $[WA]_{mixed} = 0.30 \text{ M CH}_3\text{COOH}$ $[BC]_{mixed} = 0.20 \text{ M CH}_3\text{COO}^-$
3. $\text{pH} \approx \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = -\log(1.8 \times 10^{-5}) + \log(0.20/0.30)$
 $= -(-4.74) + \log(0.67) = 4.74 - 0.18 = \boxed{4.56 = \text{pH}}$
 (To review taking logs with a calculator, see Lesson 25D).

Practice A:

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

1. If $X = 2.0 \times 10^{-12}$, $\text{p}X = ?$
2. If $K_a = 4.5 \times 10^{-7}$, $\text{p}K_a = ?$
3. If $\text{p}K_a = 5.50$, $K_a = ?$
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

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

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.

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

This converts the Henderson-Hasselbalch equation to the form

$$\text{pH} \approx \text{p}K_a + \log(\text{mol base} / \text{mol acid})$$

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,

- Fill in the *buffer chart* for moles or mol/L .
- Solve the **Henderson-Hasselbalch** equation using the *buffer chart* values and either

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

$$\text{or } \text{pH} \approx \text{p}K_a + \log (\text{mol base} / \text{mol acid})$$

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,

- If [acid] = [base], or moles acid = moles base, then $\text{pH} \approx \text{p}K_a$.**

Why? If *base/acid* in moles or mol/L = 1, then $\log(1) = \log(10^0) = 0$, and the Henderson-Hasselbalch equation becomes $\text{pH} \approx \text{p}K_a + \underline{0} \approx \text{p}K_a$

- 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.

- In buffer solutions, the **pH will be close to the $\text{p}K_a$.**

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 $\text{p}K_a$ and pH is smaller: ± 0.3 .

Adding those numbers to the $\text{p}K_a$ 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 .

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

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

$$\text{pH} \approx \text{p}K_a + \log ([\text{base}]/[\text{acid}])$$
 or

$$\text{pH} \approx \text{p}K_a + \log (\text{mol base} / \text{mol acid})$$
4. In a buffer, if *either* $[\text{WA}] = [\text{BC}]$ **or** *moles* WA = *moles* BC, then $[\text{H}^+] \approx K_a$ and $\text{pH} \approx \text{p}K_a$.
5. For a given conjugate pair in different buffer solutions, if the ratio $[\text{base}]/[\text{acid}]$ **or** mol base/mol acid is the *same*, the pH is the same, and $[\text{H}^+]$ 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 $\text{pH} = \text{p}K_a$?
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 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 in 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 $\text{NH}_3 = 1.8 \times 10^{-5}$)
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 $K_{a2} = 5.6 \times 10^{-11}$.

ANSWERS**Practice A**

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

The prefix **p** is an abbreviation for the function $-\log$.

$$? = K_a \text{ NH}_4^+ = \frac{1.0 \times 10^{-14}}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = K_a \text{ NH}_4^+$$

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

Check: K_a of $\text{NH}_4^+ = 5.6 \times 10^{-10}$, 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:** WA formula = HCO_3^- BC formula = CO_3^{2-}
 mol or $[\text{WA}]_{\text{mixed}} = 0.40 \text{ M HCO}_3^-$ mol or $[\text{BC}]_{\text{mixed}} = 0.30 \text{ M CO}_3^{2-}$

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: $K_{a2} = 5.6 \times 10^{-11}$ (see Lesson 28G on polyprotic acids).

$$\begin{aligned} \text{pH} &\approx \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = -\log(5.6 \times 10^{-11}) + \log(0.30 / 0.40) \\ &= -(-10.25) + \log(0.75) = 10.25 + (-0.12) = \boxed{10.13 = \text{pH}} \end{aligned}$$

Check: K_a of $\text{HCO}_3^- = 5.6 \times 10^{-11}$, pH should be between 9 and 13.

* * * * *

SUMMARY – Buffers

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 $[\text{H}^+]$, the methodical steps are:
 1. Fill in the buffer chart. If needed, *REC* the *salt(s)*.
 2. *WRECK* the WA ionization, then add [BC 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** = _____ **BC formula** = _____
 mol or $[WA]_{mixed}$ = _____ mol or $[BC]_{mixed}$ = _____

3. Write and solve the buffer approximation:

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

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:

$$pH \approx pK_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right)$$

$$\text{or } pH \approx pK_a + \log (\text{mol base} / \text{mol acid})$$

5. In a buffer, if *either* $[WA] = [BC]$ **or** *moles* WA = *moles* BC, then

$$[H^+] \approx K_a \text{ and } pH \approx pK_a.$$

6. For a given conjugate pair in different buffer solutions, if $[\text{base}]/[\text{acid}]$ **or** mol base/mol acid is the *same*, **pH** and $[H^+]$ in the solutions is the *same*.

7. Summary of check rules

- In aqueous solutions, $[H^+] \times [OH^-]$ must = $K_w = 10.0 \times 10^{-15}$ or 1.0×10^{-14} .
- In conjugate pairs, $K_b \times K_a$ must estimate to = $K_w = 10.0 \times 10^{-15}$ or 1.0×10^{-14} .
- 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.
- 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.
- 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 of the K_a .

#

Module 32 — pH During Titration

Prerequisites: Complete Module 31 before starting this module.

* * * * *

Lesson 32A: 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

- *Strong* acids and bases and *weak* acids and bases;
- Polyprotic acids;
- Salts with ions that are acidic, basic, or amphoteric; and
- A mixture of acid-base conjugates (a buffer).

These types of calculations have components in common, but their steps are not the same. During tests on acids and bases, it will be necessary to identify what *type* a problem is, then to apply the steps needed to solve that type of problem. A summary can help 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. Strong acids or hydroxide bases, use the *REC* steps based on ~100% ionization.
or quick steps: $[HCl \text{ or } HNO_3]_{\text{mixed}} = [H^+]$ 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 $K_a \times K_b = 1.0 \times 10^{-14}$
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 A, B, or N, *WRRECK* the A or B ion.
7. Buffer solutions:
 - Treat as a weak acid with base conjugate added.
 - Complete the buffer chart.
 - Solve the buffer approximation or the H-H equation using mol or mol/L WA and BC as mixed.

Practice A

For aqueous solutions of the following,

- | | | | | |
|---------------|-----------------------------------|--------------------|-------------------------|-----------------------|
| 1. NaF and HF | 2. NaCN | 3. NH ₃ | 4. CH ₃ COOH | 5. NaHCO ₃ |
| 6. KCl | 7. H ₂ CO ₃ | 8. KOH | 9. NH ₄ Cl | 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.

For several other types of *mixtures* at equilibrium, the [H⁺], [OH⁻], and pH are relatively easy to determine. For the purpose of discussing calculations for mixtures of acids and bases, we will adopt the following vocabulary:

- The *opposite* of an acid will mean a base, and the *opposite* of a base will mean an acid.
- *Strong* acids and bases are 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 29B).

The rules for finding pH for mixtures of *one* or *two* acids or bases include the following.

1. 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, and the mixture cannot 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.

2. 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.
 - First label each particle in the mixture as acid or base, strong or weak, or neutral.
 - Then solve for the pH as determined by the pH-*dominant* particle.

3. Specifically, apply these steps *in order* to determine the pH in a solution with *one* or *two* acidic or basic particles.
- Re-write formulas for soluble ionic solids (salts) in their *separated-ions* format.
 - 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 defined vocabulary 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.
 - If all particles in a mixture are pH neutral, solution pH = 7 .
 - 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.
 - If the mixture contains a *strong* acid or base, its concentration determines the pH.
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 $[\text{H}^+]$ in solutions containing *strong* acids or bases, either write the *REC* steps for 100% ionization *or* use the quick steps:
$$[\text{HCl or HNO}_3]_{\text{mixed}} = [\text{H}^+]_{\text{in soln.}} \quad \text{and} \quad [\text{NaOH or KOH}] = [\text{OH}^-]_{\text{in soln.}}$$
 - If a weak acid or base *and* its conjugate are present in substantial amounts, the solution is a buffer. Use the buffer chart and Henderson-Hasselbalch equation to find the pH.
 - If the only non-pH-neutral particle present is a *weak* acid or base, its K_a or K_b determines the pH. Use the K_a or K_b approximation and 5% test to determine pH.

Summary: Steps For Calculating pH in a Mixture

Apply in this order.

- Re-write soluble salts as separated ions.
- Label each particle in the mixture as SA, SB, WA, WB, or N.
- Ignore pH-neutral (N) particles if mixed with acidic or basic particles.
- If all particles are N, pH = pH of water = 7.
- If SA or SB is present, ignore other particles. Find pH based on quick steps:
$$[\text{HCl or HNO}_3] = [\text{H}^+] \quad \text{and} \quad [\text{NaOH or KOH}] = [\text{OH}^-]$$
- If a WA or WB *and* its conjugate is present, solve a buffer chart and the Henderson-Hasselbalch equation in moles or mol/L.
- If only *one* WA or WB is present, use K_a or K_b approximation, then the 5% test.

The logic of the rules is:

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

Practice B: Commit the steps in the summary above firmly to memory. Write the steps, then apply the steps to these problems. Save a few for your next practice session.

- For each mixture a-d below,
 - List the particles present in the solution in significant concentration.
 - Label each particle as acid (A), basic (B), or pH-neutral (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 mixture of 0.40 M NH_4Cl , 0.10 M NaCl , and 0.20 M HCl .
 - 0.50 L of solution containing 0.20 mol KCN , 0.20 mol HCN , and 0.10 mol KCl .
 - A solution containing 0.45 M HF and 0.50 M KCl .
 - 0.20 mol KCl and 0.35 mol KNO_3 dissolved in 75 mL of solution.

Solve these.

- A solution contains 0.350 mol KCl in 120.0 mL of solution. Calculate the solution pH.
 - A solution contains 0.010 M KOH , 0.20 M KF , and 0.10 M KCl . Find the pH.
 - A solution contains 0.0050 moles of KCN and 0.010 mol KCl in 25.0 mL of solution. Calculate the pH. ($K_b \text{CN}^- = 1.6 \times 10^{-5}$).
 - After a reaction, at equilibrium, a solution contains 0.020 mol CH_3COO^- and 0.020 M CH_3COOH . Find the pH. ($K_a \text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$)
-

ANSWERS

Practice A

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

- 1b. The particles present are K^+ CN^- HCN Cl^- Contains a weak acid and its base conjugate. Use step **f**.
N **WB** **WA** **N**
- 1c. The particles present are K^+ HF Cl^- Ignore pH-neutrals. Weak acid determines the pH. Use step **g**.
N **WA** **N**
- 1d. The particles present are K^+ Cl^- NO_3^- All are pH-neutral. Use step **d**.
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^- .
N **SB** **WB** **N**

If one strong particle is present, it determines the pH. Use the quick steps for strong bases.

For this solution: $[SB] = [OH^-] = 0.010 \text{ M} = 1.0 \times 10^{-2} \text{ M}$, $[H^+] = 1.0 \times 10^{-12} \text{ M}$, **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 **K_b** .

See pH? Write $\text{pH} \equiv -\log [H^+]$ and $[H^+] \equiv 10^{-\text{pH}}$ 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.

$$K_b \approx \frac{x^2}{[\text{WB}]_{\text{mixed}}} \quad \text{where } x = [\text{OH}^-]$$

To solve the approximation for $[\text{OH}^-]$, you need $[\text{WB}]_{\text{mixed}} = [\text{KCN}]$ or $[\text{CN}^-]_{\text{mixed}}$ in this problem.

$$? = [\text{WB}]_{\text{mixed}} = \frac{\text{mol } \text{CN}^-}{\text{L soln.}} = \frac{0.0050 \text{ mol } \text{CN}^-}{25.0 \text{ total mL soln.}} \cdot \frac{1 \text{ mL}}{10^{-3} \text{ L}} = \mathbf{0.200 \text{ M } \text{CN}^-}$$

$$K_b \approx \frac{x^2}{[\text{WB}]_{\text{mixed}}} \quad \text{Substituting: } 1.6 \times 10^{-5} \approx \frac{x^2}{\mathbf{0.200 \text{ M } \text{CN}^-}}$$

$$x^2 = (1.6 \times 10^{-5})(0.200) = 0.32 \times 10^{-5} = 3.2 \times 10^{-6}$$

$$x \approx (\text{estimate } 1.2 \times 10^{-3}) \approx \mathbf{1.8 \times 10^{-3} \text{ M} = [\text{OH}^-]} \quad (\text{In } K_b, x = [\text{OH}^-])$$

Quick 5% test: $x = 1.8 \times 10^{-3} \text{ M}$, $[\text{WB}] = 0.20 \text{ M} = 2.0 \times 10^{-1} \text{ M}$

Since the difference in the exponents is 2 or less, do the 5% test:

$$5\% \text{ test} = \frac{x}{[\text{WA or WB}]_{\text{mixed}}} \cdot 100\% = \frac{1.8 \times 10^{-3}}{2.0 \times 10^{-1}} \cdot 10^2\%$$

= **0.90 %**, which is less than 5%, so approximation is OK -- but pH was wanted.

* * * * *

$$\text{pOH} = -\log [\text{OH}^-] = -\log(1.8 \times 10^{-3}) = \mathbf{2.74 = \text{pOH}} \quad \text{pH} = 14.00 - \text{pOH} = \mathbf{11.26 = \text{pH}}$$

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: it is 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 30H).

Buffer Chart: **WA formula** = CH₃COOH **BC formula** = CH₃COO[−]
 mol WA = **0.020 mol** mol BC = **0.020 mol**

Since mol WA = mol BC, the H-H equation: $\text{pH} \approx \text{p}K_a + \log(\text{mol base/mol acid})$ simplifies to

$$\text{pH} \approx \text{p}K_a + \log(1) \approx \text{p}K_a + 0 \approx \text{p}K_a \approx -\log(1.8 \times 10^{-5}) \approx -(-4.74) = \boxed{4.74 = \text{pH}}$$

* * * * *

Lesson 32B: 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 *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: 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*. 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 reaction, if one of the reactants is *strong*, the *moles* of one of the *reactants* must be *zero*.

Using this rule, we complete a *rice moles* table for neutralization, using the same steps that were used in Lessons 10F and 10G 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 Initial row of a *rice moles* table.
3. In the Change 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 End of the reaction (in the *bottom rice* 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/Equilibrium				

* * * * *

- The initial moles of acid and base are known.
- The balanced reaction equation is: $1 \text{ HCl} + 1 \text{ NaOH} \rightarrow 1 \text{ H}_2\text{O} + 1 \text{ NaCl}$ (goes ~100%)
To balance, use the rules in Lesson 14A: acids reacted with hydroxide bases always form water as one product.

* * * * *

Among the rules that apply to *rice* tables in general:

- If a reaction starts with all reactants, the sign in the Change row for the reactants must be negative, since reactant must be used up if there is a reaction.
- In the Change row, the sign of the reactants and products must be opposites: if one is negative, the other must be positive.

- The *ratios* in the Change row and the coefficients must be the same.

(For a *rice* review, see Lesson 10F.)

* * * * *

Reaction	<u>1</u> HCl	1 NaOH	1 H ₂ O	1 NaCl
Initial	0.100 mol	0.080 mol	0 mol	0 mol
Change	− 0.080 mol	− 0.080 mol	+ 0.080 mol	+ 0.080 mol
At End/Equilibrium	+ 0.020 mol	0 mol	+ 0.080 mol	+ 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.

Calculate the pH of the solution mixture above present at the *End* of the reaction.

* * * * *

To begin, label the particles present in the bottom row as SA, SB, WA, WB, or N.

* * * * *

Water and table salt 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.

* * * * *

$$[\text{H}^+]_{\text{in solution}} = [\text{HCl or HNO}_3]_{\text{mixed}}$$

Calculate the [HCl] in the solution at the end of the reaction, then check your answer below.

* * * * *

$$? = [\text{HCl}] = \frac{\text{mol H}^+}{\text{L soln}} = \frac{0.020 \text{ mol HCl}}{120. \text{ mL soln.}} \cdot \frac{1 \text{ mL}}{10^{-3} \text{ L}} = 0.17 \text{ M HCl}$$

To finish, find the pH.

* * * * *

$$[\text{H}^+]_{\text{in solution}} = [\text{HCl or HNO}_3]_{\text{as mixed}} = 0.17 \text{ M}$$

$$? = \text{pH} = -\log [\text{H}^+] = -\log(0.17) = -(-0.77) = \boxed{0.77 = \text{pH}}$$

Practice A: Learn the rules and steps above, *then* try these problems.

- 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, we use the same steps as above.

When dealing with moles/liter and *milliliters*, it is often convenient (but not required) to solve the *rice moles* table in *millimoles*. 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.
- Calculate the millimoles of each reactant.
 - Write the balanced equation for the reaction.
 - Complete the *rice moles* table in millimoles.
 - Find the pH in the mixture after the reaction.

* * * * *

- a. For the HCl calculation, use HCl data.

$$? \text{ mmol HCl} = 50.0 \text{ mL HCl} \cdot \frac{10^{-3} \text{ L}}{1 \text{ mL}} \cdot \frac{0.100 \text{ mol HCl}}{1 \text{ L HCl}} \cdot \frac{1 \text{ mmol}}{10^{-3} \text{ mol}} = 5.00 \text{ mmol HCl}$$

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, in the mmol KF calculation in this problem.

$$? \text{ mmol KF} = 20.0 \text{ mL-KF} \cdot 0.150 \frac{\text{mol}}{\text{L}} = 3.00 \text{ mmol KF}$$

$\uparrow \qquad \qquad \uparrow \qquad \qquad \text{---} \qquad \qquad \uparrow$

This form of unit cancellation works because *milli-* is simply an abbreviation for "times 10^{-3} ." When doing the math, an exponential term is 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 $\text{mmol} = \text{mL} \times (\text{mol/L})$.

The logic is the same: a prefix can be separated from its unit: $\text{mL} \cdot \frac{\text{mol}}{\text{L}} = \text{mmol}$

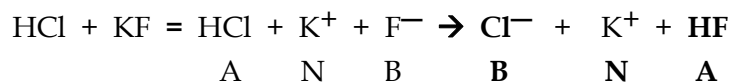
- b. The reactants are HCl + KF →

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: $\text{HCl} + \text{KF} = \text{HCl} + \text{K}^+ + \text{F}^- \rightarrow$

The *products* of the reaction are the conjugates of the acid and base.



The acid-strength table supplies the formulas for the conjugates if needed.

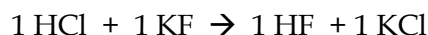
Will this reaction go to the right? Why or why not?

★ ★ ★ ★ ★

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 *Reaction* equation is:



c. If you have not already done so, complete the *rice moles* table using millimoles as units.

★ ★ ★ ★ ★

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 End/Equilibrium	+ 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 $[\text{H}^+]$ overwhelms any others. Find pH based on [HCl].

★ ★ ★ ★ ★

First find the [HCl]. How many moles of HCl are in the solution?

★ ★ ★ ★ ★

$$? \text{ mol HCl} = 2.00 \text{ mmol HCl} = 2.00 \times 10^{-3} \text{ mol HCl} \quad (\text{milli- means " } \times 10^{-3} \text{ "})$$

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 *volumes* of the combined solutions 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 amount 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 amount of water present due to the reaction can nearly always be *ignored* in calculations.

The rule is: When *solutions* are combined, their *volumes 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.

$$? = [\text{HCl}] = \frac{\text{mol H}^+}{\text{L soln}} = \frac{2.00 \times 10^{-3} \text{ mol HCl}}{70.0 \text{ mL soln.}} = \frac{2.00 \times 10^{-3} \text{ mol HCl}}{70.0 \times 10^{-3} \text{ L soln.}} = 0.0286 \text{ M HCl}$$

For *part d*, find the WANTED pH.

* * * * *

Using the quick rule: $[\text{H}^+]_{\text{in solution}} = [\text{HCl or HNO}_3]_{\text{mixed}} = 0.0286 \text{ M}$

$$? = \text{pH} = -\log [\text{H}^+] = -\log(0.0286) = -(-1.54) = \boxed{1.54 = \text{pH}}$$

* * * * *

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 = **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 reactants *before* reaction and 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 is 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: $[HCl \text{ or } HNO_3] = [H^+]$ and $[NaOH \text{ or } KOH] = [OH^-]$
- 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, use K_a or K_b approximation, then the 5% test.

Practice B: Commit the rules summary above to memory, then try these problems.

1. Complete the following *rice moles* table.

Reaction	<u>1</u> HCl	1 NaCN	1 HCN	1 NaCl
Initial	4.50 mmol	3.00 mmol	0 mol	0 mol
Change				
At End/Equilibrium				

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. ($K_a \text{ HF} = 6.8 \times 10^{-4}$)
4. To a solution containing 150. mmol NaOH is added 200. mmol HOBr (hypobromous acid). What is the pH of the solution after the reaction? ($K_a \text{ of HOBr} = 2.8 \times 10^{-9}$).

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 reactants before and pH after. For pH *after* reaction from amounts *before*, the steps are

Reactants > reactant mol > *rice* moles > mixture pH

Reaction	<u>1</u> HCl	1 NaOH	1 H ₂ O	1 NaCl
Initial	0.0250 mol	0.0300 mol	0 mol	0 mol
Change (use +, -)	- 0.0250 mol	- 0.0250 mol	+ 0.0250 mol	+ 0.0250 mol
At End/Equilibrium	0 mol	0.0050 mol	0.0250 mol	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: $[\text{NaOH or KOH}] = [\text{OH}^-]$. Find [NaOH] first.

* * * * *

DATA: 0.0050 mol NaOH in 40.0 mL total volume

$$? = [\text{NaOH}] = \frac{\text{mol NaOH}}{\text{L soln}} = \frac{0.0050 \text{ mol HCl}}{40.0 \text{ mL soln.}} \cdot \frac{1 \text{ mL}}{10^{-3} \text{ L}} = 0.125 \text{ M NaOH} = [\text{OH}^-]$$

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

and $\text{pH} + \text{pOH} = 14.00$

$\text{pOH} = -\log [\text{OH}^-] = -\log (0.125) = 0.90$; $\text{pH} = 14.00 - 0.90 = \mathbf{13.10 = \text{pH}}$

Practice B

1.

Reaction	<u>1</u> 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 End/Equilibrium	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?

* * * * *

$$\approx -(-3.17) + \log(0.67) \approx 3.17 - 0.18 = \boxed{2.99 = \text{pH}}$$

The units in the base/acid ratio of the Henderson-Hasselbalch equation can be M, mol, or mmol, 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. 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	<u>1</u> HOBr	1 NaOH	1 H ₂ O	1 NaOBr
Initial	200. mmol	150. mmol	0	0
Change (use +, -)	- 150. mmol	- 150. mmol	+150. mmol	+ 150. mmol
At End/Equilibrium	50. mmol	0 mmol	150. mmol	150. 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 base conjugate OBr⁻, which makes the solution a buffer. The solution also contains the pH-neutral ions Na⁺ and Cl⁻ 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

BC formula = OBr⁻

moles WA = 50. mmol HOBr

moles BC = 150. mmol OBr⁻

Henderson-Hasselbalch: pH \approx p*K*_a + log (mol base/mol acid)

$$\approx -\log(2.8 \times 10^{-9}) + \log(150. \text{ mmol} / 50. \text{ mmol})$$

$$\approx -(-3.17) + \log(3.0) \approx 3.17 + 0.48 \approx \boxed{3.65 = \text{pH}}$$

* * * * *

Lesson 32C: Distinguishing Types of Acid-Base Calculations

Summary of Acid-Base Problems and Calculations

We have done a wide variety of acid-base calculations. Sometimes it can be difficult to decide *which steps* to apply to a problem. Let's see if we can both summarize the rules for acid-base calculations, and note ways to distinguish the different types of acid-base calculations.

- The K_a and K_b relationships.
 - For acid-base conjugates: $K_w = \boxed{K_a \times K_b = 1.0 \times 10^{-14}}$
 - In water, amphoteric ions will form acidic solutions if their $K_a > K_b$, and basic solutions if $K_b > K_a$.
- If an acid is mixed with a base, will the reaction go? Use either one of two rules.
 - If either the acid or base is strong, the reaction goes to completion (the limiting reactant is ~100% used up).
 - Use the acid-strength table. Equilibrium favors the side with the *weaker* A and B.

pH-neutral particles do not affect the pH of a solution *nor* whether an acid-base reaction will go.
- Calculations of $[\text{H}^+]$ and/or pH can be divided into two types: those for
 - a stable solution: one that is at equilibrium (*not* changing), and
 - acid and base amounts *before* reaction that WANT pH *after* the reaction.

To find $[\text{H}^+]$ or pH, *ask*: is this DATA for a stable solution or a "before and after" reaction calculation?

 - For a *stable* solution, apply the rules for acid-base *mixtures* in step 4 below.
 - For *reaction* calculations, use a *rice moles* table to find what is in the stable solution at the end of the reaction, *then* apply the mixture rules.
- In stable mixtures, to find $[\text{H}^+]$ or pH, apply these rules in this order.
 - Re-write soluble salts as separated ions.
 - Label each particle in the mixture as SA, SB, WA, WB, or N.
 - Ignore pH-neutral (N) particles if they are mixed with other particles.
 - If all particles are N, pH = 7.
 - If SA or SB is present, ignore other particles. Find pH based on *REC* steps for 100% ionization *or* the quick steps:

$$[\text{HCl or HNO}_3] = [\text{H}^+] \quad \text{and} \quad [\text{NaOH or KOH}] = [\text{OH}^-]$$
 - If a WA or WB *and* its conjugate is present, solve a buffer chart and the buffer approximation or Henderson-Hasselbalch equation (in moles or mol/L).
 - If only *one* WA or WB is present, use K_a or K_b approximation, then the 5% test.

5. We have done two types of *reaction* calculations.
- If *given* is an amount of *one* reactant that is 100% used up (the limiting reactant), and WANTED is how much of *one* other reactant will react or *one* other product will form, we solve using the *stoichiometry* steps:

WDBB, units → moles → moles → units

IF one or both of the acid-base reactants is strong, *acid-base* reaction calculations to find an *equivalence point* can be solved by stoichiometry. This type of neutralization stoichiometry was done in Module 14.

- For all other types of reaction calculations, a *rice moles* table 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 goes to equilibrium instead of to completion, or
 - you need the amounts of *all* of the particles in the mixture after the reaction stops.
 - IF a reaction is simple, the concentrations at equilibrium (the **C rice** step) can be solved by inspection when writing the WRECK steps.
 - Once the composition of a reaction mixture at equilibrium is known, the rules to solve most calculations can be applied.

Practice

- For each number and letter below, pick the number and letter from the summary above, from 1 to 5a, that best describes the steps needed to solve.
 - Solve Problem 5d below.
- (Then, *if* you need more practice, *solve* the remaining problems. Answers are below).
- 0.050 mol HF is reacted with 0.035 mol KOH. What is the pH in the resulting solution? (K_a of HF = 6.8×10^{-4})
 - Before the endpoint in a titration, a solution contains 0.0060 mol NaOH, no HCl, and 0.0200 mole NaCl in 80.0 mL of total solution volume. What is the pH?
 - To 50.0 mL of 0.0500 M KOH is added 0.100 M HNO₃.
 - Will this reaction go to completion?
 - What is the pH before any acid is added?
 - What is the pH after 20.0 mL of HNO₃ has been added?
 - How many mL of acid must be added to neutralize all of the KOH?
 - Calculate the pH at the equivalence point of the reaction.

ANSWERS

1. To solve Problem 3: This is a “DATA before and pH after” reaction problem. Use **Step 3b**.

Problem 4: This is a stable mixture. Use **Step 3a**.

Problem 5a: Both are strong, so the reaction goes until the limiting reagent is used up. Use **Step 2a**.

Problem 5b: Before any acid is added, the solution is a stable mixture of the strong base KOH and water. For strong base solution pH, use **Step 4e**.

Problem 5c: This is a “reactants before and mixture after” reaction problem. Use **Step 3b**.

Problem 5d: Calculations to find the equivalence point are stoichiometry. Use **Step 5a**.

Problem 5e: This is a “reactants before and mixture after” problem. Use **Step 3b**. If you note that a strong acid and strong base, when neutralized exactly, form a pH-neutral salt and water, you can solve by inspection using **Step 4d**.

2. See 5d below.

3. WANTED: pH See pH? At least once per problem set, write $\text{pH} \equiv -\log [\text{H}^+] \text{ and } [\text{H}^+] \equiv 10^{-\text{pH}}$

If the final mixture turns out to be a buffer, you may instead need the Henderson-Hasselbalch approximations to find pH.

For a “DATA before and pH after” reaction problem, steps are

Reactants > reactant mol > rice moles > then mixture pH steps.

To balance: when a hydroxide is reacted with an acid, one of the products is always H₂O (Lesson 14B).

In this problem, the “convert to moles” step is done already.

Reaction	1 HF	1 KOH	1 H ₂ O	1 KF
Initial	0.050 mol	0.035 mol	0 mol formed	0 mol
Change	-0.035 mol	- 0.035 mol	+ 0.035 mol	+ 0.035 mol
At End/Equilibrium	0.015 mol	+ 0 mol	+ 0.035 mol	+ 0.035 mol

Label the particles present at equilibrium SA, SB, WA, WB, or N.

* * * * *

The pH-not-neutrals are HF (WA) and its conjugate F⁻ (WB): a buffer. To find buffer pH,

- using the “at end” conjugates, fill in a buffer chart, then
- find the pH using the Henderson-Hasselbalch equation.

* * * * *

Buffer Chart: **WA formula** = HF **BC formula** = F⁻
 moles or [WA] = 0.015 mol HF **moles** or [BC] = 0.035 mol F⁻

H-H: $\text{pH} \approx \text{p}K_a + \log (\text{mol base/mol acid})$
 $\approx -\log (6.8 \times 10^{-4}) + \log (0.035 \text{ mol} / 0.015 \text{ mol})$
 $\approx -(-3.17) + \log (2.33) \approx 3.17 + 0.37 = \boxed{3.54 = \text{pH}}$

4. WANTED = pH. The table salt NaCl contains two pH neutral ions, so NaCl has no impact on the pH.

The only particle that impacts the pH is NaOH (SB). For strong bases, the quick rule is:

$$[\text{NaOH or KOH}]_{\text{mixed}} = [\text{OH}^-]_{\text{in solution}}$$

$$? [\text{NaOH}] = \frac{\text{mol NaOH}}{\text{L soln}} = \frac{0.0060 \text{ mol NaOH}}{80.0 \text{ total mL soln.}} \cdot \frac{1 \text{ mL}}{10^{-3} \text{ L}} = 0.075 \text{ M NaOH} = [\text{OH}^-]_{\text{in solution}}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log(7.5 \times 10^{-2}) = 1.12 = \text{pOH} \quad \text{pH} = 14.00 - \text{pOH} = \boxed{12.88 = \text{pH}}$$

A solution dominated by a strong base should have a high pH, and it does.

- 5a. If an acid and base are mixed, and one or both components is strong, the reaction will go to completion.

- 5b. WANTED: **pH of a KOH solution**

Begin by asking: what type of problem is this: solution or reaction? This is a stable solution.

The initial solution is a strong base solution at equilibrium. Use the rules for strong base pH.

DATA: $\boxed{\text{pH} \equiv -\log [\text{H}^+] \quad \text{and} \quad [\text{H}^+] \equiv 10^{-\text{pH}}}$ and $\boxed{\text{pH} + \text{pOH} = 14.00}$

Quick rule: $[\text{NaOH or KOH}] = [\text{OH}^-]$

$$[\text{NaOH}] = 0.0500 \text{ M} = [\text{OH}^-] ; \text{pOH} = -\log [\text{OH}^-] = -\log (0.0500) = 1.30 = \text{pOH}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.30 = \mathbf{12.70}$$

- 5c. WANTED: **pH after reaction**

Begin by asking: what type of problem is this: solution or “before and after” reaction? This is a *reaction*.

For pH after reaction from amounts before, the steps are

$$\boxed{\text{Reactants} > \text{reactant mol or mmol} > \text{rice moles} > \text{mixture pH rules}}$$

$$? \text{ mmol KOH} = 50.0 \text{ mL KOH} \times 0.0500 \text{ mol/L KOH} = 2.50 \text{ mmol KOH}$$

$$? \text{ mmol HCl} = 20.0 \text{ mL HNO}_3 \times 0.100 \text{ mol/L HNO}_3 = 2.00 \text{ mmol HNO}_3$$

Reaction	1 HNO ₃	1 KOH	1 H ₂ O	1 KNO ₃
Initial	2.00 mmol	2.50 mmol	0 mmol formed	0 mmol
Change (use +, -)	- 2.00 mmol	-2.00 mmol	+ 2.00 mmol	+ 2.00 mmol
At End/Equilibrium	+0 mmol	+ 0.50 mmol	+ 2.00 mmol	+ 2.00 mmol

At equilibrium, what kind of solution is this?

* * * * *

A mixture with a strong base KOH, water, and the pH-neutral ions K⁺ and NO₃⁻. If a strong base is present, it's 100% ionization determines the pH. [SB] = [OH⁻]

WANTED = pH Find [OH⁻] = [SB] = [KOH]

DATA: 0.50 mmol KOH is dissolved in 50.0 mL + 20.0 mL = 70.0 mL of total solution volume.

$$? [\text{KOH}] = \frac{\text{mol KOH}}{\text{L soln}} = \frac{0.50 \text{ mmol NaOH}}{70.0 \text{ total mL soln.}} = 0.0071 \text{ M NaOH} = [\text{NaOH}] = [\text{OH}^-]_{\text{in solution}}$$

Milli- is an abbreviation for “ $\times 10^{-3}$ ”, and “ $\times 10^{-3}$ ” on the top and bottom can cancel.

$$\text{pOH} = -\log [\text{OH}^-] = -\log(7.1 \times 10^{-3}) = 2.15 = \text{pOH} \quad \text{pH} = 14.00 - \text{pOH} = \boxed{11.85 = \text{pH}}$$

5d. WANTED: ? 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 12D. When solving for a single unit, the *stoichiometry* steps are

WDBB, units \rightarrow moles \rightarrow moles \rightarrow units

Balance: $1 \text{ HNO}_3 + 1 \text{ KOH} \rightarrow 1 \text{ H}_2\text{O} + 1 \text{ KNO}_3$

Bridge: $1 \text{ mol HNO}_3 = 1 \text{ mol KOH}$

SOLVE: $? \text{ mL HNO}_3 = 50.0 \text{ mL KOH} \cdot \frac{0.0500 \text{ mol KOH}}{1 \text{ L KOH}} \cdot \frac{1 \text{ mol HNO}_3}{1 \text{ mol KOH}} \cdot \frac{1 \text{ L HNO}_3}{0.100 \text{ mol HNO}_3} =$

$= \boxed{25.0 \text{ mL HNO}_3}$ 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*.

5e. You could do a *rice* table for the reaction, or, since this is at the equivalence point, recall that the reactants have been exactly used up and only products are present. The products are an aqueous solution of the soluble salt KNO_3 . What's the pH?

* * * * *

KNO_3 contains two ions that are pH-neutral: K^+ and NO_3^- . They won't change the pH of the water in which they are dissolved. The pH at the equivalence point is 7.

* * * * *

Lesson 32D: pH During Titration of an SA and SB

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,

- 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 29B).

The substance gradually added to a sample during a titration is the **titrant**.

Indicating the Endpoint

An acid-base *titration* is a gradual neutralization with an indicator present. An indicator is a small amount of pH-sensitive dye that is added to the reaction mixture.

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. The endpoint is detected by a change in the *color* of the indicator:

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). 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 and the equivalence point for the titration will be the *same*.

A number of different substances can be used as acid-base indicators. These indicators change color in different pH ranges. In order to choose an indicator that accurately signals an equivalence point, the pH of the acid-base mixture at points *during* a titration must be determined.

Principles of Acid-Base Titration

The following fundamentals apply when calculating pH during titration.

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 titration is simply carefully measured *neutralization*. The key rule in neutralization is

When an acid and a base are combined, if *either* component is *strong*, the neutralization goes to *completion*: the *limiting* reactant is ~100% used up.

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.

4. 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. As K goes 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.

5. 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.

6. A titration of a substance with a single acidic or basic group 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 (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
<i>Before</i> titrant is added	original acid or base
<i>Between</i> the beginning and endpoint	original acid or base plus products
<i>At the endpoint</i>	Products only
<i>After the endpoint</i>	products plus titrant added <i>after</i> endpoint

Practice A. Check your answers after each part.

- Write the products using molecular (solid) formulas, then balance these equations for reactions in aqueous solution.
 - $\text{KOH} + \text{HNO}_3 \rightarrow$
 - $\text{HCN} + \text{RbOH} \rightarrow$
 - $\text{NH}_3 + \text{HCl} \rightarrow$
 - $\text{NaHCO}_3 + \text{NaOH}$
- Which compounds among the 7 *products* above are not pH-neutral?
- Assuming for the reactions in problem 1 that the 2nd reactant listed is gradually titrated into the first, what substances will be present in the reaction mixture
 - In problem 1a before the titration begins.
 - In problem 1b just before the endpoint of a titration.
 - In problem 1c at the endpoint.
 - In problem 1d three drops after the endpoint.
- In which answer to *question 3* is the solution a buffer?
- 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).

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.
- Since most titrations measure volumes in mL, you can calculate in moles, but it is usually easier to solve in *millimoles*.

Acid-base *titration* calculations are the same as *neutralization* calculations. We have done each type of neutralization calculation in previous lessons. However, 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, and even let us solve by inspection, during the stages of titration.

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.

- What is the pH of the solution before any base is added?
- Write the balanced reaction equation.
- What is the pH at the equivalence point of the titration?
- How many mL NaOH must be added to reach the equivalence point?
- 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 $\text{pH} \equiv -\log [\text{H}^+]$ and $[\text{H}^+] \equiv 10^{-\text{pH}}$

The initial solution is a strong acid. Use the strong acid rules to find pH.

★ ★ ★ ★ ★

For any ~100% ionization, *REC*: $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$ (goes 100%)
~~0.100 M~~ 0 M 0.100 M 0.100 M

or by the quick rule: $[\text{H}^+]_{\text{in solution}} = [\text{HCl or HNO}_3]_{\text{mixed}} = 0.100 \text{ M} = [\text{H}^+]$;

$$\text{pH} = -\log [\text{H}^+] = -\log (0.100) = -\log (1.00 \times 10^{-1}) = -\log (10^{-1}) = -(-1) = 1.00$$

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: $1 \text{ HCl} + 1 \text{ NaOH} \rightarrow 1 \text{ H}_2\text{O} + 1 \text{ NaCl}$ (goes ~100%)

★ ★ ★ ★ ★

c. The rules are

At the equivalence point in any 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.

(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 somewhat easier to solve *rice* tables in millimoles.

★ ★ ★ ★ ★

Find **mmol HCl** using HCl DATA: Want a single unit? Start with a single unit.

$$\text{WANTED} = ? \text{ mmol HCl} = 50.0 \text{ mL HCl} \cdot \frac{0.100 \text{ mol HCl}}{1 \text{ L HCl soln.}} = 5.00 \text{ mmol HCl}$$

★ ★ ★ ★ ★

For NaOH calculations, use NaOH DATA:

$$? \text{ mmol NaOH} = 10.0 \text{ mL NaOH} \cdot \frac{0.250 \text{ mol NaOH}}{1 \text{ L NaOH soln.}} = 2.50 \text{ mmol NaOH}$$

Now complete the *rice* table below for the reaction.

★ ★ ★ ★ ★

Reaction	<u>1</u> HCl	1 NaOH	1 H ₂ O	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 End/Equilibrium	+ 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 *End* row above.

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The HCl at the end determines the pH. Use the quick SA rule to find $[H^+]$, then pH.

* * * * *

$$[H^+]_{\text{in solution}} = [HCl \text{ or } HNO_3]_{\text{mixed}}$$

Calculate the $[HCl]_{\text{mixed}}$ 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. $[HCl] = ?$

* * * * *

$$? = [HCl] = \frac{\text{mol } H^+}{\text{L soln}} = \frac{2.50 \text{ mmol HCl}}{60.0 \text{ mL soln.}} = 0.0417 \text{ M HCl}$$

Since *milli* is simply an abbreviation for “ $\times 10^{-3}$ ” it can cancel. If needed, finish *part e*.

* * * * *

Using the quick rule: $[HCl \text{ or } HNO_3]_{\text{mixed}} = [H^+]_{\text{in solution}} = 0.0417 \text{ M}$

$$? = \text{pH} = -\log [H^+] = -\log(0.0417) = -(-1.38) = \boxed{1.38 = \text{pH}}$$

* * * * *

One of our goals in these calculations is to track what happens to *pH* during a titration.

Let's summarize what we have calculated so far. For this strong acid-strong base titration,

- 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 the *rice* table in the same units used for **Q1**.

* * * * *

The steps can be summarized as

To find pH *after* reaction, given amounts of reactants *before* the reaction:
 Reactants > **reactant mol or prefix-mol** > *rice moles* > **mixture pH steps.**

Complete the table using the increased millimoles of NaOH.

* * * * *

The mmol HCl *being* titrated is the same, but the mmol NaOH added have increased.

$$? \text{ mmol NaOH} = 19.8 \text{ mL NaOH} \cdot \frac{0.250 \text{ mol NaOH}}{1 \text{ L NaOH soln.}} = 4.95 \text{ mmol NaOH}$$

* * * * *

Reaction	<u>1</u> HCl	1 NaOH	1 H ₂ O	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 End/Equilibrium	+ 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. It will determine the pH. HCl is a strong acid. 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.

* * * * *

$$? [\text{HCl}] = \frac{\text{mol HCl}}{\text{L soln}} = \frac{0.05 \text{ mmol HCl}}{69.8 \text{ total mL soln.}} = 0.0007 \text{ mol/L HCl} \quad \text{pH} = ?$$

* * * * *

$$? = \text{pH} = -\log [\text{H}^+] \quad \text{Since HCl is a strong acid, } [\text{H}^+] = [\text{HCl}] = 0.0007 \text{ M}$$

$$? = \text{pH} = -\log [\text{H}^+] = -\log 0.0007 = -(-3.1) = \boxed{3.1 = \text{pH}}$$

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 be 7 – a comparatively large change for the small amount of additional added titrant.

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 would take us to 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.

$$? \text{ mmol NaOH} = 20.1 \text{ mL NaOH} \cdot \frac{0.250 \text{ mol NaOH}}{1 \text{ L NaOH soln.}} = \mathbf{5.02 \text{ mmol NaOH}}$$

Complete the *rice* table using the increased initial millimoles of NaOH.

★ ★ ★ ★ ★

Reaction	<u>1</u> HCl	1 NaOH	1 H ₂ O	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 End/Equilibrium	+ 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 NaOH. It will determine the pH. 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.

★ ★ ★ ★ ★

$$? [\text{NaOH}] = \frac{\text{mol NaOH}}{\text{L soln}} = \frac{0.02 \text{ mmol NaOH}}{70.1 \text{ total mL soln.}} = 0.0003 \text{ mol/L NaOH} \quad \mathbf{pH = ?}$$

★ ★ ★ ★ ★

Since NaOH is a strong base, [NaOH] = [OH[−]] = 0.0003 M

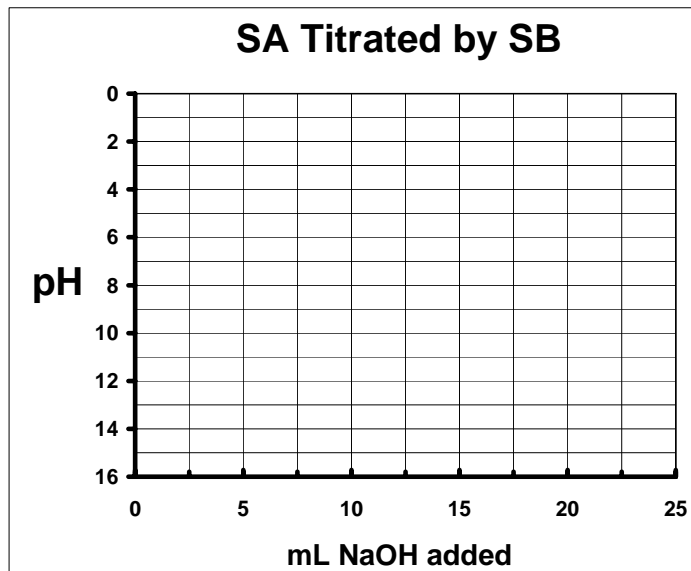
$$\mathbf{pOH} = -\log [\text{OH}^-] = -\log(3 \times 10^{-4}) = 3.5 \quad \mathbf{pH} = 14.00 - \mathbf{pOH} = \mathbf{10.5 = pH}$$

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 B:

- 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.
- 50.0 mL of 0.0500 M KOH is titrated by 0.150 M HNO₃.
 - What is the pH before any acid is added?
 - What is the pH at the endpoint?
 - Calculate the pH after 20.0 mL of HNO₃ has been added.

ANSWERS**Practice A**

- All coefficients are one.
 - $\text{KOH} + \text{HNO}_3 \rightarrow \text{H-OH} + \text{KNO}_3$
 - $\text{HCN} + \text{RbOH} \rightarrow \text{H-OH} + \text{RbCN}$
 - $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$
 - $\text{NaHCO}_3 + \text{NaOH} \rightarrow \text{H-OH} + \text{Na}_2\text{CO}_3$
- RbCN is a salt that is a weak base: it contains the weak base conjugate CN[−] and pH-neutral Rb⁺.
 NH₄Cl is a weakly acidic salt containing the weak acid ion NH₄⁺ and pH-neutral Cl[−].
 Na₂CO₃ is a basic salt containing the moderately weak base CO₃^{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: **NH₄Cl** dissolved in water.
- d. In 1d, three drops after the endpoint are the products **H-OH** and **Na₂CO₃**, plus the **NaOH** added after the endpoint. After the endpoint, the original acid is 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**)
- 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. NH₄Cl (**WA**) is a salt composed of NH₄⁺ 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. H-OH (**N**) Na₂CO₃ (**WB**) is a salt containing the moderately weak carbonate ion ($K_b = 1.9 \times 10^{-4}$). NaOH (**SB**)

Practice B

1. The mmol HCl *being* titrated is the same, but the mmol NaOH added have increased.

$$? \text{ mmol NaOH} = 25.0 \text{ mL NaOH} \cdot \frac{0.250 \text{ mol NaOH}}{1 \text{ L NaOH soln.}} = \mathbf{6.25 \text{ mmol NaOH}}$$

Reaction	<u>1</u> HCl	1 NaOH	1 H ₂ O	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 End/Equilibrium	+ 0 mmol	+ 1.25 mmol	+ 5.00 mmol	+ 5.00 mmol

The NaOH determines the pH. Find [NaOH], then [OH⁻], then pH.

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To 50.0 mL original acid solution has been added 25.0 mL base = 75.0 mL total volume.

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$$? [\text{NaOH}] = \frac{\text{mol NaOH}}{\text{L soln}} = \frac{\mathbf{1.25 \text{ mmol NaOH}}}{75.0 \text{ total mL soln.}} = \mathbf{0.0167 \text{ mol/L NaOH}} \quad \text{pH} = ?$$

★ ★ ★ ★ ★

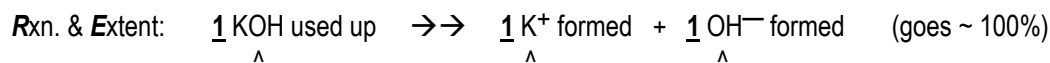
Since NaOH is a strong base, [NaOH] = [OH⁻] = **0.0167 M**

$$\text{pOH} = -\log [\text{OH}^-] = -\log(1.67 \times 10^{-2}) = \mathbf{1.78} \quad \text{pH} = 14.00 - \text{pOH} = \mathbf{12.22 = \text{pH}}$$

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 is a strong base. Strong bases ionize 100% in water.

To find the ion concentrations in strong acid or base, either use the *REC* steps,Or recall the quick rule: $[\text{NaOH or KOH}]_{\text{mixed}} = [\text{OH}^-]_{\text{in solution}}$ (see Lesson 27E)Since $[\text{OH}^-] = 0.0500 \text{ M}$; $\text{pOH} = -\log [\text{OH}^-] = -\log(0.0500) = \mathbf{1.30} = \text{pOH}$

$$\text{pH} = 14.00 - \text{pOH} = \boxed{\mathbf{12.70 = \text{pH}}}$$

2b. In this reaction: $\text{KOH} + \text{HNO}_3 \rightarrow \rightarrow \text{H}_2\text{O} + \text{KNO}_3$ (goes $\sim 100\%$)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, 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, *millimoles*).
- 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

$$? \text{ mmol KOH} = 50.0 \text{ mL KOH} \cdot \frac{0.0500 \text{ mol KOH}}{1 \text{ L KOH}} = \mathbf{2.50 \text{ mmol KOH}}$$

The millimoles of acid added so far are

$$? \text{ mmol HNO}_3 = 20.0 \text{ mL HNO}_3 \cdot \frac{0.150 \text{ mol HNO}_3}{1 \text{ L HCl soln.}} = \mathbf{3.00 \text{ mmol HNO}_3}$$

Reaction	1 HNO ₃	1 KOH	1 H ₂ O	1 KNO ₃
Initial	3.00 mmol	2.50 mmol	0 mmol	0 mmol
Change	− 2.50 mmol	− 2.50 mmol	+ 2.50 mmol	+ 2.50 mmol
At End/Equilibrium	0.50 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, $[\text{H}^+]$ is needed. To find $[\text{H}^+]$, $[\text{SA}]$ is needed: its moles and its liters.

The total volume in the flask is 50.0 mL original base + 15.0 mL acid solution added = 65.0 mL total.

$$? = [\text{HNO}_3] = \frac{\text{mol HNO}_3}{\text{L soln}} = \frac{0.50 \text{ mmol HNO}_3}{65.0 \text{ total mL soln.}} = 0.0077 \text{ M HNO}_3$$

Since HNO_3 is a strong acid,

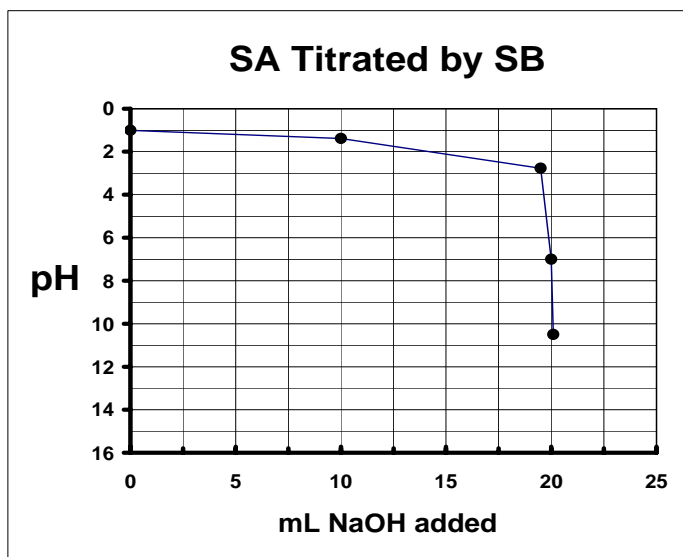
$$[\text{H}^+] = [\text{HNO}_3] = 0.0077 \text{ M H}^+$$

$$\text{pH} = -\log [\text{H}^+] = -\log(0.0077)$$

$$= \boxed{2.11 = \text{pH}}$$

The graph at the right is the answer to Q4 in the lesson.

* * * * *



Lesson 32E: Titration pH: Weak by Strong

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 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 they are 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 *initial* [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	<u>1</u> HCl	1 KOH		
Initial (after combining, but before reacting)	0.025 M	0.035 M	0 mol	0 mol
Change				
At End/Equilibrium				

* * * * *

Since the table shows the *initial* 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	<u>1</u> HCl	1 KOH	1 H ₂ O	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 End/Equilibrium	0 M	+ 0.010 M	+ 0.025 M	+ 0.025 M

After the reaction, the $[KOH]$ at equilibrium determines the pH.

$$[KOH] = [OH^-] = 0.010 \text{ M} = 1.0 \times 10^{-2} \text{ M}; \text{ pOH} = 2.00; \text{ pH} = 12.00$$

Using Mol/L Before Reaction With A Rice Table

The question above was solved relatively quickly. Why haven't we solved all neutralization calculations that 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*, *K*, and *Q* calculations can be solved in mol/L IF all 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 *initial* row of a *rice* 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

$$V_{\mathbf{C}} \times M_{\mathbf{C}} = V_{\mathbf{D}} \times M_{\mathbf{D}} \quad \text{in which } \mathbf{C} \text{ means concentrated and } \mathbf{D} \text{ diluted.}$$

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

$$M_{\mathbf{Diluted}} - \text{after combining} = \frac{V_{\mathbf{Conc}} - \text{before combining} \times M_{\mathbf{Conc}} - \text{before combining}}{V_{\mathbf{Diluted-Total}} \text{ after combining}}$$

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 for the particles of each substance is doubled, and the concentration of both substances is *cut in half*.

Practice A: For additional review, see Lesson 12A.

- If 20.0 mL of 0.100 M NaOH is combined with 20.0 mL of 0.200 M HCl, after mixing,
 [HCl] = _____ [NaOH] = ?

2. If 10.0 mL of 0.45 M KOH is combined with 20.0 mL of 0.300 M HCN, after combining, but before reacting,

$$[\text{HCN}] = \qquad \qquad \qquad [\text{KOH}] = ?$$

3. If 25.0 mL of 0.250 M HF is combined with 21.5 mL of 0.120 M KOH,
- [HF] after combining, before reacting = ?
 - [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. The unit that best makes sense of most chemical 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: the buffer chart and then the 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 end row of the *rice* 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 = 6.8×10^{-4}). Solve the *rice* table in mol/L.

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When any acid (H^+) 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 ₂ O	1 KF
Initial	0.100 M	0.0600 M	0 M	0 M
Change	− 0.0600 M	− 0.0600 M	+ 0.0600 M	+ 0.0600 M
At End/Equilibrium	+ 0.040 M	0 M	+ 0.0600 M	+ 0.0600 M

What type solution is this?

★ ★ ★ ★ ★

A buffer. Solve for buffer pH.

★ ★ ★ ★ ★

Buffer Chart:

WA formula = HF

BC formula = F[−]

moles or [WA] = **0.040 M HF**

moles or [BC] = **0.0600 M F[−]**

★ ★ ★ ★ ★

H-H equation:

$$pH \approx pK_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right)$$

$$\approx -\log (6.8 \times 10^{-4}) + \log (0.0600 \text{ M} / 0.040 \text{ M})$$

$$\approx -(-3.17) + \log (1.5) \approx 3.17 + 0.18 = \boxed{3.35 = \text{pH}}$$

Buffer check: $K_a = 6.8 \times 10^{-4}$, buffer pH estimate $4+2 = 2$ 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

In buffer solutions, if either $[WA] = [BC]$ or moles WA = moles BC, 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 BC, 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, to provide more accurate results, 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-Strong	If Weak-Strong
<i>Before start</i>	[Initial SA or SB]	[Weak Acid or Base] & K
<i>Between start & endpoint</i>	[SA or SB remaining]	<i>Buffer</i>
<i>Halfway to endpoint</i>	$1/2$ [Initial SA or SB]	$[H^+] \approx K_a$ and $pH \approx pK_a$
<i>At endpoint</i>	pH = 7	[Conjugate] and its K
<i>After endpoint</i>	[strong titrant]	[strong 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, and save Problem 3 for your next practice session. The final problem is more challenging.

- 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. Solve in millimoles (K_a of HCN = 6.2×10^{-10}).
- What is the $[H^+]$ half-way to the equivalence point
 - When a strong acid is titrated by a strong base?
 - When a weak acid is titrated by a strong base?
 - When a weak base is titrated by a strong acid?
- 20.0 mL of 0.200 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) is titrated by 0.200 M NaOH.
 - How many mL of NaOH is required to reach the endpoint?
 - When $pH = pK_a$, how many mL of NaOH have been added?
 - Calculate the pH in the solution after 19.0 mL NaOH is added.
 - Calculate the pH at the endpoint of the titration.
- New synthesized *organic* acids (those that include carbon and hydrogen) are frequently tested for their effects on biological systems. To determine the K_a of a new weak acid (call it HbC), 20.0 mL of a 0.150 M 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

- When equal volumes are combined, the concentrations of both substances are cut in half.
 $[HCl] = 0.100 \text{ M}$; $[NaOH] = 0.0500 \text{ M}$
- The total volume after mixing is 30.0 mL. The volume of the KOH is tripled, so its concentration is 1/3 the original. $[KOH] = 0.45 \text{ M} \times 1/3 = 0.15 \text{ M}$ after mixing.

If needed, for $[HCN]$, you can use $V_C \times M_C = V_D \times M_D$

$$? M_D \text{ HCN} = \frac{V_C \times M_C}{V_D} = \frac{20.0 \text{ mL} \times 0.300 \text{ M HCN}}{30. \text{ mL total}} = 0.200 \text{ M HCN diluted} = [HCN] \text{ after mixing.}$$

Using the dilution equation with M, the units will cancel properly, but the labels often will not.

3a. To use the dilution equation, $V_C \times M_C = V_D \times M_D$, 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

$$\text{SOLVE: } ? M_D = \frac{V_C \times M_C}{V_D} = \frac{25.0 \text{ mL} \times 0.150 \text{ M HF}}{46.5 \text{ mL total}} = 0.806 \text{ M HF diluted}$$

Using the dilution equation with M, the units will cancel properly, but the 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, $V_C \times M_C = V_D \times M_D$, 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

$$\text{SOLVE: } ? M_D = \frac{V_C \times M_C}{V_D} = \frac{21.5 \text{ mL} \times 0.120 \text{ M KOH}}{46.5 \text{ mL}} = 0.00558 \text{ M KOH diluted}$$

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	<u>1</u> 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 End/Equilibrium	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

BC formula = CN^-

moles or [WA] = 0.0350 M HCN

moles or [BC] = 0.0150 M CN^-

* * * * *

H-H equation: $\text{pH} \approx \text{p}K_a + \log \left(\frac{[\text{base}]}{[\text{acid}]}\right)$

$$\approx -\log(6.2 \times 10^{-10}) + \log(0.0150 \text{ M} / 0.0350 \text{ M})$$

$$\approx -(-9.20) + \log(0.429) \approx 9.20 - 0.37 = 8.83 = \text{pH}$$

Check: $K_a = 5.6 \times 10^{-10}$, 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.
 $[H^+] = 1/2 [SA \text{ initial}]$
- 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 base conjugate. As in part 2c, $[H^+] \approx K_a$ All buffers can be treated as a weak acid mixed with its base conjugate.
3. WANTED: mL NaOH to neutralize the acetic acid.
 In this reaction, one mole of base neutralizes one mole of acid:
 $1 \text{ CH}_3\text{COOH} + 1 \text{ NaOH} \rightarrow 1 \text{ H}_2\text{O} + 1 \text{ CH}_3\text{COONa}$
 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. $\text{pH} = \text{p}K_a$ half-way to the end point. so $\text{pH} = \text{p}K_a$ 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 (one option), the moles of acid and base before reacting are

$$? \text{ mmol CH}_3\text{COOH} = 20.0 \text{ mL CH}_3\text{COOH} \cdot \frac{0.200 \text{ mol CH}_3\text{COOH}}{1 \text{ L CH}_3\text{COOH soln.}} = 4.00 \text{ mmol CH}_3\text{COOH}$$

$$? \text{ mmol NaOH} = 19.0 \text{ mL NaOH} \cdot \frac{0.200 \text{ mol NaOH}}{1 \text{ L NaOH soln.}} = 3.80 \text{ mmol NaOH}$$

Reaction	1 CH ₃ COOH	1 NaOH	1 H ₂ O	1 CH ₃ COONa
Initial	4.00 mmol	3.80 mmol	-	-
Change	-3.80 mmol	-3.80 mmol	+ 3.80 mmol	+ 3.80 mmol
At End/Equilibrium	+ 0.20 mmol	0 mmol	+ 3.80 mmol	+ 3.80 mmol

Label the particles at the end as SA, SB, WA, WB, or N.

* * * * *

This is a buffer. The pH-not-neutrals are CH₃COOH and its conjugate CH₃COO⁻. To find buffer pH,

- for the two “at end” conjugates, fill in a buffer chart, and
- find the pH using the Henderson-Hasselbalch equation.

* * * * *

Buffer Chart: **WA formula** = CH_3COOH **BC formula** = CH_3COO^-
moles WA = **0.20 mmol** CH_3COOH **moles BC** = **3.80 mmol** CH_3COO^-

Henderson-Hasselbalch: **pH** $\approx \text{p}K_a + \log(\text{mol base/mol acid})$
 $\approx -\log(1.8 \times 10^{-5}) + \log(3.80 \text{ mmol} / 0.20 \text{ mmol})$
 $\approx -(-4.74) + \log(19) \approx 4.74 + 1.28 = \boxed{6.02 = \text{pH}}$

Buffer check: $K_a = 1.8 \times 10^{-5}$, buffer pH estimate $5 \pm 2 = 3-7$. 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 $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{CH}_3\text{COOH}$ (goes slightly)

R+E: general $\underset{\wedge}{\text{WB}} + \text{H}_2\text{O} \rightleftharpoons \underset{\wedge}{\text{OH}^-} + \underset{\wedge}{\text{acid conjugate}}$ (goes slightly)

Conc. at Eq:	$[\text{WB}]_{\text{mixed}} - x$	x	x	
--------------	----------------------------------	-----	-----	--

(rice bottom row)

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

Solve the K_b approximation for x .

* * * * *

To solve the approximation, you need K_b and $[\text{WB}]_{\text{mixed}}$. Find K_b first.

* * * * *

You don't know K_b , but you know that K_a of acid conjugate = 1.8×10^{-5}

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

$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 0.56 \times 10^{-9} = \boxed{5.6 \times 10^{-10} = K_b}$

Now find $[\text{WB}]_{\text{mixed}}$.

* * * * *

$[\text{WB}]_{\text{mixed}} = [\text{CH}_3\text{COO}^-]_{\text{at the endpoint}}$. At and after the endpoint,

? = mol salt ion formed = mol of initial weak acid used up = 0.00400 mol 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.

$$? [\text{CH}_3\text{COO}^-] = \frac{\text{mol CH}_3\text{COO}^-}{\text{L soln}} = \frac{0.00400 \text{ mol CH}_3\text{COO}^-}{40.0 \text{ total mL soln.}} \cdot \frac{1 \text{ mL}}{10^{-3} \text{ L}} = 0.100 \text{ M CH}_3\text{COO}^-$$

Solve the approximation.

* * * * *

$K_b \approx \frac{x^2}{[\text{WB}]_{\text{mixed}}}$	Substituting: $5.6 \times 10^{-10} \approx \frac{x^2}{0.100 \text{ M}}$
--	---

$$x^2 = (5.6 \times 10^{-10})(0.100) = 5.6 \times 10^{-11} = 56 \times 10^{-12}$$

$$x \approx (\text{estimate } 7.8 \times 10^{-6}) \approx \boxed{7.5 \times 10^{-6} \text{ M} = [\text{OH}^-]}$$

Since the approximation was used, do the:

Quick 5% test: $x = 7.5 \times 10^{-6} \text{ M}$, $[\text{WB}] = 0.10 \text{ M} = 1.0 \times 10^{-1} \text{ M}$

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

But pH was WANTED.

* * * * *

$$\text{pOH} = -\log [\text{OH}^-] = -\log(7.5 \times 10^{-6}) = 5.12 = \text{pOH} \quad \text{pH} = 14.00 - \text{pOH} = \boxed{8.88 = \text{pH}}$$

4. WANTED = K_a of HBc

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

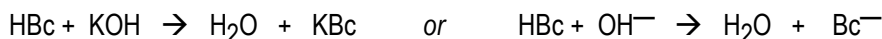
To solve for $\text{p}K_a$ then K_a , you need to find the moles of acid and base at the point where the pH = 5.25

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



Both give the same results. Find the initial mmol, before the reactants react.

* * * * *

$$? \text{ mmol KOH} = 10.0 \text{ mL KOH} \cdot \frac{0.200 \text{ mol KOH}}{1 \text{ L KOH soln.}} = 2.00 \text{ mmol KOH} = 2.00 \text{ mmol OH}^-$$

The millimoles of acid mixed is

$$? \text{ mmol HBc} = 20.0 \text{ mL HBc} \cdot \frac{0.150 \text{ mol HBc}}{1 \text{ L HCl soln.}} = 3.00 \text{ mmol HBc}$$

Reaction	1 HBc	1 OH ⁻	1 H ₂ O	1 Bc ⁻
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 End/Equilibrium	+ 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 HBc (WA) and its conjugate Bc⁻. Solve H-H.

Buffer Chart: **WA formula** = HBc **BC formula** = Bc⁻
 moles or [WA] = 1.00 mmol HBc **moles** or [BC] = 2.00 mmol Bc⁻
 H-H: pH ≈ pK_a + log (mol base/mol acid)

You want K_a. Solve for pK_a first. From the above equation,

$$\begin{aligned} \text{pK}_a &\approx \text{pH} - \log (\text{mol base/mol acid}) \\ &\approx 5.25 - \log (2.00 \text{ mmol} / 1.00 \text{ mmol}) \approx 5.25 - \log (2.00) \approx \\ &\approx 5.25 - 0.30 \approx \boxed{4.95 = \text{pK}_a} \end{aligned}$$

But we WANT K_a. Since $\text{pH} \equiv -\log [\text{H}^+]$ and $[\text{H}^+] \equiv 10^{-\text{pH}}$

$\text{pK}_a \equiv -\log K_a$ and $K_a \equiv 10^{-\text{pK}_a}$ Finish from here.

* * * * *

$$? = K_a \equiv 10^{-\text{pK}_a} = 10^{-4.95} = ?? \times 10^{-5} = \boxed{1.1 \times 10^{-5} = K_a \text{ of HBc}}$$

Check: Buffer pH and -K_a exponent should be +2. pH is 5.25. K_a estimate = ? x 10⁻³ 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.

- Re-write soluble salts as separated ions.
 - Label the particles in the mixture as SA, SB, WA, WB, or N, based on K_a or K_b .
 - In pH calculations, ignore pH-neutral (N) particles.
 - If all particles are N, pH = 7.
 - If SA or SB is present, ignore other particles. Find pH based on 100% ionization:

$$[\text{HCl or HNO}_3] = [\text{H}^+] \quad \text{and} \quad [\text{NaOH or KOH}] = [\text{OH}^-]$$
 - If a WA or WB *and* its conjugate is present, solve a buffer chart and the Henderson-Hasselbalch equation in moles or mol/L.
 - If only *one* WA or WB is present, use K_a or K_b approximation, then the 5% test.
- Rice* tables must have consistent units. The values that go into the initial row of a *rice* table can be *moles*, or *prefix-moles*, or *mol/L* after combining but before reacting.
 - To Calculate pH After Reaction From Amounts Before Reaction
 - Convert the initial amounts of acid and base to *moles*, or *prefix-moles*, or *mol/L* after combining, but before reacting.
 - Enter those values in the initial row of a *rice moles* table.
 - In the change row, use the rule: when acid and base are combined, if *one* or both are strong, the one reactant is 100% used up.
 - Calculate pH based on the mixture at the end of the reaction (in *bottom rice* row).
Those four steps can be summarized as:

To find pH *after* 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**.

- To solve calculations for $[\text{H}^+]$ or **pH**,
 - Ask: Is the problem about a stable solution at equilibrium, or reactants reacting that then become a stable solution?
 - If about a stable solution, apply the steps for finding **mixture pH**.
 - IF about a reaction use the steps for pH *after* from amounts *before* combining.
- The millimoles shortcut for *rice moles* tables: millimoles = **mmol = mL x (mol/L)**.
- When solutions are combined, their volumes add.

8. For reactions, to choose between using stoichiometry steps or the *rice moles* table:
- 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.

- 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
- 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.
 - 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.
 - For the titration of *any* strong acid and strong base, at the endpoint: $\text{pH} = 7$.
 - Half-way to the endpoint in the titration of a *weak* acid or base, a buffer solution exists in which moles WA = moles BC, and $[\text{H}^+] \approx K_a$ and $\text{pH} \approx \text{p}K_a$.

10. Summary: Strong-Strong vs. Weak Strong Titration

Stage	[H ⁺] and pH Determined By	
	If Strong By Strong	If Weak By Strong
<i>Before start</i>	[Strong Acid or Base]	[Weak Acid or Base] & <i>K</i>
<i>Between start & endpoint</i>	[Strong Acid or Base]	<i>Buffer</i>
<i>Half-way to endpoint</i>	1/2 [Initial SA or SB]	$[\text{H}^+] \approx K_a$ and $\text{pH} \approx \text{p}K_a$
<i>At endpoint</i>	$\text{pH} = 7$	[Conjugate] and its <i>K</i>
<i>After endpoint</i>	[strong titrant]	[strong titrant]

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