Student Name: $\qquad$
Class period:

## RRHS AP Chemistry



## Unit 8: Acids, Bases © Buffers Unit 9: Titrations

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## Mastering Chemistry (Pearson textbook/homework)

https://www.pearsonmylabandmastering.com/northamerica/masteringchemistry/
You will need to get your course ID and access code from your teacher!

| What to Do |
| :--- |
| Be $\underline{\text { ACTIVE in while learning/studying: }}$ |
| - Close your booklet and try problems on your own with |
| just a periodic table and formula chart! Only check your |
| answer/work when you've finished, or you can't go any |
| farther. |
| - Use flashcards (physical or digital) |
| - Struggle with challenging problems and keep trying, even |
| if you're stuck initially (or convinced you're doing it |
| wrong) |

## What NOT to Do

Be passive while learning/studying:

- Re-read over your booklet and practice problems you've already completed
- Ask your friend or look up the answer if you don't immediately know how to do the problem

Focus when studying

- Decrease distractions while studying; don't read texts, check social media, or watch Netflix while studying. Put your phone out of sight/hearing.


## Use Intensity when studying

- You control the effort that you apply in your work! 30 minutes of high focus, high intensity study can be better than 2 hours of unfocused, low energy multi-tasking.


## Space out studying over time

- Study a little bit of chemistry most days
- Start long-term homework (like Mastering Chem or lab reports) the day they're assigned, and work a little bit every day or two
- Less is more! Spaced practice studying is more effective than LONG hours of "studying" with multitasking and little focus.

| Focus when studying |
| :--- |
| -Decrease distractions while studying; don't read texts, <br> check social media, or watch Netflix while studying. Put <br> your phone out of sight/hearing. |
| Use Intensity when studying |
| - You control the effort that you apply in your work! 30 |
| minutes of high focus, high intensity study can be better |
| than 2 hours of unfocused, low energy multi-tasking. |

- Study while checking/writing texts, checking social media, and/or watching Netflix.
- Keep your computer or tv on in the background


## Low intensity/low effort

- Look over problems and try them "in your head" but then just look up the answer
- Use flashcards but don't try to recall the info on the other side before looking at the answer


## Cram

- Only study for quizzes/tests the night before
- Start Mastering Chem or your lab report only 1-2 days before it's due
- Study for many hours at a time all at once


## Interleave your Studying

- Study more than just one type of problem; mix it up and jump between different concepts
- Review and practice old units while studying (especially important since AP Chem assessments are cumulative!)


## One Concept Studying

- Study only one type of problem, and practice those problems over and over
- Don't review older content or units while studying


## Test Yourself!

- The best way to prepare for a test is to take a test!
- Time yourself while trying practice problems
- Access only the AP Periodic Table and Formula Chart when practicing problems

Open Notes Practice

- Use your notes, friends, and/or the internet while trying practice problems
- Give yourself unlimited time for each problem

| $3^{\text {rd }}$ Marking Period: J anuary-March 2023 |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Sunday | Monday | Tuesday | Wednesday | Thursday | Friday | Saturday |
| 1 J an. | 2 <br> Student Holiday/ Staff Developmen | 3 <br> Student Holiday/ Staff Development | 4 A | 5 B | 6 A | 7 |
| 8 | 9 B | 10 A | 11 B | 12 A | 13 B | 14 |
| 15 | 16 <br> Student AND Staff Holiday. Hooray! | 17 A | 18 B | 19 A | 20 B | 21 |
| 22 | $23 \quad \text { A }$ | 24 B | 25 A | $26 \quad B$ | 27 A | 28 |
| 29 | 30 B | 31 A | 1 Feb. B | $2 \quad \mathbf{A}$ | 3 B | 4 |
| 5 | 6 A | 7 B | 8 A | 9 B | $10$ <br> A | 11 |


|  | $\stackrel{\infty}{\sim}$ | $\stackrel{\sim}{\sim}$ |  | $\checkmark$ | F |  | $\stackrel{\infty}{\sim}$ | $\stackrel{\sim}{\sim}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\boldsymbol{\sim}$ | - |  | ¢ |  | $\begin{aligned} & \mathbf{U} \\ & \mathbf{Q} \\ & \mathbf{U N} \\ & \mathbf{N} \\ & \mathbf{N} \end{aligned}$ |  | $\mathbb{4}$ <br> N |
|  | 4 <br> 0 <br> -1 | ¢ |  | $\boldsymbol{\sim}$ | ¢ |  |  | $\begin{gathered} \boldsymbol{\infty} \\ \underset{\mathbf{N}}{2} \end{gathered}$ |
| $\begin{aligned} & \text { त } \\ & \frac{10}{0} \\ & 0 \\ & \frac{1}{0} \\ & 3 \end{aligned}$ | 0 $\square$ $\sim$ | $\boldsymbol{\sim}$ |  |  | $\boldsymbol{\infty}$ |  | $\underbrace{\frac{0}{2}}_{n}$ | $\underset{N}{N}$ |
| $\begin{aligned} & \lambda \\ & \frac{\pi}{0} \\ & 0 \\ & \vdots \\ & 1 \end{aligned}$ | $\begin{gathered} \mathbb{4} \\ \underset{H}{+} \end{gathered}$ | $\begin{aligned} & \mathbb{4} \\ & \underset{N}{N} \end{aligned}$ |  | $\underset{\mathbf{N}}{\boldsymbol{\infty}}$ | 4 |  |  | $\underset{\sim}{\boldsymbol{N}}$ |
|  | $\underset{\sim}{\mathbf{n}}$ | 우N |  | $\mathbb{4}$ <br> $N$ | $\boldsymbol{\bullet}$ |  | $m_{i}^{\frac{v}{n}}$ | 아N |
| $\begin{aligned} & \text { त } \\ & \frac{\sqrt{0}}{0} \\ & \frac{1}{5} \\ & \dot{U} \end{aligned}$ | $\begin{aligned} & \text { O} \\ & \text { U } \\ & \text { N } \\ & \underset{\sim}{n} \end{aligned}$ | $\underset{\sim}{7}$ |  | $\stackrel{\ominus}{N}$ | ค |  | $\underset{\sim}{\sim}$ | 9 |

## AP ${ }^{\circledR}$ CHEMISTRY EQUATIONS AND CONSTANTS

Throughout the exam the following symbols have the definitions specified unless otherwise noted.

```
L,mL = liter(s), milliliter(s) mm Hg = millimeters of mercury
g = gram(s) J, kJ = joule(s), kilojoule(s)
nm = nanometer(s) V = volt(s)
atm = atmosphere(s) mol = mole(s)
```


## ATOMIC STRUCTURE

$$
\begin{aligned}
& E=h v \\
& c=\lambda v
\end{aligned}
$$

$$
\begin{aligned}
E & =\text { energy } \\
\nu & =\text { frequency } \\
\lambda & =\text { wavelength }
\end{aligned}
$$

Planck's constant, $h=6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}$
Speed of light, $c=2.998 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$
Avogadro's number $=6.022 \times 10^{23} \mathrm{~mol}^{-1}$
Electron charge, $e=-1.602 \times 10^{-19}$ coulomb

## EQUILIBRIUM

$$
\begin{aligned}
K_{c} & =\frac{[\mathrm{C}]^{c}[\mathrm{D}]^{d}}{[\mathrm{~A}]^{a}[\mathrm{~B}]^{b}}, \text { where } a \mathrm{~A}+b \mathrm{~B} \rightleftarrows c \mathrm{C}+d \mathrm{D} \\
K_{p} & =\frac{\left(P_{\mathrm{C}}\right)^{c}\left(P_{\mathrm{D}}\right)^{d}}{\left(P_{\mathrm{A}}\right)^{a}\left(P_{\mathrm{B}}\right)^{b}} \\
K_{a} & =\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]} \\
K_{b} & =\frac{\left[\mathrm{OH}^{-}\right]\left[\mathrm{HB}^{+}\right]}{[\mathrm{B}]} \\
K_{w} & =\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} \text { at } 25^{\circ} \mathrm{C} \\
& =K_{a} \times K_{b} \\
\mathrm{pH} & =-\log \left[\mathrm{H}^{+}\right], \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] \\
14 & =\mathrm{pH}+\mathrm{pOH} \\
\mathrm{pH} & =\mathrm{p} K_{a}+\log \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]} \\
\mathrm{p} K_{a} & =-\log K_{a}, \mathrm{p} K_{b}=-\log K_{b}
\end{aligned}
$$

## Equilibrium Constants

$K_{c}$ (molar concentrations)
$K_{p}$ (gas pressures)
$K_{a}$ (weak acid)
$K_{b}$ (weak base)
$K_{w}$ (water)

## KINETICS

$$
\begin{aligned}
\ln [\mathrm{A}]_{t}-\ln [\mathrm{A}]_{0} & =-k t \\
\frac{1}{[\mathrm{~A}]_{t}}-\frac{1}{[\mathrm{~A}]_{0}} & =k t \\
t_{1 / 2} & =\frac{0.693}{k}
\end{aligned}
$$

$$
\begin{aligned}
k & =\text { rate constant } \\
t & =\text { time } \\
t_{1 / 2} & =\text { half-life }
\end{aligned}
$$

## GASES, LIQUIDS, AND SOLUTIONS

$$
\begin{aligned}
P V & =n R T \\
P_{A} & =P_{\text {total }} \times X_{\mathrm{A}}, \text { where } X_{\mathrm{A}}=\frac{\text { moles A }}{\text { total moles }} \\
P_{\text {total }} & =P_{\mathrm{A}}+P_{\mathrm{B}}+P_{\mathrm{C}}+\ldots \\
n & =\frac{m}{M} \\
\mathrm{~K} & ={ }^{\circ} \mathrm{C}+273 \\
D & =\frac{m}{V}
\end{aligned}
$$

$K E$ per molecule $=\frac{1}{2} m v^{2}$
Molarity, $M=$ moles of solute per liter of solution

$$
A=a b c
$$

$P=$ pressure
$V=$ volume
$T=$ temperature
$n=$ number of moles
$m=$ mass
$\boldsymbol{M}=$ molar mass
$D=$ density
$K E=$ kinetic energy
$v=$ velocity
$A=$ absorbance
$a=$ molar absorptivity
$b=$ path length
$c=$ concentration
Gas constant, $R=8.314 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$

$$
=0.08206 \mathrm{~L} \mathrm{~atm} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}
$$

$$
=62.36 \mathrm{~L}^{2} \text { torr } \mathrm{mol}^{-1} \mathrm{~K}^{-1}
$$

$1 \mathrm{~atm}=760 \mathrm{~mm} \mathrm{Hg}=760$ torr
STP $=273.15 \mathrm{~K}$ and 1.0 atm
Ideal gas at $\mathrm{STP}=22.4 \mathrm{~L} \mathrm{~mol}^{-1}$

$$
\begin{aligned}
q & =\text { heat } \\
m & =\text { mass } \\
c & =\text { specific heat capacity } \\
T & =\text { temperature } \\
S^{\circ} & =\text { standard entropy } \\
H^{\circ} & =\text { standard enthalpy } \\
G^{\circ} & =\text { standard Gibbs free energy } \\
n & =\text { number of moles } \\
E^{\circ} & =\text { standard reduction potential } \\
I & =\text { current (amperes) } \\
q & =\text { charge (coulombs) } \\
t & =\text { time (seconds) }
\end{aligned}
$$

Faraday's constant, $F=96,485$ coulombs per mole of electrons
1 volt $=\frac{1 \text { joule }}{1 \text { coulomb }}$

## Unit 8 Objectives: Acids, Bases \& Buffers

BIG IDEA 3 - Changes in matter involve the rearrangement and/or the reorganization of atoms and /or the transfer of electrons.

- Enduring Understanding 3.A: Chemical changes are represented by a balanced chemical equation that identifies the ratios with which reactants react and products form.
- Enduring Understanding 3.B: Chemical reactions can be classified by considering what the reactants are, what the products are, or how they change from one into the other. Classes of chemical reactions include synthesis, decomposition, acid-base, and oxidation-reduction reactions.

BIG IDEA 6 - Any bond or intermolecular attraction that can be formed can be broken. These processes are in a dynamic competition, sensitive to initial conditions and external perturbations.

- Enduring Understanding 6.A: Chemical equilibrium is a dynamic, reversible state in which rates of opposing processes are equal.
- Enduring Understanding 6.B: Systems at equilibrium are responsive to external perturbations, with the response leading to a change in the composition of the system.
- Enduring Understanding 6.C: Chemical equilibrium plays an important role in acid-base chemistry and solubility.
- Enduring Understanding 6.D: The equilibrium constant is related to temperature and the difference in Gibbs free energy between reactants and products.

Acids and Bases: Equilibrium that Bites Back!

## Types of Acids and Bases

|  | Arrhenius | Brønsted-- Lowry | Notes |
| :---: | :---: | :---: | :---: |
| Acids | $\ldots \ldots$ donor | $\ldots$ |  |
| Bases | $\ldots \ldots$ donor |  |  |

Note: $\mathrm{H}^{+}$ions are so reactive they cannot exist in water $\qquad$ . Instead, they react with water molecules to produce complex ions, mainly hydronium ion, $\qquad$ . Be careful: $\mathbf{H}^{+}$and $\mathbf{H}_{3} \mathbf{O}^{+}$are often used interchangeably!

$$
\mathrm{H}^{+}+\stackrel{H}{:} \mathrm{O}: \mathrm{H} \longrightarrow\left[\begin{array}{c}
\mathrm{H} \\
\mathrm{H}: \stackrel{\mathrm{O}}{:} \mathrm{H}
\end{array}\right]^{+}
$$

Chemists prefer the Brønsted-Lowry definition, because it Illustrates the $\qquad$ of acid/base reactions as a proton exchange (mmm, equilibrium). To examine why, let's look at how the Bronsted-Lowry base, $\mathrm{NH}_{3}$ (ammonia) reacts with water:

$$
\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{NH}_{4}^{+}+\mathrm{OH}^{-}
$$

Note: when a Bronsted-Lowry base reacts with water, $\qquad$ is still produced! But it comes from what's left of the water molecule after $\mathrm{NH}_{3}$ removes a proton ( $\qquad$ ).

You MUST know (i.e. memorize): $\mathbf{N H}_{3}$ is a $\qquad$ Brønsted-Lowry base!

## Terms to Know

monoprotic acids: donate $\qquad$ $\mathrm{H}^{+}\left(\right.$ex. $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ ) diprotic acids: donate $\qquad$ $\mathrm{H}^{+\prime}$ s (ex. $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ ) polyprotic acids: donate many $\mathrm{H}^{+\prime}$ s (ex. $\mathrm{H}_{3} \mathrm{PO}_{4}$ )

But be careful!
Acids only donate ONE PROTON AT A TIME!
*Don't forget the bases!
$\rightarrow$ polyprotic bases: $\qquad$ more than one $\mathrm{H}^{+}$; anions with -2 or -3 charge (ex. $\mathrm{PO}_{4}{ }^{3-} ; \mathrm{HPO}_{4}{ }^{2-}$ )

Amphoteric or amphiprotic: substances can act as $\qquad$ acids or bases (ex. $\mathrm{H}_{2} \mathrm{O}, \mathrm{HCO}_{3}{ }^{-}$, and $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{2-}$ )

- Example 1: Water as a base, accepting $\mathrm{H}^{+}$from HCl .

$$
\mathrm{HCl}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightarrow
$$

- Example 2: Water as an acid, donating $\mathrm{H}^{+}$to $\mathrm{NH}_{3}$.

$$
\mathrm{NH}_{3}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons
$$

## Conjugate Acid-Base Pairs

In a Brønsted--Lowry acid-base reaction, the original base becomes an acid in the reverse reaction, and the original acid becomes a base in the reverse process.

- Each reactant and the product it becomes is called a $\qquad$ pair.
- Conjugate pairs differ by the presence of $\qquad$ $\mathrm{H}^{+}$ion!


$$
\begin{gathered}
\underset{\text { acid }}{\mathrm{HA}}+\underset{\text { base }}{\mathrm{H}_{2} \mathrm{O}} \underset{\begin{array}{c}
\text { conjugate } \\
\text { base (CB) }
\end{array}}{\mathrm{A}^{-}}+\underset{\begin{array}{c}
\text { conjugate } \\
\text { acid (CA) }
\end{array}}{\mathrm{H}_{3} \mathrm{O}^{+}} \\
\rightarrow \text { Conjugate acid-base pair? } \\
\text { or } \quad \text { and }
\end{gathered}
$$

Note: By definition, the $\qquad$ and $\qquad$ are reactants, and the $\qquad$ of each are the products.

$$
\begin{gathered}
\text { Let's Try! } \\
\mathrm{HSO}_{4}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{H}_{2} \mathrm{SO}_{4}+\mathrm{OH}^{-}
\end{gathered}
$$

$\rightarrow$ Conjugate acid-base pair? $\qquad$ and $\qquad$
or $\qquad$ and $\qquad$

| Acid | Conjugate Base | Base | Conjugate Acid |
| :---: | :---: | :---: | :---: |
| HCl |  |  | $\mathrm{NH}_{4}{ }^{+}$ |
| $\mathrm{HPO}_{4}{ }^{2-}$ |  | $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$ |  |
|  | $\mathrm{HSO}_{4}{ }^{-}$ |  | $\mathrm{H}_{2} \mathrm{O}$ |

Now you try!

1. In the following reactions, identify the acid, base, conjugate acid (CA) and conjugate base (CB).
a) $\mathrm{HBr}(\mathrm{aq})+\mathrm{NH}_{3}(\mathrm{aq}) \rightarrow \mathrm{NH}_{4}{ }^{+}(\mathrm{aq})+\mathrm{Br}^{-}(\mathrm{aq})$
b) $\mathrm{HPO}_{4}{ }^{2-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq}) \rightarrow \mathrm{HSO}_{4}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{PO}_{4}^{-}(\mathrm{aq})$
c) $\mathrm{CO}_{3}{ }^{2-}(\mathrm{aq})+\mathrm{NH}_{4}^{+}(\mathrm{aq}) \rightleftharpoons \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{HCO}_{3}^{-}(\mathrm{aq})$
2. What is the conjugate base of $\mathrm{H}_{2} \mathrm{~S}$ ? $\qquad$ 3. What is the conjugate acid of $\mathrm{HCO}_{3}{ }^{-}$? $\qquad$
3. Which of the following represent a Bronsted-Lowry conjugate acid-base pair?
a. $\mathrm{H}_{2} \mathrm{CrO}_{4}(\mathrm{aq})$ and $\mathrm{CrO}_{4}{ }^{2-}(\mathrm{aq})$
b. $\mathrm{HCrO}_{4}{ }^{-}(\mathrm{aq})$ and $\mathrm{CrO}_{4}{ }^{2-}(\mathrm{aq})$
c. $\mathrm{HCrO}_{4}^{-}(\mathrm{aq})$ and $\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$
d. $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ and $\mathrm{OH}^{-}(\mathrm{aq})$
4. Which of the following species is amphoteric?
a. $\mathrm{H}^{+}$
b. $\mathrm{CO}_{3}{ }^{2-}$
c. $\mathrm{HCO}_{3}^{-}$
d. $\mathrm{H}_{2} \mathrm{CO}_{3}$

$$
\mathrm{HSO}_{4}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{SO}_{4}^{2-}
$$

5. In the equilibrium represented above, the species that act as bases include which of the following?
a. $\mathrm{SO}_{4}{ }^{2-}$
b. $\mathrm{HSO}_{4}^{-}$
c. $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{SO}_{4}{ }^{2-}$
d. $\mathrm{H}_{2} \mathrm{O}$

## Acid Nomenclature Review

Binary acids contain two different elements: hydrogen and one of the more electronegative elements. Aqueous solutions of these compounds are known by the acid names.

## RULES:

1. Name begins with prefix hydro-
2. Root of name of second element follows this prefix
3. Name ends with suffix -ic. Add the word acid.

## EXAMPLES:

1. HBr hydrobromic acid
2. $\mathrm{H}_{3} \mathrm{~N}$ hydronitric acid

Oxyacids are acid compounds of hydrogen, oxygen, and a third element. Usually the oxyacid is one or more hydrogen followed by a polyatomic anion.

## RULES:

1. NO PREFIX
2. Look at the polyatomic anion:
a. if name ends in $\qquad$ then the suffix is changed to $\qquad$ .
b. if name ends in $\qquad$ then the suffix is changed to $\qquad$ .
3. Add the word acid at the end.
4. NO HYDRO prefix!
5. Hint: Watch out for the dread disease called Ate-ic ite-ous $\%$

## EXAMPLES:

1. $\mathrm{H}_{2} \mathrm{SO}_{4}$ - Sulfuric Acid
2. $\mathrm{H}_{2} \mathrm{SO}_{3}$ - Sulfurous Acid

Table: Conventions for Naming Oxyacids

| Relationship | General name | Example name | Example formula |
| :--- | :---: | :---: | :---: |
| one more oxygen atom than (root)ic | per(root)ic acid | perchloric acid | $\mathrm{HClO}_{4}$ |
|  | (root)ic acid | chloric acid | $\mathrm{HClO}_{3}$ |
| one less oxygen atom than (root)ic | (root)ous acid | chlorous acid | $\mathrm{HClO}_{2}$ |
| two less oxygen atoms than (root)ic | hypo(root)ous acid | hypochlorous acid | HClO |

Time to Practice!

1. $\mathrm{H}_{2} \mathrm{CO}_{3}$
2. $\mathrm{HNO}_{2}$
3. HCl
4. $\mathrm{HBrO}_{2}$ $\qquad$
5. nitric acid $\qquad$
6. phosphoric acid $\qquad$
7. hydroiodic acid $\qquad$
8. sulfurous acid $\qquad$

## Relative Strength of Acids and Bases: All about the lonization!

## Strong acid or base:

$\qquad$

- $\qquad$ ionized in water (completely dissociates)
$>\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=$[strong acid $]$
> $\left[\mathrm{OH}^{-}\right]=$[strong base]
- $\qquad$ electrolytes (conduct electricity in solution)


## A Strong Acid

When HCl dissolves in water, it ionizes completely.


After dissociation, at equilibrium


Weak acid or base: $\qquad$

- Much less than $\qquad$ ionized in water
$>\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \ll$ [weak acid]
$>\left[\mathrm{OH}^{-}\right] \ll$ [weak base]
- $\qquad$ electrolytes
- Vast $\qquad$ of acids/bases are weak!


## A Weak Acid

When HF dissolves in water, only a fraction of the molecules ionize.


Before dissociation
After dissociation, at equilibrium


$\mathrm{K}_{\mathrm{a}}$ and $\mathrm{K}_{\mathrm{b}}$ : Equilibrium Expressions for Acids and Bases

Given the dissociation of the generic acid, $\qquad$ :

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftrightharpoons \mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})
$$

$K_{a}=$

Given the dissociation of the generic base, $\qquad$ :

$$
\mathrm{B}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftrightharpoons \mathrm{BH}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

$K_{b}=$

Memorize the following: (for reals - you MUST know these!)

1. Strong acids:
a. Hydrohalic acids: $\mathbf{H C I}, \mathbf{H B r}, \mathbf{H I}$
(note: HF is NOT a strong acid! The H-F bond is too strong.)
b. Nitric acid: $\mathbf{H N O}_{\mathbf{3}}$
c. Sulfuric acid: $\mathbf{H}_{\mathbf{2}} \mathbf{S O}_{\mathbf{4}}$
d. Perchloric acid: $\mathbf{H C l O}_{4}$
2. Strong bases:
a. Group I A and II A metal hydroxides (i.e. $\mathrm{LiOH}, \mathrm{NaOH}, \mathrm{Ca}(\mathrm{OH})_{2}$, etc)
b. Solubility plays a huge role
i. Very soluble = very strong
ii. $\mathrm{Be}(\mathrm{OH})_{2}$ and $\mathrm{Mg}(\mathrm{OH})_{2}$ are very poorly soluble, limiting their effectiveness; however, the small amount of these bases which dissolves will ionize $100 \%$, so they can be considered strong bases.

Tricks to Remember the Strong Acids

1. BriCl-SO-NO-ClO (Pronounced "Brickle-So-No-Clo; all long "oh" sounds)
2. By song! ()

The Song Acid Song!
(sung with the melody from You Are My Sunshine)
All the strong acids, They share the same fate -

To $100 \%$ dissociate!
They will never
Get back together, All their H 's are gone forever.

There's hydrochloric, And hydrobromic, And hydroiodic just says hi!

Then there's perchloric,
Of course sulfuric,
And then nitric by the by.

Oxyacid Trends: The $\qquad$ oxygen atoms present, the $\qquad$ the acid WITHIN that group..
$\rightarrow$ Why? The $\mathrm{H}^{+}$being donated is bonded to an oxygen atom.
0 The oxygen atoms are highly electronegative and are pulling the bonded pair of electrons AWAY from the site where the $\mathrm{H}^{+}$is bonded:

- More oxygen atoms = greater bond $\qquad$
- Greater bond polarity = greater $\qquad$ charge density around H
- Greater positive charge density around $H=$ easier (less energy to remove) $H$
- Easier to remove $\mathrm{H}=$ stronger acid!

Hypochlorous

> Chlorous




$K_{a}=3.0 \times 10^{-8}$
$K_{a}=1.1 \times 10^{-2}$
$\mathrm{K}_{\mathrm{a}}=$ large
$\mathrm{K}_{\mathrm{a}}=$ VERY large

## Increasing Acid Strength



Acid Ionization Constant ( $\qquad$ ): the equilibrium constant for the dissociation of an acid in water

## Larger $\mathrm{K}_{\mathrm{a}}=$ Stronger acid!

- Size of $K_{\mathrm{a}}$ depends on strength of attraction between $\qquad$ and $\qquad$
0 $\qquad$ attraction between $\mathrm{A}^{-}$and $\mathrm{H}^{+}=$ $\qquad$ acid ( $\qquad$ $\mathrm{K}_{\mathrm{a}}$ )

0 $\qquad$ attraction between $\mathrm{A}^{-}$and $\mathrm{H}^{+}=$ $\qquad$ acid ( $\qquad$ $\mathrm{K}_{\mathrm{a}}$ )

Strong acid: $\mathrm{K}_{\mathrm{a}} \gg 1$
Weak acid: $\mathrm{K}_{\mathrm{a}} \ll 1$
$\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftrightharpoons \mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$
$K_{a}=\frac{\left[H_{3} O^{+}\right]\left[A^{-}\right]}{[H A]}=\frac{\left[H^{+}\right]\left[A^{-}\right]}{[H A]}$

Base Ionization Constant ( ): the equilibrium constant for the reaction of a base with water

$$
\text { Larger } \mathrm{K}_{\mathrm{b}}=\text { Stronger base! }
$$

- Size of $K_{\mathrm{b}}$ depends on strength of attraction between $\qquad$ and $\qquad$
0 $\qquad$ attraction between B and $\mathrm{H}^{+}=$ $\qquad$ base ( $\qquad$ $\mathrm{K}_{\mathrm{b}}$ )

$$
\begin{gathered}
\mathrm{B}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftrightharpoons \mathrm{BH}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \\
K_{b}=\frac{\left[H B^{+}\right]\left[O H^{-}\right]}{[B]}
\end{gathered}
$$

In general, Brønsted-Lowry acid-base reactions are equilibrium systems meaning that $\qquad$ the forward and reverse reactions occur.

- The extent of the reaction depends on the relative $\qquad$ of the acids and bases involved, and the value of their equilibrium constants ( $\mathrm{K}_{\mathrm{a}}$ and $\mathrm{K}_{\mathrm{b}}$ ).
a. The stronger an acid is, the $\qquad$ its conjugate base.
b. The $\qquad$ a base is, the weaker its conjugate acid.
Let's look at an example to see why!
Example 1: Strong Acid $\quad \mathrm{HCl}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Cl}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \quad \mathrm{K} \gg 1$, products are favored!

But if you reverse the reaction and look at the strength of the conjugate base of HCl , $\qquad$ :

$$
\mathrm{Cl}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{HCl}+\mathrm{OH}^{-} \quad \mathrm{K} \ll 1 \text {, reactants are favored! No products. }
$$

$\rightarrow \mathrm{Cl}^{-}$is a $\qquad$ base, because it really does NOT want to accept that $\mathrm{H}^{+}$!

## Important Notes:

- The favored direction of the reaction is the one in which the $\qquad$ acid/base are produced.
- The $\qquad$ acid and base will always be on the $\qquad$ side of the equation (which means the acid and base will also always be on the same side of the equation.)


## Example 1: K >> 1

$\mathrm{HClO}_{4(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \leftrightharpoons \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}+\mathrm{ClO}_{4}{ }^{-}{ }_{(\mathrm{aq})}$

Favored:
Stronger acid:
Weaker acid:
Stronger base:
Weaker base:

Example 2: $\mathrm{K}=1.76 \times 10^{-5}$

$$
\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}{ }_{(\mathrm{aq})}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}
$$

Favored:

| Stronger acid: | Weaker acid: |
| :--- | :--- |
| Stronger base: | Weaker base: |

Consider the following acids and their $\mathrm{K}_{\mathrm{a}}$ values.

| $\quad$ Acid | $\mathrm{K}_{\mathrm{a}}$ | Conjugate Base? |
| :--- | :---: | :---: |
| $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | $1.8 \times 10^{-5}$ |  |
| HOCN | $3.5 \times 10^{-4}$ |  |
| HF | $6.8 \times 10^{-4}$ |  |

1. Rank these acids in order of increasing strength:
2. Rank the conjugate bases of the acids in order of increasing strength:

Using $K_{a}$ 's to determine $K_{\text {eq }}$ for a given reaction: You can compare the $K_{a}$ values of two acids to determine if a given acid/base reaction is reactant or product favored!

Example: $\quad \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq})+\mathrm{HCO}_{3}^{-}(\mathrm{aq}) \leftrightharpoons \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq})$

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}} \text { of } \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}=1.8 \times 10^{-5} \\
& \mathrm{~K}_{\mathrm{a}} \text { of } \mathrm{H}_{2} \mathrm{CO}_{3}=4.3 \times 10^{-7}
\end{aligned}
$$

1. What are the two conjugate acid-base pairs in this reaction?
2. What are the two acids in this reaction? $\qquad$ and $\qquad$
3. Which acid is stronger, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ or $\mathrm{H}_{2} \mathrm{CO}_{3}$ ? $\qquad$
4. Is the example reaction reactant or product favored? $\qquad$
5. Is the $K$ value of this reaction less than 1 , equal to 1 , or greater than 1 ? $\qquad$

## Practice Problems!

1. Consider the reaction of an acid in water: $\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \leftrightharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})$
a. If $\mathrm{A}^{-}$is a stronger base than $\mathrm{H}_{2} \mathrm{O}$, is the value of K greater or less than 1 ?
b. If $\mathrm{A}^{-}$is a stronger base than $\mathrm{H}_{2} \mathrm{O}$, is HA a weak acid or a strong acid?
2. Given the following acid/base reaction: $\mathrm{NO}_{2}^{-}+\mathrm{NH}_{4}^{+} \leftrightharpoons \mathrm{NH}_{3}+\mathrm{HNO}_{2}$

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}} \text { of } \mathrm{NH}_{4}{ }^{+}=5.6 \times 10^{-10} \\
& \mathrm{~K}_{\mathrm{a}} \text { of } \mathrm{HNO}_{2}=4.5 \times 10^{-4}
\end{aligned}
$$

a. What are the two conjugate acid-base pairs in this reaction?
b. What are the two acids in this reaction? $\qquad$ and $\qquad$
c. Which acid is stronger? $\qquad$
d. Is the example reaction reactant or product favored? $\qquad$
e. Is the $K$ value of this reaction less than 1 , equal to 1 , or greater than 1 ? $\qquad$
3. The hypochlorite ion, $\mathrm{ClO}^{-}$, is a weaker base than the cyanide ion, $\mathrm{CN}^{-}$. Which is a stronger acid, HClO or HCN , and why?
4. The term " $\mathrm{K}_{\mathrm{a}}$ for chlorous acid" refers to what chemical reaction?

## Multiple Choice Practice!

5. You prepare a 0.100 M solution of acid. For which of the following acids will $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.100 \mathrm{M}$ ?
a. $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
b. $\mathrm{H}_{2} \mathrm{SO}_{3}$
c. $\mathrm{HNO}_{3}$
d. $\mathrm{HIO}_{3}$
6. All of the following can function as Brønsted-Lowry bases in solution EXCEPT:
a. $\mathrm{H}_{2} \mathrm{O}$
b. $\mathrm{NH}_{3}$
c. $\mathrm{H}_{3} \mathrm{PO}_{4}$
d. $\mathrm{HCO}_{3}^{-}$
7. You prepare a 2.0 M solution of acid. For which of the following acids will $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \ll 2.0 \mathrm{M}$ ?
a. HBr
b. HF
c. HI
d. HCl
8. Which of the following is true for all bases?
a. All bases donate $\mathrm{OH}^{-}$ions into solution.
b. Only strong bases create solutions in which $\mathrm{OH}^{-}$ions are present.
c. Only strong bases are good conductors when dissolved in solution.
d. For weak bases, the concentration of the $\mathrm{OH}^{-}$ions equals to concentration of the base in solution.
9. A 0.5-molar solution of which of the following bases will have $\left[\mathrm{OH}^{-}\right] \ll 0.5 \mathrm{M}$ ?
a. $\mathrm{Mg}(\mathrm{OH})_{2}$
b. LiOH
c. $\mathrm{Al}(\mathrm{OH})_{3}$
d. $\mathrm{Sr}(\mathrm{OH})_{2}$
10. The structure of two oxyacids is shown below:


Which would be a stronger acid and why?
a. HOCl , because the $\mathrm{H}-\mathrm{O}$ bond is stronger than in HOF as chlorine is larger than fluorine.
b. HOCl, because the $\mathrm{H}-\mathrm{O}$ bond is weaker than in HOF as chlorine has a higher electronegativity than fluorine.
c. HOF, because the $\mathrm{H}-\mathrm{O}$ bond is weaker than in HOCl as fluorine has a higher electronegativity than chlorine.
d. HOF, because the $\mathrm{H}-\mathrm{O}$ bond is stronger than in HOCl as fluorine is smaller than chlorine.
11. A 0.5 -molar solution of which of the following acids will be the best conductor of electricity?
a. $\mathrm{H}_{2} \mathrm{CO}_{3}$
b. $\mathrm{H}_{2} \mathrm{~S}$
c. HF
d. $\mathrm{HNO}_{3}$

## $\mathrm{K}_{\mathrm{w}}$ : The Self-Ionization of Water

## Self-Ionization of Water

- To understand whether a solution is acidic or basic, we use pure water as a $\qquad$ starting point.
- In the $\qquad$ of water, a water molecule produces a hydronium ion, $\mathrm{H}_{3} \mathrm{O}^{+}$, and a hydroxide ion, $\mathrm{OH}^{-}$.

| Water acting as both |
| :--- |
| an acid and a base |


| Acid |
| :--- |
| (proton donor) |


| Base |
| :--- |
| (proton acceptor) |

A. The self-ionization of water produces $\qquad$ amounts of hydronium and hydroxide ions.

- Each ion has a concentration of $\qquad$ .
- Since each ion has equal concentration, we say that pure water is $\qquad$ .
B. The equilibrium constant for the self-ionization of water, $\mathrm{K}_{\mathrm{w}}$, is $\qquad$ .

$$
\begin{gathered}
\boldsymbol{K}_{w}=\frac{[\text { products }]}{[\text { reactants }]}=[\text { products }]=\left[\boldsymbol{H}^{+}\right]\left[\mathrm{OH}^{-}\right](\text {reactants get crossed out because reactants are liquids) } \\
\left.K_{w}=\left(1.0 \times 10^{-7}\right)\left(1.0 \times 10^{-7}\right)=1.0 \times 10^{-14} \quad \text { (at } 25^{\circ} \mathrm{C}\right)
\end{gathered}
$$

Neutral, Acidic, and Basic Solutions: A solution is then determined to be acidic or basic depending on which ion is in greater concentration.

Acidic: $\left[\mathrm{H}^{+}\right]$ $\qquad$ $\left[\mathrm{OH}^{-}\right]$

Neutral: $\left[\mathrm{H}^{+}\right]$ $\qquad$ $\left[\mathrm{OH}^{-}\right]$

Basic: $\left[\mathrm{H}^{+}\right]$ $\qquad$ $\left[\mathrm{OH}^{-}\right]$

Why is $\mathrm{K}_{\mathbf{w}}$ useful? If you know the concentration of $\mathrm{H}^{+}$in solution, $\left[\mathrm{H}^{+}\right]$, you can calculate $\left[\mathrm{OH}^{-}\right]$(and vice versa).
Example 1: Given an aqueous solution of $2.7 \times 10^{-4} \mathrm{M} \mathrm{Ba}(\mathrm{OH})_{2}$ :
a. Calculate $\left[\mathrm{OH}^{-}\right]$:
b. Calculate $\left[\mathrm{H}^{+}\right]$:
c. Is the solution acidic, basic, or neutral? $\qquad$

Example 2: An aqueous solution of $\mathrm{HNO}_{3}$ has an $\left[\mathrm{OH}^{-}\right]$concentration of $5.1 \times 10^{-11} \mathrm{M}$.
a. Calculate the $\left[\mathrm{H}^{+}\right]$.
b. What is the molarity of $\mathrm{HNO}_{3}$ ?
c. Is the solution acidic, basic, or neutral? $\qquad$

## The pH Scale

pH and $\mathbf{p O H}$ scale: Another way to express if a solution is acid or basic is to use the pH scale.

1. The letters pH stand for the French words pouvoir hydrogène, meaning "hydrogen $\qquad$ $"$
2. The letter " p " is short for " $\qquad$ " (just like "x" means multiply)
3. The pH of a solution is defined as the negative $\qquad$ of the $\qquad$ ion concentration, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$.

$$
\mathbf{p H}=-\log \left[\mathrm{H}^{+}\right] \quad \text { OR } \quad \mathbf{p H}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

The pH Scale

| 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |

Acidic

| $10^{-0}$ | $10^{-1}$ | $10^{-2}$ | $10^{-3}$ | $10^{-4}$ | $10^{-5}$ | $10^{-6}$ | $10^{-7}$ | $10^{-8}$ | $10^{-9}$ | $10^{-10}$ | $10^{-11}$ | $10^{-12}$ | $10^{-13}$ | $10^{-14}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |

$\left[\mathrm{H}^{+}\right]$
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4. The pOH of a solution is defined as the negative $\qquad$ of the $\qquad$ ion concentration, $\left[\mathrm{OH}^{-}\right]$.

$$
\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]
$$

| 14 | 13 | 12 | 11 | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 | 0 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |

Acidic

| $10^{-14}$ | $10^{-13}$ | $10^{-12}$ | $10^{-11}$ | $10^{-10}$ | $10^{-9}$ | $10^{-8}$ | $10^{-7}$ | $10^{-5}$ | $10^{-9}$ | $10^{-4}$ | $10^{-3}$ | $10^{-2}$ | $10^{-1}$ | $10^{-0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |

$\left[\mathrm{OH}^{-1}\right.$

## The best part:

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

Why? It all comes back to the expression for $\mathrm{K}_{\mathrm{w}}$.

$$
\begin{gathered}
\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} \quad \text { (at } 25^{\circ} \mathrm{C} \text { ) } \\
\text { Take the log of both sides! } \\
-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]+-\log \left[\mathrm{OH}^{-}\right]=14 \\
\mathrm{pH}+\mathrm{pOH}=14 \\
\text { Yay math! }
\end{gathered}
$$



## Significant Figures and Logarithmic Scales

Sig. figs. are the digits $\qquad$ the decimal point in the log

2 significant digits


More Examples: $\quad \log \left(2.25 \times 10^{6}\right)=6.352$
$\log (0.03)=-1.5 \quad 10^{1.18}=15 \quad 10^{1.9}=80$
Now you try!

1. $\log \left(4 \times 10^{3}\right)$
$=$ $\qquad$ 3. $10^{0.8}=$ $\qquad$
2. $\log \left(6.6667 \times 10^{-8}\right)$ $\qquad$ 4. $10^{4.92}=$ $\qquad$
3. Calculate $\left[\mathrm{H}^{+}\right],\left[\mathrm{OH}^{-}\right], \mathrm{pH}$ and pOH of a $0.25 \mathrm{M} \mathrm{Ca}(\mathrm{OH})_{2}$ solution.
4. The pH of a sample of human blood was measured to be 7.41 at $25^{\circ} \mathrm{C}$. Calculate $\mathrm{pOH},\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$for the sample.

## OPTIONAL Pre-AP pH ${ }^{2}$ Notes $\&$ Extra Practice

pH and pOH scale: Another way to express if a solution is acid or basic is to use the pH scale.

- The letters pH stand for the French words pouvoir hydrogène, meaning "hydrogen $\qquad$ "
- The letter " p " is short for " $\qquad$ " (just like "x" means multiply)

$$
\mathbf{p H}=-\log \left[\mathbf{H}^{+}\right] \quad \text { OR } \quad \mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

|  | Solution 1 | Solution 2 | Change? |
| :---: | :---: | :---: | :---: |
| $\left[\mathrm{H}^{+}\right]$ | $1 \times 10^{-3} \mathrm{M}$ | $1 \times 10^{-2} \mathrm{M}$ |  |
| pH |  |  |  |

The pH Scale

| 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $10^{-0}$ | $10^{-1}$ | $10^{-2}$ | $10^{-3}$ | $10^{-4}$ | $10^{-5}$ | $10^{-6}$ | $10^{-7}$ | $10^{-8}$ | $10^{-9}$ | $10^{-10}$ | $10^{-11}$ | $10^{-12}$ | $10^{-13}$ | $10^{-14}$ |
| Acidic |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

$\left[\mathrm{H}^{+}\right.$]

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$$
\begin{array}{r}
\quad \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] \\
\rightarrow \ldots \\
\rightarrow \quad\left[\mathrm{H}^{+}\right]=\ldots \ldots \mathrm{pH}=\text { more acidic } \leftarrow \\
\\
\left.\rightarrow \mathrm{OH}^{-}\right]=\ldots \ldots \mathrm{pOH}=\ldots \ldots \mathrm{pH}=\text { more basic } \leftarrow
\end{array}
$$

The best part: $\mathrm{pOH}+\mathrm{pH}=14$

But why? $\mathrm{K}_{\mathrm{w}}$, of course!
In summary:

|  | Acidic | Neutral | Basic |
| :---: | :---: | :---: | :---: |
| All the Time | $\left[\mathrm{H}^{+}\right]>\left[\mathrm{OH}^{-}\right]$ | $\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]$ | $\left[\mathrm{H}^{+}\right]<\left[\mathrm{OH}^{-}\right]$ |
| At $25^{\circ} \mathrm{C}$ | $\mathrm{pH}<7.0$ | $\mathrm{pH}=7.0$ | $\mathrm{pH}>7.0$ |

Very Important
If Temperature __, pH AND pOH $\qquad$
If Temperature $\qquad$ , pH AND pOH $\qquad$
$\rightarrow$ This is an $\qquad$ relationship! $\leftarrow$

## What Equations are Given on the Formula Chart?

$$
\begin{aligned}
& \mathrm{pH}=-\log \left[\mathrm{H}^{+}\right] \\
& \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] \\
& \mathrm{pH}+\mathrm{pOH}=14
\end{aligned}
$$

$K_{w}$ relationships are given on the formula chart as well!
$K_{w}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]$, where $\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \quad K_{w}=1.0 \times 10^{-14}$ at $25^{\circ} \mathrm{C}$ $K_{w}=K_{a} \times K_{b}$

## Significant Figures and Logarithmic Scales

- Sig. figs. are the digits $\qquad$ the decimal point in the log

2 significant digits


3 significant digits

Now you try! Calculator Answer Rounded Answer

| 1. $-\log \left(4 \times 10^{-3}\right)$ | = | 2.39794 | $=$ |
| :---: | :---: | :---: | :---: |
| 2. $-\log \left(6.6667 \times 10^{-8}\right)$ | = | 7.17609 | $=$ |
| 3. $-\log (0.00032)$ | $=$ | 3.49485 | = |
| 4. $-\log \left(3.98 \times 10^{-9}\right)$ | = | 8.40012 | $=$ |
| 5. $-\log \left(2 \times 10^{-6}\right)$ | = | 5.69897 |  |
| 6. $10^{-0.8}$ | = | 0.15849 | $=$ |
| 7. $100^{-4.920}$ | = | $1.20226 \times 10^{-5}$ | $=$ |
| 8. $10^{-6.12}$ | = | $7.58578 \times 10^{-7}$ | $=$ |
| 9. $10^{-0.50}$ | = | 0.31623 | $=$ |
| 10. $10^{-7.2}$ | $=$ | $6.30957 \times 10^{-8}$ | $=$ |

## A Brief Reminder about Polyprotic Bases:

1. If you're given solution concentration, multiply by the \# of $\mathrm{OH}^{-}$'s to convert into $\left[\mathrm{OH}^{-}\right]$.
2. If you're given [ $\mathrm{OH}^{-}$], divide by the \# of $\mathrm{OH}^{-’}$ s to convert into solution concentration.

| Solution concentration | [ $\mathrm{OH}^{-}$] | Solution concentration | [ $\mathrm{OH}^{-}$] |
| :---: | :---: | :---: | :---: |
| $2.0 \mathrm{M} \mathrm{Ca}(\mathrm{OH})_{2}$ | $\left[\mathrm{OH}^{-}\right]=\ldots \mathrm{M}$ | M NaOH | $\left[\mathrm{OH}^{-}\right]=0.25 \mathrm{M}$ |
| $3 \times 10^{-4} \mathrm{M} \mathrm{Al}(\mathrm{OH})_{3}$ | $\left[\mathrm{OH}^{-}\right]=\ldots \mathrm{M}$ | _ $\mathrm{M} \mathrm{Mg}(\mathrm{OH})_{2}$ | $\left[\mathrm{OH}^{-}\right]=1.0 \mathrm{M}$ |
| 0.50 M LiOH | $\left[\mathrm{OH}^{-}\right]=\ldots \mathrm{M}$ | $\ldots \mathrm{M} \mathrm{Ga}(\mathrm{OH})_{3}$ | $\left[\mathrm{OH}^{-}\right]=2.8 \times 10^{-7} \mathrm{M}$ |

## Examples

| Solution concentration | $\left[\mathrm{H}^{+}\right]$or $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ | pH | pOH | Acidic (A), <br> Basic (B), <br> or Neutral (N)? |  |
| :--- | ---: | ---: | ---: | :---: | :---: | :---: |
| 1. | 0.003 M HCl |  |  |  |  |  |
| 2. | $-\mathrm{M} \mathrm{Mg}(\mathrm{OH})_{2}$ |  |  |  | 2.0 |  |
| 3. | M HClO 4 |  | 13.00 |  |  |  |
| 4. | M HBr | $4.9 \times 10^{-13} \mathrm{M}$ |  |  |  |  |
| 5. | $\mathrm{M} \mathrm{Al}(\mathrm{OH})_{3}$ |  |  | 12.1 |  |  |
| 6. | M LiOH |  | $4.9 \times 10^{-13} \mathrm{M}$ |  |  |  |

7. If 0.029 mol of HCl is dissolved into $150 . \mathrm{mL}$ of distilled water, what is the pH of the solution which forms?
8. How many moles of $\mathrm{HClO}_{4}$ would be needed to create $500 . \mathrm{mL}$ of a solution which has a $\mathrm{pH}=3.200$ ?
9.If $1.7 \times 10^{-4} \mathrm{~mol}$ of $\mathrm{Ba}(\mathrm{OH})_{2}$ is dissolved into $100 . \mathrm{mL}$ of distilled water, what is the pH of the solution formed?


## Practice Makes Perfect!

|  | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right.$] | pH | pOH | [ $\mathrm{OH}^{-}$] | Solution Concentration |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1. |  | 3.78 |  |  | _ $\mathrm{M} \mathrm{Al}(\mathrm{OH})_{3}$ |
| 2. |  |  |  | $4.5 \times 10^{-4} \mathrm{M}$ | $\ldots \mathrm{M} \mathrm{LiOH}$ |
| 3. | $2.01 \times 10^{-3} \mathrm{M}$ |  |  |  | $\ldots \mathrm{M} \mathrm{Sr}(\mathrm{OH})_{2}$ |
| 4. |  | 2.9 |  |  | $\ldots \mathrm{M} \mathrm{HBr}$ |
| 5. |  |  |  |  | $5.66 \times 10^{-4} \mathrm{M} \mathrm{Ca}(\mathrm{OH})_{2}$ |

6. Calculate the concentration of hydroxide ions in a solution that is $3.00 \times 10^{-4} \mathrm{M} \mathrm{HCl}$.
7. Determine the molarity of $\mathrm{Sr}(\mathrm{OH})_{2}$ solution with a $\mathrm{pH}=10.32$.
8. A nitric acid solution is found to have a pH of 2.70. Calculate the number of moles of $\mathrm{HNO}_{3}$ required to prepare 5.50 L of this solution.
9. The pH of a sample of human blood was measured to $2^{4} \mathrm{e} 7.41$ at $25^{\circ} \mathrm{C}$. Calculate the concentration of hydroxide in the blood sample.
10. The pH of a solution changes from 3.00 to 6.00 . By what factor does the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$change?
a. 3
b. 30
C. 100
d. 1000

$$
\mathrm{HClO}(\mathrm{aq})+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}(\mathrm{aq}) \leftrightarrow \mathrm{ClO}_{2}^{-}(\mathrm{aq})+\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq})
$$

11. The equilibrium constant for the reaction represented by the equation above is greater than 1.0 . Which of the following gives the correct relative strength of the acids and bases in the reaction?

## Acids

a. $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}>\mathrm{HClO}$
b. $\mathrm{HClO}>\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
c. $\mathrm{HClO}>\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
d. $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}>\mathrm{HClO}$

## Bases

$$
\mathrm{ClO}_{2}^{-}>\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}
$$

$$
\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}>\mathrm{ClO}_{2}^{-}
$$

$$
\mathrm{ClO}_{2}^{-}>\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}
$$

$$
\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}>\mathrm{ClO}_{2}^{-}
$$

12. Which of the following will change the value of $K_{w}$ ?
a. increasing pH
c. increasing temperature
b. increasing pOH
d. $\mathrm{K}_{\mathrm{w}}$ is a constant and can never change
13. What is the conjugate acid and the conjugate base of $\mathrm{HPO}_{4}{ }^{2-}$ ?

## Conjugate Acid Conjugate Base

a. $\mathrm{PO}_{4}{ }^{3-}$
$\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$
b. $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$
$\mathrm{PO}_{4}{ }^{3-}$
c. $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$
$\mathrm{H}_{3} \mathrm{PO}_{4}$
d. $\mathrm{H}_{3} \mathrm{PO}_{4}$
$\mathrm{PO}_{4}{ }^{3-}$
14. When comparing 1.0 M solutions of bases, the base with the lowest $\left[\mathrm{OH}^{-}\right]$is the
a. weakest base and it has the largest $K_{b}$ value.
b. strongest base and it has the largest $K_{b}$ value.
c. weakest base and it has the smallest $K_{b}$ value.
d. strongest base and it has the smallest $K_{b}$ value.
15. What is the concentration of $\mathrm{Sr}(\mathrm{OH})_{2}$ in a solution with a $\mathrm{pH}=11.00$ ?
a. $\quad 2.0 \times 10^{-11} \mathrm{M}$
b. $\quad 1.0 \times 10^{-11} \mathrm{M}$
C. $5.0 \times 10^{-4} \mathrm{M}$
d. $\quad 1.0 \times 10^{-3} \mathrm{M}$

Consider the simple dissociation of water:

$$
\mathrm{H}-\mathrm{OH} \rightleftharpoons \mathrm{H}^{+}+\mathrm{OH}^{-}
$$

1. Is the dissociation of water an endothermic or exothermic process? Why? (Hint: is a bond breaking or forming?)
2. Rewrite the dissociation of water as a thermochemical equation:
3. If you cool a solution of pure water,
a. which direction should the reaction shift and why?
b. would you expect $K_{w}$ to increase, decrease, or stay the same? Why?
c. would you expect $\left[\mathrm{H}^{+}\right]$to increase, decrease, or stay the same? Why?
d. would you expect pH to increase, decrease, or stay the same? $\qquad$
e. would you expect $\left[\mathrm{OH}^{-}\right]$to increase, decrease, or stay the same? Why?
f. would you expect pOH to increase, decrease, or stay the same? $\qquad$
g. does the equation $\mathrm{pH}+\mathrm{pOH}=14$ still hold true? Why or why not? Why?
4. If you heat a solution of pure water,
a. Would you expect pH to increase, decrease, or stay the same? $\qquad$
b. Does this mean your solution of water is now more acidic, more basic, or still neutral? Explain.
$\qquad$ thermic!

## Estimations with pH and pOH : so much pHun!

Quick Reminder: a logarithm is the power to which a number must be raised in order to get some other number, or, more formally, a logarithm is the inverse function of an exponent.

This is great - it means that $\log \left(\mathbf{1} \boldsymbol{x} \mathbf{1 0}^{\boldsymbol{x}}\right)=x \quad$ by definition!

$$
\text { Thus, } \quad \mathbf{p H}=-\log \left(1 x \mathbf{1 0}^{-x}\right)=x
$$

## Let's Practice with Pretty Numbers!

|  | $\left[\mathrm{H}_{3} \mathbf{O}^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ | pOH | pH |
| :---: | :--- | :--- | :---: | :---: |
| 1. |  |  | 4.0 |  |
| 2. |  | $0.100 \mathrm{M}=$ |  |  |
| 3. | $0.010 \mathrm{M}=$ |  |  |  |
| 4. |  |  |  | 10.00 |
| 5. |  |  |  |  |

But what about when the numbers aren't so pretty? Round to the nearest exponent!

| Concentration | Rounded Concentration | Concentration | Rounded Concentration |
| :---: | :---: | :---: | :---: |
| $3.95 \times 10^{-2} \mathrm{M}$ |  | $8.9 \times 10^{-11} \mathrm{M}$ |  |
| $5.2 \times 10^{-8} \mathrm{M}$ |  | $4.01 \times 10^{-9} \mathrm{M}$ |  |

## Let's Practice!

|  |  | $\left[\mathrm{H}_{3} \mathbf{}^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ | pOH |
| :---: | :---: | :---: | :---: | :---: |
| 1. |  |  | 4.67 | pH |
|  |  |  |  |  |
| 2. |  | $0.600 \mathrm{M}=$ |  |  |
| 3. | $0.004 \mathrm{M}=$ |  |  |  |
| 4. |  |  |  |  |
| 5. |  |  |  |  |

## Dilution Calculations: Water, water everywhere

Dilution: adding water to a concentrated solution to decrease the molarity

- Stock solutions: concentrated solutions that labs purchase to save time and space in the laboratory.
- _____ is then added to the stock solution to achieve the desired molarity.

Remember: when diluting solutions with pure $\qquad$ , the number of moles of solute do $\qquad$ change.

## The Dilution Equation

$M_{1} V_{1}=M_{2} V_{2}$

Stock solution
before dilution


The two beakers contain the same number of moles of solute.

For the dilution of acidic and basic solutions, it's important to be able to do simple estimations without a calculator! For example,

1. Doubling the volume of solution by adding an amount of distilled water $\qquad$ to the original volume of solution will decrease the concentration by $\qquad$ .
2. Increasing the volume of solution by adding $\qquad$ parts distilled water to $\qquad$ part original solution with decrease the concentration by a factor of $\qquad$ .

## Guided Practice

1. Consider a $200 . \mathrm{mL}$ solution of 0.200 M HBr after the addition of $200 . \mathrm{mL}$ of distilled water.
a. What will the new concentration of HBr be?
b. What will be the pH of the new solution?
2. Consider a $100 . \mathrm{mL}$ solution of 1.0 M LiOH after the addition of $900 . \mathrm{mL}$ of distilled water.
a. What will the new concentration of LiOH be?
b. What will be the pH of the new solution?

## Multiple Choice Practice

3. How can 100. mL of sodium hydroxide solution with a pH of 13.00 be converted to a sodium hydroxide solution with a pH of 12.00 ?
a. By diluting the solution with distilled water to a total volume of 1.00 L .
b. By adding $100 . \mathrm{mL}$ of 0.10 M HCl .
c. By diluting the solution with distilled water to a total volume of $200 . \mathrm{mL}$
d. By adding $100 . \mathrm{mL}$ of 0.10 M NaOH
4. The pH of a $500 . \mathrm{mL}$ solution of 0.60 M HCl if $500 . \mathrm{mL}$ of distilled water is added to the solution is closest to:
a. 0
b. 1
c. 3
d. 6
5. How many liters of distilled water must be added to 1 liter of an aqueous solution of HCl with a pH of 1 to create a solution with a pH of 2 ?
a. 0.1 L
b. 0.9 L
c. 2 L
d. 9 L
6. Which change in the $\mathrm{H}^{+}$ion concentration of an aqueous solution represents a decrease of one unit on the pH scale?
a. a tenfold increase
c. a hundredfold increase
b. a tenfold decrease
d. a hundredfold decrease
7. Four different acids are added to beakers of water, and the following diagrams represent the species present in each solution at equilibrium. Which acid has the highest pH ?

a. Acid 1

b. Acid 2

c. Acid 3

d. Acid 4
8. Estimate the pH of a $100 . \mathrm{mL}$ solution of 0.01 M NaOH if $900 . \mathrm{mL}$ of distilled water is added to the solution.
a. 2
b. 3
c. 11
d. 12
9. A bottle of water is left outside early in the morning. The bottle warms gradually over the course of the day. What happens to the pH of the water as the bottle warms?
a. Nothing; pure water always has a pH of 7.00 .
b. Nothing; the volume would have to change in order for any ion concentration to change.
c. It will increase because the concentration of $\mathrm{H}^{+}$is increasing.
d. It will decrease because the auto-ionization of water is an endothermic process.
10. Solution $A$ has a pH of 7 , and solution $B$ has a pOH of 9 . Which solution has a higher concentration of hydroxide ions?
a. Solution A
c. They have the same concentration of hydroxide ions.
b. Solution B
d. The concentration of hydroxide ions cannot be determined.

$$
\mathrm{ClO}_{2}^{-}(\mathrm{aq})+\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq}) \leftrightarrow \mathrm{HClO}(\mathrm{aq})+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}(\mathrm{aq})
$$

11. The equilibrium constant for the reaction represented by the equation above is less than 1.0. Which of the following gives the correct relative strength of the acids and bases in the reaction?

## Acids

## Bases

a. $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}>\mathrm{HClO}$
$\mathrm{ClO}_{2}{ }^{-}>\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$
b. $\mathrm{HClO}>\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
$\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}>\mathrm{ClO}_{2}^{-}$
c. $\mathrm{HClO}>\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
$\mathrm{ClO}_{2}^{-}>\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$
d. $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}>\mathrm{HClO}$
$\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}>\mathrm{ClO}_{2}{ }^{-}$

## Percent lonization

Percent lonization: percentage of acid molecules that $\qquad$ (ionize) when dissolved in water
$\rightarrow$ Another way to measure acid strength!

$$
\% \text { Ionization }=\frac{\text { molarity of ionized acid }}{\text { initial molarity of acid }} \times 100=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]_{\text {equil }}}{[\mathrm{HA}]_{0}} \times 100
$$

$$
\mathrm{HA}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \leftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{A}^{-}(a q)
$$

## Effect of Dilution on Percent Ionization

- Diluting an acid will $\qquad$ the percent ionization.
- A more concentrated acid will $\qquad$ the percent ionization.


In summary: we now know 5 ways to compare acid strength!

| Various Ways to Describe Acid Strength |  |  |
| :--- | :---: | :---: |
| Property | Strong Acid | Weak Acid |
| Ionization constant ( $\mathrm{K}_{\mathrm{a}}$ ) value | $\mathrm{K}_{\mathrm{a}}$ is large | $\mathrm{K}_{\mathrm{a}}$ is small |
| Percent lonization | \% lonization $=100 \%$ | \% lonization << $100 \%$ |
| Position of the dissociation <br> (ionization) equilibrium | Far to the right | Far to the left |
| Equilibrium concentration of $\mathrm{H}^{+}$when <br> compared to original [HA] | $\left[\mathrm{H}^{+}\right] \approx[\mathrm{HA}]_{0}$ | $\left[\mathrm{H}^{+}\right] \ll[\mathrm{HA}]_{0}$ |
| Strength of conjugate base compared <br> with that of water ( $\mathrm{K}_{\mathrm{b}}$ value of <br> conjugate base) | $\mathrm{A}^{-}$much weaker base than $\mathrm{H}_{2} \mathrm{O}$ <br> $\mathrm{K}_{\mathrm{b}}$ (conjugate base) is small/weak | $\mathrm{A}^{-}$much stronger base than $\mathrm{H}_{2} \mathrm{O}$ <br> $\mathrm{K}_{\mathrm{b}}$ (conjugate base) is large/strong |

## pH Calculations with Weak Acids and Bases: Yummy RICE!

Unlike strong acids and bases, weak acids and bases do $\qquad$ dissociate completely, so calculation of pH or pOH for these solutions requires the ability to calculate delicious equilibrium concentrations of $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$, using RICE tables and $K_{a}$ or $K_{b}$ values.

Example 1: Calculate the pH of a 0.10 M solution of acetic acid, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$. The $\mathrm{K}_{\mathrm{a}}$ of acetic acid is $1.8 \times 10^{-5}$.

Example 2: A 0.200 M weak acid solution (HA) has a pH of 4.25 . Find the ionization constant for the acid.

Example 3: Determine the $\left[\mathrm{OH}^{-}\right]$and pH of a $0.100 \mathrm{M} \mathrm{NH}_{3}$ solution. The $\mathrm{K}_{\mathrm{b}}$ of $\mathrm{NH}_{3}$ is $1.76 \times 10^{-5}$.

Example 4: Calculate the percent ionization of a $2.5 \mathrm{M} \mathrm{HNO}_{2}$ solution ( $\mathrm{K}_{\mathrm{a}}=4.0 \times 10^{-4}$ ).

1. What is the pH of a 0.200 M solution of $\mathrm{HNO}_{2}$ ? The $\mathrm{K}_{\mathrm{a}}$ of $\mathrm{HNO}_{2}$ is $4.6 \times 10^{-4}$.
2. The carbonate ion, $\mathrm{CO}_{3}{ }^{2-}$, is a weak base $\left(\mathrm{K}_{\mathrm{b}}=2.13 \times 10^{-4}\right)$. Calculate the pH of a 1.3 M carbonate solution.
3. The pH of a 0.010 M solution of benzoic acid, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}$ (a monoprotic acid), is 3.09 . What is the ionization constant for benzoic acid?

## Multiple Choice Practice

1. Which of the following could be added to an aqueous solution of the weak acid HF to increase the percent dissociation?
a. $\mathrm{NaF}(\mathrm{s})$
b. $\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$
c. $\mathrm{NaOH}(\mathrm{s})$
d. $\mathrm{NH}_{3}(\mathrm{aq})$
2. Which of the following solutions will have the highest pH ?
a. 0.20 M HCl
b. $\quad 0.10 \mathrm{M} \mathrm{HCl}$
c. $\quad 0.20 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
d. $\quad 0.10 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
3. A weak monoprotic acid has an ionization constant of $1.0 \times 10^{-8}$. What will be the percent dissociation of the acid in a 4.0-molar solution?
a. $0.8 \%$
b. $0.05 \%$
c. $0.005 \%$
d. $0.0002 \%$
4. Which of the following solutions has the greatest percent ionization?
a. $0.20 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
b. $\quad 0.10 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
c. $\quad 0.050 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
d. $\quad 0.010 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
5. A weak monoprotic acid, HA , has a pH of 5.00 when $[\mathrm{HA}]=0.25 \mathrm{M}$. Calculate the ionization constant of this acid.
a. $2.5 \times 10^{-5}$
b. $2.5 \times 10^{-10}$
c. $4.0 \times 10^{-10}$
d. $4.0 \times 10^{-11}$
6. Acetic acid has an ionization constant that is approximately equal to $2.0 \times 10^{-5}$. What will be the percent dissociation of acetic acid in a 0.20 M solution?
a. $1.0 \%$
b. $0.20 \%$
c. $0.010 \%$
d. $0.0020 \%$
7. Which of the following solutions has the smallest percent ionization?
a. $\quad 0.20 \mathrm{M} \mathrm{HNO}_{2}$
b. $\quad 0.10 \mathrm{M} \mathrm{HNO}_{2}$
c. $\quad 0.20 \mathrm{M} \mathrm{HNO}_{3}$
d. $\quad 0.10 \mathrm{M} \mathrm{HNO}_{3}$
8. A 1-molar solution of a very weak monoprotic acid has a pH of 5 . What is the value of $\mathrm{K}_{\mathrm{a}}$ for the acid?
a. $1 \times 10^{-10}$
b. $1 \times 10^{-7}$
c. $1 \times 10^{-5}$
d. $1 \times 10^{-2}$

## Let's Mix it Up: Calculating pH of a Mixture of Weak Acids

Determination of the pH of a Mixture of Weak Acids: Luckily, only the acid with the $\qquad$ $K_{a}$ will contribute an appreciable $\left[\mathrm{H}^{+}\right]$. Determine the pH based on this acid and ignore all others!

- This is what we've been doing with the autoionization of water. Although hydronium ions are being produced through the equation below, $\mathrm{K}_{\mathrm{w}}=1 \times 10^{-14}$ which is usually $\ll \mathrm{K}_{\mathrm{a}}$ for other acids in solution.

$$
2 \mathrm{H}_{2} \mathrm{O}(I) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{OH}^{-}(a q)
$$

## Let's Try!

1. A solution contains $1.00 \mathrm{M} \mathrm{HCN}\left(\mathrm{K}_{\mathrm{a}}=6.2 \times 10^{-10}\right)$ and $5.00 \mathrm{M} \mathrm{HNO}_{2}\left(\mathrm{~K}_{\mathrm{a}}=4.0 \times 10^{-4}\right)$. Calculate the pH of the solution.

## Determination of the pH of Polyprotic Acids:

- Acids with more than one ionizable hydrogen will ionize in steps, and each dissociation has its own $\qquad$ value.
- As the negative charge on the acid increases it becomes more difficult to remove the positively charged proton.
- As each $\mathrm{H}^{+}$is removed, the remaining acid gets weaker and therefore has a smaller $\mathrm{K}_{\mathrm{a}}$.

$$
\mathrm{K}_{\mathrm{a} 1}>\mathrm{K}_{\mathrm{a} 2}>\mathrm{K}_{\mathrm{a} 3}
$$

Generally, the difference between $K_{a}$ values is great enough so the second ionization doesn't affect the pH value!
For most polyprotic pH problems, just do first ionization.

## Exception: $\mathrm{H}_{2} \mathrm{SO}_{4}$

- The ionization constants for $\mathrm{H}_{2} \mathrm{SO}_{4}$ are listed below:

$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{SO}_{4}+\mathrm{H}_{2} \mathrm{O} \vec{r} \\
& \mathrm{HSO}_{4}^{-}+\mathrm{HSO}_{2} \mathrm{O} \rightleftharpoons+\mathrm{H}_{3} \mathrm{C}^{4} \\
& \mathrm{SO}_{4}^{2-1}+\mathrm{H}_{3} \mathrm{O}^{+}
\end{aligned} \quad \mathrm{K} \mathrm{~K}_{\mathrm{a} 2}=1.2 \times 10^{-2}
$$

both present in solution!

- The
- Because sulfuric acid is a strong acid in its first dissociation, use $\left[\mathrm{H}_{2} \mathrm{SO}_{4}\right]_{\text {nintial }}=\left[\mathrm{HSO}_{4}^{-}\right]_{\text {equil }}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]_{\text {equil }}$
- Because sulfuric acid is a weak acid in its second dissociation, the second dissociation will contribute a negligible amount for concentrations less than 1.0 M .
- Luckily, the AP test only considers quantitative calculations for $\left[\mathrm{H}_{2} \mathrm{SO}_{4}\right]<1.0 \mathrm{M}$. ©

1. Sulfurous acid, $\mathrm{H}_{2} \mathrm{SO}_{3}$, is a diprotic acid with $\mathrm{K}_{1}=1.3 \times 10^{-2}$ and $\mathrm{K}_{2}=6.2 \times 10^{-8}$. Which of the following best represents the relative concentrations of ions in a 2.0 M solution of $\mathrm{H}_{2} \mathrm{SO}_{3}$ ?
a. $\left[\mathrm{H}_{2} \mathrm{SO}_{3}\right]<\left[\mathrm{SO}_{3}{ }^{2-}\right]=\left[\mathrm{HSO}_{3}{ }^{-}\right]$
b. $\left[\mathrm{SO}_{3}{ }^{2-}\right]<\left[\mathrm{HSO}_{3}^{-}\right] \ll\left[\mathrm{H}_{2} \mathrm{SO}_{3}\right]$
c. $\left[\mathrm{H}_{2} \mathrm{SO}_{3}\right]<\left[\mathrm{HSO}_{3}^{-}\right]<\left[\mathrm{SO}_{3}{ }^{2-}\right]$
d. $\left[\mathrm{H}_{2} \mathrm{SO}_{3}\right]=\left[\mathrm{SO}_{3}{ }^{2-}\right]<\left[\mathrm{HSO}_{3}{ }^{-}\right]$
2. Which of the following ions will have the lowest concentration in a 0.50 -molar solution of $\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})$ ?
a. $\mathrm{SO}_{4}{ }^{2-}$
b. $\mathrm{HSO}_{4}^{-}$
c. $\mathrm{H}_{2} \mathrm{SO}_{4}$
d. $\mathrm{H}_{3} \mathrm{O}^{+}$
3. Which of the following chemicals will have the greatest concentration in a 0.02 -molar solution of $\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})$ ?
a. $\mathrm{SO}_{4}{ }^{2-}$
b. $\mathrm{HSO}_{4}^{-}$
c. $\mathrm{H}_{2} \mathrm{SO}_{4}$
d. $\mathrm{OH}^{-}$
4. As the concentration of a weak acid increases, its percent dissociation $\qquad$ and the pH $\qquad$ .
a. increases, increases
c. increases, decreases
b. decreases, decreases
d. decreases, increases
5. The acid dissociation constants of phosphoric acid $\left(\mathrm{H}_{3} \mathrm{PO}_{4}\right)$ are $\mathrm{K}_{\mathrm{a} 1}=8 \times 10^{-3}, \mathrm{~K}_{\mathrm{a} 2}=6 \times 10^{-8}$ and $\mathrm{K}_{\mathrm{a} 3}=4 \times 10^{-13}$ at 298 K . What is the pH of a 5.0 M aqueous solution of phosphoric acid?
a. 0.70
b. $\quad 1.7$
c. 2.7
d. 3.7
6. A 0.10 M acid solution has a pH of 1.00 . The acid could be:
a. $\mathrm{HNO}_{3}$
b. $\mathrm{H}_{2} \mathrm{SO}_{3}$
c. $\mathrm{CH}_{3} \mathrm{COOH}$
d. $\mathrm{HClO}_{3}$
7. When a solution of pure water has a pH of 7.5 , the temperature is $\qquad$ and the solution is $\qquad$ .
a. less than $25^{\circ} \mathrm{C}$, basic
c. greater than $25^{\circ} \mathrm{C}$, basic
b. less than $25^{\circ} \mathrm{C}$, neutral
d. greater than $25^{\circ} \mathrm{C}$, neutral

Between any acid/conjugate base pair, the following relationships will always be true:

$$
\begin{gathered}
K_{\mathrm{w}}=K_{\mathrm{a}} \times K_{\mathrm{b}} \\
K_{\mathrm{w}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} \quad \text { at } 25^{\circ} \mathrm{C}
\end{gathered}
$$

And because of yummy math, this means:

$$
\begin{gathered}
-\log K_{\mathrm{w}}=-\log K_{\mathrm{a}}-\log K_{\mathrm{b}} \\
14=\mathrm{p} K_{a}+\mathrm{p} K_{b} \quad \text { at } 25^{\circ} \mathrm{C}
\end{gathered}
$$

Example 1: The $\mathrm{K}_{\mathrm{a}}$ for $\mathrm{HCO}_{3}{ }^{-}$is $4.7 \times 10^{-11}$. What is the conjugate base and the value of $\mathrm{K}_{\mathrm{b}}$ and $\mathrm{pK} \mathrm{K}_{\mathrm{b}}$ ?

Example 2: The $\mathrm{pK}_{\mathrm{b}}$ for $\mathrm{CN}^{-}$is 4.80. What is the conjugate acid and its $\mathrm{K}_{\mathrm{a}}$ value?

## Neutralization Reactions

Neutralization reaction: when an Arrhenius acid and base react to produce a $\qquad$ and $\qquad$

- $\mathrm{H}^{+}+\mathrm{OH}^{-} \rightarrow$ $\qquad$ $=$ $\qquad$

General Neutralization Reaction:

$$
\begin{aligned}
\mathrm{HX}(\mathrm{aq})+\mathrm{MOH}(\mathrm{aq}) & \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{MX}(\mathrm{aq}) \\
\text { acid }+ \text { base } & \rightarrow \text { water }+ \text { salt }
\end{aligned}
$$

Net lonic:
Let's Try! Complete and balance the following neutralization reactions.

1. $\qquad$ $\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})+$ $\qquad$ $\mathrm{NaOH}(\mathrm{aq}) \rightarrow$
2. What is the net ionic for the reaction shown above?

## Net Ionic Equations for Weak/Strong Neutralization Reactions

In the net ionic equation for a weak acid/base + a strong base/acid, the weak species will $\qquad$ dissociate!

Wait, but why? Remember that a weak species is defined to be weak BECAUSE it doesn't dissociate in solution, so we need to accurately represent that in our net ionic equation.
*Note about arrows: if either the acid or base reactant is strong, use a one-way (completion) arrow. Otherwise, use an equilibrium (both ways) arrow.
3. Write the balanced neutralization reaction for ammonia, $\mathrm{NH}_{3}$, and $\mathrm{HClO}_{4}$.
4. What is the net ionic equation for the reaction in \#2?
5. Write the balanced neutralization reaction for acetic acid, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, and $\mathrm{Sr}(\mathrm{OH})_{2}$.
6. What is the net ionic equation for the reaction in \#5?

## More Practice!

7. $\quad \_\mathrm{Mg}(\mathrm{OH})_{2}(\mathrm{aq})+\ldots \mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{aq}) \rightarrow$
8. What is the net ionic for the reaction in \#7?
9. $\qquad$ $\mathrm{HNO}_{3}(\mathrm{aq})+$ $\qquad$ $\mathrm{NH}_{3}(\mathrm{aq}) \rightarrow$
10. What is the net ionic for the reaction in \#9?

## Feeling Salty? Acid-Base Properties of Salts

Any salt can be written as the $\qquad$ of an acid-base neutralization rxn.

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{M}(\mathrm{OH})\left((\mathrm{aq}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{MA}(\mathrm{aq}) \longleftarrow\right. \text { salt }
$$

Salts are $\qquad$ always neutral! Some salts hydrolyze water to produce aqueous solutions with pHs other than 7.00.

To determine if and how a salt will affect the pH of a solution, you must determine whether or not the salt ions will hydrolyze ( $\qquad$ ) water to any significant extent.

Hydrolysis reaction of the conjugate $\qquad$ of the weak acid HA:

$$
\begin{gathered}
\mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HA}+\mathrm{OH}^{-} \\
\text {OH- }{ }^{-} \text {produced = alkaline solution: } \mathrm{pH}>7
\end{gathered}
$$

Hydrolysis reaction of the conjugate $\qquad$ of the weak base $\mathbf{M}$ :

$$
\mathrm{MH}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{M}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

$$
\mathrm{H}^{+} \text {produced = acidic solution: } \mathrm{pH}<7
$$

## How to Tell if an Ion will Hydrolyze Water

1. If given an anion (-),
a. Add $\qquad$
b. Ask: is this conjugate acid a strong acid or weak acid?
i. Conjugate $=$ strong acid ? $\qquad$ water hydrolysis
ii. Conjugate = weak acid? $\qquad$ water hydrolysis
2. If given a cation (+),
a. Add $\qquad$
b. Ask: is this conjugate base a strong base or weak base?
i. Conjugate $=$ strong base ? $\qquad$ water hydrolysis
ii. Conjugate = weak base? $\qquad$ water hydrolysis

Let's Practice! If the ion below will hydrolyze water, write the hydrolysis reaction that occurs, and determine if the solution is acidic or basic.

1. Will $\mathrm{HCO}_{3}^{-}$hydrolyze water?
2. Will $\mathrm{NH}_{4}{ }^{+}$hydrolyze water?
3. Will $\mathrm{NO}_{3}{ }^{-}$hydrolyze water?

Feeling Salty? How to recognize a salt
Remember, in chemistry, salts are neutral $\qquad$ compounds (not acids or bases, although an acid or base can be made into a salt (O)).
$\rightarrow$ Look for the presence of commonly $\qquad$ cations (like alkali metal cations, especially $\qquad$ ) and commonly soluble anions (like halogen anions, especially $\qquad$ ).

| Reactants | Strong Acid + Strong Base | Weak Acid + Strong Base | Strong Acid + Weak Base | $\underline{\text { Weak Acid }+\underline{\text { Weak }} \text { Base }}$ |
| :---: | :---: | :---: | :---: | :---: |
| Product <br> Salt: | neutral salt | basic salt | acidic salt | $\mathrm{K}_{\mathrm{a}}>\mathrm{K}_{\mathrm{b}}$ acidic salt |
| $\mathrm{K}_{\mathrm{b}}>\mathrm{K}_{\mathrm{a}}$ basic salt |  |  |  |  |

## More Practice!

1. Which of the following are salts? Circle them.

$$
\mathrm{NH}_{3}, \mathrm{NH}_{4} \mathrm{Cl}, \mathrm{H}_{2} \mathrm{PO}_{4}^{-}, \mathrm{FeBr}_{2}, \mathrm{NaOH}, \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3}^{+}, \mathrm{HCl}, \mathrm{NaHCO}_{3}
$$

2. Which of the following ions will hydrolyze water? Circle them

$$
\mathrm{NH}_{3}, \quad \mathrm{Cl}^{-}, \quad \mathrm{H}_{2} \mathrm{PO}_{4}^{-}, \quad \mathrm{ClO}_{4}^{-}, \mathrm{Na}^{+}, \mathrm{F}^{-}, \quad \mathrm{NO}_{3}^{-}, \mathrm{ClO}_{2}^{-}
$$

3. Write the hydrolysis reaction for each of the following ions, and determine if it will produce an acidic or basic solution:
a. $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}$
b. $\mathrm{CO}_{3}{ }^{2-}$
4. Determine if the solution formed from each salt below is acidic, basic, or neutral.
a. $\mathrm{SrCl}_{2}$
b. $\mathrm{AlBr}_{3}$
c. $\mathrm{NH}_{4} \mathrm{NO}_{3}$
d. $\mathrm{NaCHO}_{2}$

## Calculating the pH of a Salt Solution: Salty and Delicious!

To calculate the pH of a salt solution, follow the thrilling three step process shown below!

1. Identify the ion of the salt that is acting as a $\qquad$ acid or base. (This will be the ion that came from the weak acid/base in the neutralization reaction).
a. If the ion is acting as a weak $\qquad$ , write the hydrolysis reaction of the ion with water and set up a RICE table using the $\qquad$ expression.
i. The hydrolysis reaction for an acidic salt will always be the $\qquad$ reacting with water to
form $\qquad$ and a weak $\qquad$ _.
b. If the ion is acting as a weak $\qquad$ , write the hydrolysis reaction of the ion with water and set up a RICE table using the $\qquad$ expression.
i. The hydrolysis reaction for an basic salt will always be the $\qquad$ reacting with water to form $\qquad$ and a weak $\qquad$ .
c. WATCH OUT: A classic trick question is to only provide $K_{a}$ values even when $a K_{b}$ value is needed. Use the relationship below to convert if needed!

$$
1 \times 10^{-14}=K_{\mathrm{a}} \times K_{\mathrm{b}}
$$

2. Use one of the equations below to solve for $\qquad$ or $\qquad$ .

$$
K_{a}=\frac{[x][x]}{[H A]_{0}} \text { where } \mathrm{x}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \quad \text { or } \quad K_{b}=\frac{[x][x]}{[B]_{0}} \text { where } \mathrm{x}=\left[\mathrm{OH}^{-}\right]
$$

3. Once you've calculated $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$or $\left[\mathrm{OH}^{-}\right]$, solve for $\qquad$ or $\qquad$ .

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \quad \text { or } \quad \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]
$$

## Guided Practice

1. Calculate the pH of a $0.10 \mathrm{M} \mathrm{NH}{ }_{4} \mathrm{Cl}$ solution. The $\mathrm{K}_{\mathrm{a}}$ value for $\mathrm{NH}_{4}{ }^{+}$is $5.6 \times 10^{-10}$.
2. Calculate the pH of a 0.30 M NaF solution. The $\mathrm{K}_{\mathrm{a}}$ value for HF is $7.2 \times 10^{-4}$.

## Multiple Choice Practice

3. What is the pH of a $1.0 \times 10^{-2} \mathrm{M}$ solution of NaCN ? (For $\mathrm{HCN}, \mathrm{K}_{\mathrm{a}}=1.0 \times 10^{-10}$ ).
a. between 0 and 3
c. between 7 and 10
b. between 3 and 7
d. between 10 and 14

$$
650 \mathrm{~kJ}+\mathrm{HCO}_{3}^{-}(\mathrm{aq})+\mathrm{HC}_{2} \mathrm{O}_{4}^{-}(\mathrm{aq}) \leftrightarrow \mathrm{CO}_{3}^{2-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}(\mathrm{aq})
$$

4. If $K>1$, all of the following statements are true about the reaction above EXCEPT:
a. $\mathrm{HC}_{2} \mathrm{O}_{4}^{-}$is a weaker base than $\mathrm{CO}_{3}{ }^{2-}$.
b. $\mathrm{HCO}_{3}^{-}$and $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ are both acting as acids in the reaction.
c. The reaction lies far to the right (favors products).
d. Lowering the temperature of the solution will decrease the value of $K$.
5. Which of the following would form a basic solution when dissolved in water?
a. HCl
b. LiCl
c. $\quad \mathrm{NH}_{4} \mathrm{Cl}$
d. $\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
6. Estimate the pH of a $1.0 \times 10^{-5} \mathrm{M}$ solution of the weak base $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}$ ? $\left(\mathrm{K}_{\mathrm{b}}=4.0 \times 10^{-10}\right)$.
a. between 0 and 3
c. between 7 and 10
b. between 3 and 7
d. between 10 and 14
7. Which of the following would a solution with the lowest pH ?
a. NaOH
b. LiCl
c. $\mathrm{HClO}_{4}$
d. $\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
8. A solution of a monoprotic acid, HA, has a pH of 5.00. Calculate the acid dissociation constant for the weak acid if the solution has a molar concentration of 0.50 M .
a. $2.0 \times 10^{-11}$
b. $2.0 \times 10^{-10}$
c. $2.0 \times 10^{-7}$
d. $2.0 \times 10^{-6}$
9. Which of the following can act as an amphoteric species?
I. $\mathrm{SO}_{4}{ }^{2-}$
II. $\mathrm{HCO}_{3}{ }^{-}$
III. $\mathrm{NH}_{4}{ }^{+}$
a. I only
b. II only
c. II and III only
d. I, II, and III
10. What is the equilibrium expression for the hydrolysis of $\mathrm{NH}_{4} \mathrm{Cl}$ ?
a. $K=\frac{[\mathrm{HCl}]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{Cl}^{-}\right]}$
b. $K=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{NH}_{4}{ }^{+}\right]}$
c. $K=\frac{\left[\mathrm{Cl}^{-}\right]}{[\mathrm{HCl}]\left[\mathrm{OH}^{-}\right]}$
d. $\quad K=\frac{\left[\mathrm{NH}_{4}{ }^{+}\right]}{\left[\mathrm{NH}_{3}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}$
11. The pH of a 0.10 M KOH solution is:
a. $\quad 0.10$
b. 1.00
c. $\quad 13.00$
d. 14.00

Purpose: Confirm the effects of salt hydrolysis on acid/base properties of a salt solution.
Table 14.6 | Acid-Base Properties of Various Types of Salts

| Type of Salt | Examples | Comment | pH of Solution |
| :---: | :---: | :---: | :---: |
| Cation is from strong base; anion is from strong acid | $\mathrm{KCl}, \mathrm{KNO}_{3}$, $\mathrm{NaCl}, \mathrm{NaNO}_{3}$ | Neither acts as an acid or a base | Neutral |
| Cation is from strong base; anion is from weak acid | $\begin{aligned} & \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}, \\ & \mathrm{KCN}, \mathrm{NaF} \end{aligned}$ | Anion acts as a base; cation has no effect on pH | Basic |
| Cation is conjugate acid of weak base; anion is from strong acid | $\begin{aligned} & \mathrm{NH}_{4} \mathrm{Cl}, \\ & \mathrm{NH}_{4} \mathrm{NO}_{3} \end{aligned}$ | Cation acts as an acid; anion has no effect on pH | Acidic |
| Cation is conjugate acid of weak base; anion is conjugate base of weak acid | $\begin{gathered} \mathrm{NH}_{4} \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2} \\ \mathrm{NH}_{4} \mathrm{CN} \end{gathered}$ | Cation acts as an acid; anion acts as a base | $\begin{aligned} & \text { Acidic if } K_{\mathrm{a}}>K_{\mathrm{b}}, \\ & \text { basic if } K_{\mathrm{b}}>K_{\mathrm{a}}, \\ & \text { neutral if } K_{\mathrm{a}}=K_{\mathrm{b}} \end{aligned}$ |
| Cation is highly charged metal ion; anion is from strong acid | $\mathrm{Al}\left(\mathrm{NO}_{3}\right)_{3}, \mathrm{FeCl}_{3}$ | Hydrated cation acts as an acid; anion has no effect on pH | Acidic |

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Shortcut (non-thinking) way to figure out acid/base properties of salt:

## *Great for MC, BAD for FR explanations*

- If parent acid is strong and parent base is weak, the salt solution is acidic (strongwins)
- If parent acid is weak and parent base is strong, the salt solution is basic (strongwins)
- If parent acid and base are both strong, the salt solution is neutral (tie)
- If parent acid and base are both weak, you cannot predict $A / B / N$ without knowing $K_{a}$ and $K_{b}$ values for the cation and anion. Whichever one has the bigger $K$ is the way the salt solution will go. If they happen to be the same, it is neutral.


## Table of $\mathrm{K}_{\mathrm{a}}$ Values

| acid | $\mathrm{K}_{\mathrm{a}}$ |
| :---: | :---: |
| $\mathrm{NH}_{4}^{+}$ | $5.6 \times 10^{-10}$ |
| $\mathrm{H}_{2} \mathrm{CO}_{3}$ | $4.5 \times 10^{-7}$ |
| $\mathrm{Al}^{3+}$ | $1.4 \times 10^{-5}$ |
| $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | $1.8 \times 10^{-5}$ |

## Procedure:

1. Make predictions for whether each salt solution will be acidic, basic, neutral, or unsure (cannot determine without more info). Record predictions in the data table.
2. Cover experiment surface with paper towel (to better see colors under the well plate)
3. Fill wells about halfway with each solution (after you've made your predictions).
4. Add 2 drops of universal indicator solution to each solution. (after you've made your predictions).
5. Note color of solution and approximate pH , and record both in the data table.
6. Write any applicable hydrolysis reactions to support your observations of pH .

Data Table:

| Salt | Predict: <br> A/B/N/U | Color <br> with UI | Approximate <br> $\mathbf{p H}$ | Calculated <br> $\mathbf{p H}$ | Relevant hydrolysis reaction(s): |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{NH}_{4} \mathrm{NO}_{3}$ |  |  |  |  |  |
| $\mathrm{NaHCO}_{3}$ |  |  |  |  |  |
| NaCl |  |  |  |  |  |
| $\mathrm{AlCl}_{3}$ |  |  |  |  |  |
| $\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ |  |  |  |  |  |

Analysis questions:

1. Why can sodium bicarbonate, $\mathrm{NaHCO}_{3}$, be used to neutralize acid spills?
2. Use the $\mathrm{K}_{\mathrm{a}}$ values from the table to determine whether a solution of $\mathrm{NH}_{4} \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ will be acidic, basic, or neutral. Remember, $\mathrm{K}_{\mathrm{a}} \times \mathrm{K}_{\mathrm{b}}=1.00 \times 10^{-14}$ for any conjugate $\mathrm{A} / \mathrm{B}$ pair.
3. Calculate the pH for each salt above. Each solution is 0.10 M . Record your calculations in the data table. Show your work for one acidic salt AND for one basic salt below.

Acidic Salt pH Calculation:

Basic Salt pH Calculation:

## Buffers

Buffer: A solution that maintains a relatively $\qquad$ pH (aka relatively constant $\qquad$ _)

## if an acid or base is added

Buffers have many applications, but are especially important in biochemistry (blood, amino acids, and proteins in the body). Many biochemical reactions are pH sensitive.

## But wait... How Can a Buffer Neutralize Added Acid or Base?

Buffer solutions contain significant amounts of:
o weak acid molecules, $\qquad$
o conjugate base anion, $\qquad$

- If you add $\qquad$ to a buffer solution, the weak acid ( $\qquad$ ) reacts with it.

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{aq})
$$

- If you add $\qquad$ to a buffer solution, the conjugate base ( $\qquad$ ) reacts with it.

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



- Weak acids and their conjugate bases make $\qquad$ buffers.
- Strong acids and bases do $\qquad$ make good buffers, because their $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$ions are already dissociated into solution.
- It takes much $\qquad$ base to change the pH of a weak acid solution because there is a large reservoir of $\qquad$ weak acid.

What happens to a given buffer system when it is "attacked" with an acid or a base?

1. Acid added?
a. The conjugate base in the buffer neutralizes the added acid, producing $\qquad$ weak acid.
b. The pH of the solution will $\qquad$ slightly.

## 2. Base added?

a. The weak acid in the buffer neutralizes the added base, producing $\qquad$ conjugate base.
b. The pH of the solution will $\qquad$ slightly.

Example: Combining HF and NaF creates a buffer system containing the weak acid HF and its conjugate base, $\mathrm{F}^{-}$.
a. Write an equilibrium reaction to describe the HF/ $\mathrm{F}^{-}$buffer system.
b. Write a net ionic equation that demonstrates why the pH of this buffer would remain relatively constant if a small amount of $\mathrm{HNO}_{3}$ was added to the buffer solution.
c. Write a net ionic equation that demonstrates why the pH of this buffer would remain relatively constant if a small amount of LiOH was added to the buffer solution.

1. Combining $\mathrm{NH}_{4} \mathrm{Cl}$ and $\mathrm{NH}_{3}$ creates a buffer system containing the weak acid $\mathrm{NH}_{4}{ }^{+}$and its conjugate base, $\mathrm{NH}_{3}$.
a. Write an equilibrium reaction to describe the $\mathrm{NH}_{4}{ }^{+} / \mathrm{NH}_{3}$ buffer system.
b. Write a net ionic equation that demonstrates why the pH of this buffer would remain relatively constant if a small amount of $\mathrm{HNO}_{3}$ was added to the buffer solution.
c. Write a net ionic equation that demonstrates why the pH of this buffer would remain relatively constant if a small amount of LiOH was added to the buffer solution.

Buffer capacity is determined by how $\qquad$ acid and base can be neutralized by a buffer system.

- $\qquad$ capacity: $\qquad$ of weak acid and conjugate base present, so large amounts of added acid and base can be neutralized before the pH changes significantly.
- $\qquad$ capacity: only a small amount of weak acid and/or conjugate base is present, so only small amounts of added acid and base can be neutralized before the pH changes significantly.
*Watch out! If you add more acid than the CB present in your buffer (or more base than the acid in your buffer), you have exceeded the capacity of the buffer!

Example: A buffer system is created by combining $300 . \mathrm{mL}$ of $0.200 \mathrm{M} \mathrm{HNO}_{2}$ with $0.400 \mathrm{M} \mathrm{LiNO}_{2}$.
a. What is the maximum amount of acid that can be neutralized by the buffer system?
b. What is the maximum amount of base that can be neutralized by the buffer system?

1. A 500. mL buffer is created by combining 0.30 M ammonia, $\mathrm{NH}_{3}$, with $0.20 \mathrm{NH}_{4} \mathrm{Cl}$. Adding which of the following would destroy the buffering ability of the solution?
a. 0.13 mol HBr
b. $0.13 \mathrm{~mol} \mathrm{NH}_{4} \mathrm{Br}$
c. $\quad 0.13 \mathrm{~mol} \mathrm{LiOH}$
d. $\quad 0.13 \mathrm{~mol} \mathrm{NH}_{3}$
2. 0.50 mol of KOH is added to an $\mathrm{HF} / \mathrm{F}^{-}$buffer system containing 0.75 mol of HF and $0.60 \mathrm{~mol} \mathrm{~F}^{-}$. When equilibrium is reestablished, what happened to the system?
a. The pH increases slightly, $\left[\mathrm{HF}\right.$ ] decreases and $\left[\mathrm{F}^{-}\right]$increases.
b. The pH decreases slightly, $[\mathrm{HF}]$ increases and $\left[\mathrm{F}^{-}\right]$decreases.
c. The pH remains constant, $[\mathrm{HF}]$ decreases and $\left[\mathrm{F}^{-}\right]$increases.
d. The pH remains constant, [HF] increases and [ $\mathrm{F}^{-}$] decreases.
3. A 500. mL buffer is created by combining 0.50 M acetic acid, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, with $0.30 \mathrm{M} \mathrm{NaC} \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$. Which of the following additions would destroying the buffering capacity of the system?
a. $\quad 0.30 \mathrm{~mol} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
b. $\quad 0.30 \mathrm{~mol} \mathrm{LiC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
c. $\quad 0.20 \mathrm{~mol} \mathrm{KOH}$
d. $\quad 0.20 \mathrm{~mol} \mathrm{HBr}$

## Two Requirements for a Good Buffer:

1. Large $\qquad$ : lots of weak acid AND lots of conjugate base, or vice versa
2. $\qquad$ (or equimolar) ratio of HA:A- so buffer can neutralize $\qquad$ added acid and added base

## Identifying a Buffer

Recall the word conjugate means that the pair differs by a single proton. For example:

|  | Acid | Base | Buffer? |
| :--- | :---: | :---: | :--- |
| Example 1 | $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | $\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | Yes, weak acid and base differ by one proton. |
| Example 2 | $\mathrm{NH}_{4}{ }^{+}$ | $\mathrm{NH}_{3}$ | Yes, weak acid and base differ by one proton. |
| Example 3 | HCl | $\mathrm{Cl}^{-}$ | No, strong acids and their bases can't be buffers. |
| Example 4 | $\mathrm{H}_{2} \mathrm{CO}_{3}$ | $\mathrm{CO}_{3}{ }^{2-}$ | No, the acid and base differ by two protons. |

1. Circle all the combinations below that would make a buffer solution when mixed in equal volumes. For each solution, explain why the solution is/is not a buffer.
1.0 M HCl and 1.0 M KCl
$1.0 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ and 0.5 M NaCl
$0.5 \mathrm{M} \mathrm{HNO}_{2}$ and $1.0 \mathrm{M} \mathrm{NaNO}_{2}$
1.0 M HBrO and 1.0M LiBrO
1.0 M NH 4 Br and $0.5 \mathrm{M} \mathrm{NH}_{3}$
$1.0 \mathrm{M} \mathrm{LiHSO}_{4}$ and $0.8 \mathrm{M} \mathrm{Li}_{2} \mathrm{SO}_{4}$
2. Choose a $1: 1$ buffer from the buffers you circled above.
a. Write an equilibrium reaction to describe this buffer system. What is true about the weak acid/conjugate base ratio?
b. Write a net ionic equation to demonstrate how the buffer system would neutralize the addition of HCl to keep the pH fairly constant.
c. After the addition of HCl in part (b), what happened to the weak acid/conjugate base ratio? Explain why this occurs.

## The Buffering Shortcut: Henderson-Hasselbach Equation

Although RICE table calculations can always be used to determine $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right.$] and thus pH , there is a more $\qquad$ way. This process works because buffers are always weak acids or bases and their conjugate, so the " x is negligible" approximation will $\qquad$ be accurate: we can consider the equilibrium concentrations of the weak acid, HA , and its conjugate base, $\mathrm{A}^{-}$to be essentially $\qquad$ to their initial concentrations.

## I'm not lazy <br> 

We can derive an equation that relates the pH of a buffer solution to the initial concentration of the buffer components by rearranging the acid ionization constant expression.

$$
\begin{array}{cc}
K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[A^{-}\right]}{[H A]} \\
{\left[\mathrm{H}^{+}\right]=K_{a} \frac{[H A]}{\left[A^{-}\right]}} & \text {or } \quad\left[\mathrm{H}^{+}\right]=K_{a} \frac{[\text { Acid }]}{[\text { Base }]}
\end{array}
$$

This equation can also be written in the following format:

$$
\mathrm{pH}=\mathrm{pKa}+\log \left(\frac{\left[A^{-}\right]}{[H A]}\right) \quad \text { or } \quad \mathrm{pH}=\mathrm{pKa}+\log \left(\frac{[\text { Base }]}{[\text { Acid }]}\right)
$$

$\mathrm{K}_{\mathrm{a}}$ - is the acid dissociation constant
[Acid] - is the concentration of the substance behaving as the weak acid in the buffered solution
o Either the weak acid or the salt of the conjugate base
[Base] - is the concentration of the substance behaving as the weak base in the buffered solution
o Either the weak base or the salt of the conjugate acid

## How To Solve Buffer Problems

- If the buffer is a weak acid, HA , and its conjugate salt, $\mathrm{A}^{-}$, then $\qquad$ is the acid and $\qquad$ is the base.
- If the buffer is a weak base, B , and its conjugate salt, $\mathrm{BH}^{+}$, then $\qquad$ is the base and $\qquad$ is the acid.
o Even if the buffer uses a weak base, you still use $\qquad$ : you must calculate it first using the $K_{b}$ provided.

1. A buffered solution contains $0.250 \mathrm{M} \mathrm{NH}_{3}\left(\mathrm{~K}_{\mathrm{b}}=1.80 \times 10^{-5}\right)$, and $0.400 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}$.
a. What species is the acid and which is the base?
b. Write an equilibrium reaction to describe this buffer.
c. Calculate the pH .
2. A student makes a 0.500 L of a buffer solution of pH 3.89 by combining formic acid, HCOOH , and sodium formate, NaHCOO . The $\mathrm{K}_{\mathrm{a}}$ of formic acid is $1.8 \times 10^{-4}$.
a. Write an equilibrium reaction to describe this buffer.
b. What ratio of formic acid to sodium formate would be required to make this buffer?

## Multiple Choice

3. Acid is added to a buffer solution. When equilibrium is reestablished the buffering effect has resulted in $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$:
a. increasing slightly
c. decreasing considerably
b. decreasing slightly
d. remaining constant
4. The value of $\mathrm{K}_{\mathrm{a}}$ for $\mathrm{HSO}_{4}^{-}$is $1 \times 10^{-2}$. What is the value of $\mathrm{K}_{\mathrm{b}}$ for $\mathrm{SO}_{4}{ }^{2-}$ ?
a. $\mathrm{K}_{\mathrm{b}}=1 \times 10^{2}$
b. $\mathrm{K}_{\mathrm{b}}=1 \times 10^{-7}$
c. $K_{b}=1 \times 10^{-2}$
d. $K_{b}=1 \times 10^{-12}$
5. Which of the following would make a good buffer when dissolved in formic acid, $\mathrm{HCO}_{2} \mathrm{H}$ ?
a. $\mathrm{NH}_{3}$
b. $\mathrm{H}_{2} \mathrm{O}$
c. $\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
d. $\mathrm{NaCO}_{2} \mathrm{H}$
$\mathrm{CH}_{3} \mathrm{NH}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \leftrightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
6. The above equation represents the reaction between the base methylamine $\left(K_{b}=4.38 \times 10^{-4}\right)$ and water. Which of the following best represents the concentrations of the various species at equilibrium?
a. $\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]<\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right]$
c. $\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]=\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right]$
b. $\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]>\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right]$
d. cannot be determined without more info.
7. Consider the following:
l. $\mathrm{H}_{3} \mathrm{O}^{+}$
II. $\mathrm{CH}_{3} \mathrm{COO}^{-}$
III. $\mathrm{CH}_{3} \mathrm{COOH}$

The purpose of a buffer system consisting of $\mathrm{CH}_{3} \mathrm{COOH}$ and $\mathrm{CH}_{3} \mathrm{COONa}$ is to maintain a relatively constant concentration of
a. I only
b. I and II only
c. II and III only
d. I, II, and III
8. A buffer solution is formed by adding which of the following to water?
a. HCl and KOH
b. HCN and RbCN
c. NaBr and NaOH
d. $\mathrm{HNO}_{3}$ and $\mathrm{LiNO}_{3}$
9. Which of the following would make the most effective buffer when added to 750 mL of distilled water?
a. 2.5 moles $\mathrm{HNO}_{2}+2.5$ moles $\mathrm{LiNO}_{2}$
b. 5.5 moles $\mathrm{HNO}_{2}+5.5$ moles $\mathrm{KNO}_{2}$
c. 5.0 moles $\mathrm{HNO}_{2}+6.0$ moles $\mathrm{NaNO}_{2}$
d. 5.5 moles $\mathrm{HNO}_{3}+5.5$ moles $\mathrm{NaNO}_{3}$

## Let's Explore Buffers!

## Procedure (Teacher Demo):

1. Obtain two beakers, one containing water and the other a (1:1) $0.10 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} / \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$buffer system.
2. Add thymol blue indicator to each.
3. Add 0.10 M HCl dropwise to the water.
a. Students: Predict how many drops of acid it will take to change the color of the water solution
4. Add 0.10 M HCl dropwise to the buffer.
a. Students: Predict how many drops of acid it will take to change the color of the buffer solution
5. Repeat Steps 1-5 with the same solutions but adding 0.10 M NaOH dropwise.

| Thymol blue indicator |  |  |  |
| :---: | :---: | :---: | :---: |
| pH range | $1-3$ | $3-8$ | $8-14$ |
| color | red | yellow | blue |

Data Table

| Solution | \# of drops <br> predicted to <br> change color | \# of drops <br> actually to <br> change color | Relevant Reaction |
| :---: | :---: | :---: | :--- |
| Water +HCl |  |  |  |
| Buffer +HCl |  |  |  |
| Water +NaOH |  |  |  |
| Buffer +NaOH |  |  |  |

Analysis:

1. Describe how a buffer system is effective at maintaining a constant pH when strong acid/base is added.
2. Describe buffer capacity. (Questions to consider: a buffer's "capacity" is its capacity to do what? What would you need to change to increase/decrease a buffer capacity?)
3. The buffer is made from equal volumes 0.10 M acetic acid, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, and 0.10 M sodium acetate, $\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$. Given this, the $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} / \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$ratio is equal to 1.
a. What color was the solution when just buffer and indicator were present? $\qquad$
b. Calculate the pH of this buffer. $\left(\mathrm{K}_{\mathrm{a}}\right.$ of $\left.\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}=1.8 \times 10^{-5}\right)$
4. When strong acid is added to the buffer,
a. What color is the solution (eventually)? $\qquad$
b. Is the $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} / \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$ratio greater than, less than, or equal to 1 ? Why?
5. When strong base is added to the buffer,
a. What color is the solution (eventually)? $\qquad$
b. Is the $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} / \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$ratio greater than, less than, or equal to 1 ? Why?
6. Consider a solution of only acetic acid, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\left(\mathrm{~K}_{\mathrm{a}}=1.8 \times 10^{-5}\right)$.
a. What color is the solution (eventually)? $\qquad$
b. Is the $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} / \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$ratio greater than, less than, or equal to 1 ? Why?

## How to Make a Buffer

## Making Your Own Buffer, Part I:

1. The most effective buffer contains $\qquad$
$\qquad$ amounts of the proton donor and proton acceptor.
2. The $\qquad$ of a buffer (its ability to continue to absorb any acid or base added) is dependent upon the concentrations of the two components of the buffer; the higher the concentrations, the higher the capacity.
3. If you have equal amounts of the weak acid and conjugate base:
a. $[H A]=\left[A^{-}\right]$
b. Therefore, your $K_{a}$ equation would simplify to:

$$
K_{a}=\frac{\left[H_{3} \mathrm{O}^{+}\right]\left[A^{-}\right]}{[H A]}=\left[H_{3} \mathrm{O}^{+}\right]
$$

c. And thus, to get the best possible buffer, you want to choose a weak acid such that
$=$
(because
$=$
_)

Example: An industrial process requires a constant pH of 3.00 . The weak acids available in the warehouse are:

$$
\begin{array}{ll}
\text { benzoic acid }\left(\mathrm{HC}_{7} \mathrm{H}_{3} \mathrm{O}_{2}\right) & \mathrm{K}_{\mathrm{a}}=6.3 \times 10^{-5} \\
\text { nitrous acid }\left(\mathrm{HNO}_{2}\right) & \mathrm{K}_{\mathrm{a}}=7.2 \times 10^{-4} \\
\text { phosphorous acid acid }\left(\mathrm{H}_{3} \mathrm{PO}_{3}\right) & \mathrm{K}_{\mathrm{a}}=3.7 \times 10^{-2} \\
\text { hydrocyanic acid }(\mathrm{HCN}) & \mathrm{K}_{\mathrm{a}}=6.2 \times 10^{-10}
\end{array}
$$

a. Which of the four acids would be the best choice for the industrial process? Explain with a calculation.
b. What other chemical(s) are needed to prepare the buffer? Give at least one possible chemical which could be used.
c. How much of the chemical from (b) should you add to achieve a buffer with a pH of 3.00 ?

1. A student wishes to create a buffered solution with a pH of 5 . Which of the following acids would be the best choice for the buffer?
a. $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \quad \mathrm{~K}_{\mathrm{a}}=5.9 \times 10^{-2}$
b. $\mathrm{H}_{3} \mathrm{AsO}_{4} \quad \mathrm{~K}_{\mathrm{a}}=5.6 \times 10^{-3}$
c. $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} \quad \mathrm{~K}_{\mathrm{a}}=1.8 \times 10^{-5}$
d. HOCl
$\mathrm{K}_{\mathrm{a}}=3.0 \times 10^{-8}$

## Making Your Own Buffer, Part II:

Let's see what happens if you add a strong base, NaOH , to the weak acid, HA :

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{NaA}(\mathrm{aq})
$$

Welp, it got neutralized. (I know, I know: what else did I expect?)

But WAIT! Let's see what happens if I add only $\qquad$ the amount of strong base:

## Now only half of the weak acid is neutralized:

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{NaA}(\mathrm{aq})
$$

## but the other half of the weak acid, HA , is still there!

Did you see what just happened?? After adding half the amount of strong base to a given amount of weak acid, the species floating around in my reaction vessel include:
$\qquad$ , $\qquad$ , and $\mathrm{H}_{2} \mathrm{O}$

## That's a buffer!!!!

This means that any titration involving a weak acid and/or weak base is a buffer problem.
If I titrate HA with NaOH , then as soon as the first drop splashes into the container, I've made NaA which promptly dissociates into $\mathrm{A}^{-}$. More on titrations soon!

Now we have lots of different ways to create a buffer! But be careful: if you're mixing a weak acid/base with a strong base/acid to make a buffer, you have to be careful to not to completely neutralize your weak species.

|  | Species 1 | Species 2 | Buffer? |
| :---: | :---: | :---: | :---: |
| Example 1 | $100 \mathrm{~mL} \mathrm{0.20} \mathrm{M}$ <br> $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | $100 \mathrm{~mL} \mathrm{0.10} \mathrm{M}$ <br> NaOH | Yes, moles of strong base < moles of weak acid. |
| Example 2 | $100 \mathrm{~mL} \mathrm{0.20} \mathrm{M}$ <br> $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | 50 mL 0.20 M <br> NaOH | Yes, moles of strong base < moles of weak acid. |
| Example 3 | $100 \mathrm{~mL} \mathrm{0.20} \mathrm{M}$ <br> $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | $100 \mathrm{~mL} \mathrm{0.20} \mathrm{M}$ <br> NaOH | Nope, moles of strong base completely neutralized |
| weak acid. |  |  |  |

Circle all the combinations below that would make a buffer solution when mixed. Note: in most cases, a neutralization reaction will occur. Consider what the products of the neutralization will be and how much of each species will be present when the reaction is complete.

100 mL of 1.0 M HCl with 100 mL of 1.0 M NaOH

100 mL of $1.0 \mathrm{M} \mathrm{HNO}_{2}$ with 100 mL of 1.0 M NaOH

100 mL of $1.0 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ with 100 mL of 0.50 M HCl

100 mL of 1.0 M HCl with 50 mL of 1.0 M NaOH

100 mL of $1.0 \mathrm{M} \mathrm{HNO}_{2}$ with 50 mL of 1.0 M NaOH

50 mL of $1.0 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ with 100 mL of 0.50 M LiOH

## Free Response Practice

1. A chemist creates a buffer at pH 4.30 by combining one of the acids from the following list and their soluble salt in a solution.

- chloroacetic acid, $\mathrm{HC}_{2} \mathrm{H}_{2} \mathrm{ClO}_{2}$
$\mathrm{K}_{\mathrm{a}}=1.35 \times 10^{-3}$
- propanoic acid, $\mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{2}$
$K_{a}=7.3 \times 10^{-4}$
- benzoic acid, $\mathrm{HC}_{6} \mathrm{H}_{5} \mathrm{CO}_{2} \quad \mathrm{~K}_{\mathrm{a}}=6.4 \times 10^{-5}$
- hypochlorous acid, $\mathrm{HClO} \quad \mathrm{K}_{\mathrm{a}}=3.5 \times 10^{-8}$
a. Which weak acid would work best? Justify your choice with calculations.
b. Identify an appropriate salt that can be used with the weak acid chosen above to complete the buffer system.
c. Write an equilibrium reaction to describe this buffer.
d. What would be true about the weak acid/conjugate base ratio ( $\left(\frac{H A}{A^{-}}\right)$in your buffer system if the acid chosen above was used to prepare the desired buffer at pH 4.30? Justify your answer.
e. How would adding HBr to the buffer system change the weak acid/conjugate base ratio $\left(\frac{H A}{A^{-}}\right)$identified in part (d)? Explain.
f. How could you prepare a buffer solution from the weak acid chosen in part (a) if you were NOT provided with the conjugate salt, but instead solutions of a strong acid and a strong base?

| Acid | Acid Dissociation <br> Constant, $K_{a}$ |
| :---: | :---: |
| $\mathrm{H}_{3} \mathrm{PO}_{4}$ | $7 \times 10^{-3}$ |
| $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$ | $8 \times 10^{-8}$ |
| $\mathrm{HPO}_{4}{ }^{2-}$ | $5 \times 10^{-13}$ |

2. On the basis of the information above, a buffer with a $\mathrm{pH}=9$ can best be made by using
a. $\mathrm{H}_{3} \mathrm{PO}_{4}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$
b. $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{HPO}_{4}{ }^{2-}$
c. $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{PO}_{4}{ }^{3-}$
d. $\mathrm{HPO}_{4}{ }^{2-}+\mathrm{PO}_{4}{ }^{3-}$

|  | Initial pH | pH after NaOH addition |
| :---: | :---: | :---: |
| Acid 1 | 3.0 | 3.5 |
| Acid 2 | 3.0 | 5.0 |

3. Two different acids with identical pH are placed in separate beakers. Identical portions of NaOH are added to each beaker, and the resulting pH is indicated in the table above. What can be determined about the strength of each acid?
a. Acid 1 is a strong acid and acid 2 is a weak acid because acid 1 resists change in pH more effectively.
b. Acid 1 is a strong acid and acid 2 is a weak acid because the NaOH is more effective at neutralizing acid 2 .
c. Acid 1 is a weak acid and acid 2 is a strong acid because the concentration of the weak acid must be significantly greater to have the same pH as the strong acid.
d. Acid 1 is a weak acid and acid 2 is a strong acid because the concentration of the hydrogen ions will be greater in acid 2 after the NaOH addition.
4. A 1.0 L buffer is prepared by combining 0.200 M acetic acid and $0.500 \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$. This solution is capable of buffering the addition of which of the following without being destroyed?
a. 0.35 moles NaOH
b. 0.62 moles HI
c. $\quad 0.40 \mathrm{M} \mathrm{LiOH}$
d. $\quad 0.45 \mathrm{M} \mathrm{HBr}$
5. Which of the following techniques can be used to prepare a buffer solution?
I. Titrate a weak acid with a strong base.
II. Titrate a weak base with a strong acid.
III. Combine a solution of weak acid with a salt containing its conjugate base.
a. I only
c. I and II
b. III only
d. I, II and III
6. Which of the following should be true when preparing a buffer solution?
I. The acid dissociation constant will have an exponent close in value to the buffer pH .
II. The $\mathrm{pK}_{\mathrm{a}}$ of the weak acid will be close in value to the buffer pH .
III. The acid/base ratio is solution will be approximately 10:1.
a. I only
c. I and II
b. II only
d. I, II and III
pH vs $\mathrm{pK}_{\mathrm{a}}$ : Which form dominates?

Given the generic weak acid reaction: $\quad \mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$
$\mathrm{pH}<\mathrm{pK}_{\mathbf{a}} \quad$ Added acid = MORE Acidic: ___ $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\ldots \ldots$ [products]; according to Le Chatelier, reaction will shift left to favor reactants, thus the ___ form predominates: $\frac{H A}{A^{-}}>1$
$\mathrm{pH}=\mathrm{pK}_{\mathrm{a}} \quad$ Ideal buffer ratio, $\qquad$ $=$ $\qquad$ thus $\qquad$ form predominates: $\frac{H A}{A^{-}}=1$
$\mathrm{pH}>\mathrm{pK}_{\mathrm{a}} \quad$ Added base $=$ MORE Basic: $\qquad$ $\left[\mathrm{OH}^{-}\right]=$ $\qquad$ $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=$ $\qquad$ [products]; according to Le Chatelier, reaction will shift right to favor products, thus the $\qquad$ form predominates: $\frac{H A}{A^{-}}<1$
*This is why, during a titration, you want to choose an indicator with a $\mathrm{pK}_{\mathrm{a}} \approx \mathrm{pH}$ at equivalence point (if the indicator is a weak acid). An indicator works because the acid form of the indicator, HA, is a different color than the conjugate base form, $\mathrm{A}^{-}$.

## Let's Practice!

1. A buffer is made using $\mathrm{HNO}_{2}$ as one of the ingredients. $\left(\mathrm{K}_{\mathrm{a}}=4.0 \times 10^{-4}, \mathrm{pKa}=3.40\right)$. A particulate representation of a small portion of the buffer is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40 ? Justify your answer.
$\mathrm{O} \mathrm{HNO}_{2}$ molecule $\mathrm{ONO}_{2}^{-}$ion


Acids, Bases \& Buffers Cheat Sheet: The 6 Ways to Determine pH

## 1) Strong Acids/ Strong Bases

## You MUST memorize:

Strong Acids: $\mathrm{HCl}, \mathrm{HBr}, \mathrm{HI}, \mathrm{HNO}_{3}, \mathrm{HClO}_{4}, \mathrm{H}_{2} \mathrm{SO}_{4}$
Strong Bases: Groups IA and IIA metal hydroxides
100\% Dissociation! Easy life:

$$
\begin{gathered}
p H=-\log \left[H^{+}\right]=-\log [H A]_{o} \\
p O H=-\log \left[O H^{-}\right]=-\log [B]_{o} \\
p H+p O H=14
\end{gathered}
$$

## 2) Weak Acids/ Weak Bases

If it's not strong, it's weak!

## $<1 \%$ Dissociation $\rightarrow$ Equilibrium!

Time saver!! Since acids ionize $1 \mathrm{H}^{+}$at a time, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=$ $\left[\mathrm{A}^{-}\right]$, and $\left[\mathrm{OH}^{-}\right]=\left[\mathrm{BH}^{+}\right]$. For weak acids and bases, make the assumption $[\mathrm{HA}]_{0}-\boldsymbol{x} \approx[\mathrm{HA}]_{0}$ and $[\mathrm{B}]_{0}-\boldsymbol{x} \approx[\mathrm{B}]_{0}$.

## Weak Acids:

$K_{a}=\frac{[x][x]}{[H A]_{o}-x} \approx \frac{[x][x]}{[H A]_{o}}$ where $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{x} \ll[\mathrm{HA}]_{\circ}$

## Weak Bases:

$K_{b}=\frac{[x][x]}{[B]_{o}-x} \approx \frac{[x][x]}{[B]_{o}}$ where $\left[\mathrm{OH}^{-}\right]=\mathrm{x} \ll[\mathrm{B}]_{\circ}$

## 3) Salty Salts

To know if a salt will affect pH , determine: $\quad \rightarrow$ Will the salt ions will hydrolyze (or split) water?
Conjugates of Strong Acids/Bases: do NOT hydrolyze water, and thus don't affect pH
Conjugates of Weak Acids/Bases: DO hydrolyze water, and thus do affect pH !

## How to Determine the pH of a Salt

1. Dissociate your salt.

Make the cation into a base: is it strong or weak?
2. Make the anion into an acid: is it strong or weak?
3. Strong wins!
4. If either is weak, write the hydrolysis reaction:

Conjugate base of WA: $\quad \mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{OH}^{-}+\mathrm{HA}$
Conjugate acid of WB: $\quad \mathrm{BH}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{B}$

Example

$$
\mathrm{CaSO}_{3} \rightarrow \mathrm{Ca}^{2+}+\mathrm{SO}_{3}^{2-}
$$

$\mathrm{Ca}^{2+}+2 \mathrm{OH}^{-} \rightarrow \mathrm{Ca}(\mathrm{OH})_{2}$ Strong base
$\mathrm{H}^{+}+\mathrm{SO}_{3}^{-} \rightarrow \mathrm{HSO}_{3}^{-} \quad$ Weak acid
$\mathrm{SB}+\mathrm{WA}$, so this salt is basic!
$\mathrm{SO}_{3}{ }^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{OH}^{-}+\mathrm{HSO}_{3}{ }^{-}$
5. Use your hydrolysis equation to calculate the pH using the Weak Acids/Bases method.
6. Be careful. Did the problem give you $K_{a}$, or $K_{b}$ instead? Do you need to convert based on your hydrolysis reaction? Remember: $\quad \mathrm{K}_{\mathrm{w}}=\mathrm{K}_{\mathrm{a}} \times \mathrm{K}_{\mathrm{b}}=1.0 \times 10^{-14}$

## 4) Adding Strong Acids + Strong Bases (Yes, this includes titrations!)

These are really just stoichiometry problems with a limiting reagent! ©)

- What is "excess" determines the $\mathbf{p H}$ (since all strong/strong combos neutralize)
- Beware the change in volume if multiple solutions are being added! (calculate moles of either $\mathrm{H}^{+}$or $\mathrm{OH}^{-}$in excess, and divide by total volume to determine concentration of $\left[\mathrm{H}^{+}\right]$or $\left[\mathrm{OH}^{-}\right]$, and go from there)


## 5) Buffers

Whenever a weak acid or base is present with its conjugate salt - YOU HAVE A BUFFER!!! Four ways to get a buffer:

1. Weak acid and its conjugate base (HA and $\mathrm{A}^{-}$OR HA and NaA ) $1: 1$ mole ratio
2. Weak base and its conjugate acid ( B and $\mathrm{BH}^{+} \mathrm{OR} B$ and BHCl ) 1:1 mole ratio
3. Weak base with strong acid (titration) $1 \mathrm{WB}: 0.5 \mathrm{SA}$ mole ratio
$\rightarrow$ strong acid reacts with weak base, producing conjugate acid
4. Weak acid with strong base (titration) $\mathbf{1} \mathbf{W A}: \mathbf{0 . 5}$ SB mole ratio
$\rightarrow$ strong base reacts with weak acid, producing conjugate base
The best buffer has: 1) High capacity (lots of acid and base), 2) [HA] =[ $\left.\mathrm{A}^{-}\right], 3$ ) pH (of buffer) $=\mathrm{pK}_{\mathrm{a}}$ (of acid form)
Two calculation options: $\quad\left[H_{3} \mathrm{O}^{+}\right]=K_{a} \frac{[H A]}{\left[A^{-}\right]} \quad$ or $\quad \mathrm{pH}=\mathrm{pKa}+\log \left(\frac{\left[\mathrm{A}^{-}\right]}{[H A]}\right)$
[HA] = Weak acid or salt ot conjugate base or added strong base (in a WB/SA titration)
$\left[A^{-}\right]=$Weak base or salt of conjugate acid or added strong acid (in a WA/SB titration)
Shortcut!!! Since $\frac{[\text { Acid }]}{[\text { Base }]}$ is a ratio in the equations, the amount of moles may be substituted in place of concentration because the final volumes will be the same, and thus cancel out.
6) Adding Strong Acids/Bases + Weak Bases/Acids (Yes, this includes titrations!)

Buffers make the titration curve "flat" at the region where buffering occurs. On a titration curve, this is the point of inflection (buffer arrow) = maximum buffering capacity!

Weak Acid Titrated with Strong Base


Weak Base Titrated with Strong Acid


There are 4 zones of interest along a titration curve for a Weak Acid/Base and Strong Base/Acid:

1. Initial pH : simply a weak acid or weak base problem!
2. During titration, before equivalence point: BUFFER! The amount of conjugate formed = the amount of strong acid or base added. (Amount of weak left $=\mathrm{HA}_{\mathrm{o}}$ - strong added)
3. Equivalence point: only salt and water are left; salt is either a weak base (if a weak acid was titrated) or a weak acid (if a weak base was titrated); remember to convert $K_{a}$ to $K_{b}$ or vice versa! (Use $M_{A} V_{A}=M_{B} V_{B}$ )
4. Beyond the equivalence point: Stoichiometry! Calculate how much STRONG (acid or base) is left after equivalence, recalculate its molarity (remember, volume increased during titration), and calculate using the strong acid/base method.

Best Indicator: Choose indicator with $\mathrm{pK}_{\mathrm{a}}$ (of indicator) $\approx \mathrm{pH}$ (at equivalence point of titration). This means that $\mathrm{K}_{\mathrm{a}}$ of the indicator $\approx 1 \times 10^{-\mathrm{pH}}$ @ eq pt $)$

Remember: if $\mathbf{p H} \leq \mathrm{pK}_{\mathrm{a}}$ the acid form (HA) predominates, if $\mathrm{pH}>\mathrm{pK}_{\mathrm{a}}$ the conjugate base form ( $\mathrm{A}^{-}$) predominates

## Unit 8 Multiple Choice Practice

1. Nitrous acid, $\mathrm{HNO}_{2}$, has a $\mathrm{pK}_{\text {a }}$ value of 3.3. If a solution of nitrous acid is found to have a pH of 4.2 , what can be said about the concentration of the conjugate acid/base pair found in solution?
a. $\left[\mathrm{HNO}_{2}\right]>\left[\mathrm{NO}_{2}^{-}\right]$
b. $\left[\mathrm{NO}_{2}^{-}\right]>\left[\mathrm{HNO}_{2}\right]$
c. $\left[\mathrm{H}_{2} \mathrm{NO}_{2}{ }^{+}\right]>\left[\mathrm{HNO}_{2}\right]$
d. $\left[\mathrm{HNO}_{2}\right]>\left[\mathrm{H}_{2} \mathrm{NO}_{2}{ }^{+}\right]$
2. A buffer solution can be formed by dissolving equal moles of:
a. HF and NaOH
b. KBr and $\mathrm{Na}_{3} \mathrm{PO}_{4}$
c. $\mathrm{CH}_{3} \mathrm{COOH}$ and NaCl
d. HF and NaF
3. How many liters of distilled water must be added to $10 . \mathrm{mL}$ of an aqueous solution of $\mathrm{HNO}_{3}$ with a pH of 2 to create a solution with a pH of 3 ?
a. $10 . \mathrm{mL}$
b. $20 . \mathrm{mL}$
c. $40 . \mathrm{mL}$
d. $90 . \mathrm{ml}$
4. Which of the following changes would affect the pH of a buffer solution?
I. Doubling the amount of acid and conjugate base used.
II. Doubling the amount of water in the solution.
III. Adding a small amount of strong acid or strong base.
a. III only
b. I and II only
c. II and III only
d. I, II, and III
5. The $\left[\mathrm{OH}^{-}\right]$in a solution with a pH of 3.00 is
a. $1.0 \times 10^{-11} \mathrm{M}$
b. $\quad 1.0 \times 10^{-9} \mathrm{M}$
c. $\quad 1.0 \times 10^{-6} \mathrm{M}$
d. $\quad 1.0 \times 10^{-3} \mathrm{M}$
6. Consider the following:
I. $\mathrm{H}_{2} \mathrm{SO}_{4}$
II. $\mathrm{HSO}_{4}^{-}$
III. $\mathrm{SO}_{4}{ }^{2-}$

Which of the chemical species above are present in a reagent bottle labeled $1.0 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})$ ?
a. I only
b. I and II only
c. II and III only
d. I, II, and III
7. The pH of a 1.0 mL solution of 0.30 M NaOH if 9.0 mL of distilled water is added to the solution is closest to:
a. 3
b. 11
c. 12
d. 13
8. A 0.25 M solution of a weak monoprotic acid has a pH of 6 . What is the value of $\mathrm{K}_{\mathrm{a}}$ for the acid?
a. $4 \times 10^{-12}$
b. $4 \times 10^{-11}$
c. $2.5 \times 10^{-6}$
d. $\quad 2.5 \times 10^{-5}$
9. Consider the following equilibrium: $\quad 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+$ energy $\leftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$

Which of the following describes the result of decreasing the temperature?
$\left[\begin{array}{lll}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]} & {\left[\mathrm{OH}^{-}\right]} & \mathrm{K}_{\mathrm{w}}\end{array}\right.$
a. increases increases increases
b. decreases increases decreases
c. increases decreases no change
d. decreases decreases decreases
10. The pH of a solution changes from 3.00 to 6.00 . By what factor does the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$change?
a. 3
b. 30
c. 100
d. 1000

$$
\mathrm{HClO}_{2}(\mathrm{aq})+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}(\mathrm{aq}) \leftrightarrow \mathrm{ClO}_{2}^{-}(\mathrm{aq})+\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq})
$$

11. The equilibrium constant for the reaction represented by the equation above is greater than 1.0. Which of the following gives the correct relative strength of the acids and bases in the reaction?

## Acids

a. $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}>\mathrm{HClO}_{2}$
b. $\mathrm{HClO}_{2}>\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
c. $\mathrm{HClO}_{2}>\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
$\mathrm{ClO}_{2}{ }^{-}>\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$
d. $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}>\mathrm{HClO}_{2}$
12. When 10.0 mL of 0.10 M HCl is added to 10.0 mL of water, the concentration of $\mathrm{H}_{3} \mathrm{O}^{+}$in the final solution is:
a. $\quad 0.010 \mathrm{M}$
b. $\quad 0.050 \mathrm{M}$
c. $\quad 0.10 \mathrm{M}$
d. $\quad 0.20 \mathrm{M}$
13. A 0.50 M solution of a weak monoprotic acid has a pH of 4 . Calculate the ionization constant, $\mathrm{K}_{\mathrm{a}}$, for the acid.
a. $5 \times 10^{-9}$
b. $2 \times 10^{-8}$
c. $2 \times 10^{-4}$
d. $5 \times 10^{-5}$
14. A bottle of water is placed in an ice bath to chill. What happens to the pH of the water as it cools?
a. It will increase because the auto-ionization of water is an endothermic process.
b. Nothing; the volume would have to change in order for any ion concentration to change.
c. Nothing; pure water always has a pH of 7.00 .
d. It will decrease because the concentration of $\mathrm{H}^{+}$is decreasing.
15. Which of the following 1.0 M solutions would have a pH greater than 7.00 ?
a. HCN
b. $\mathrm{KNO}_{3}$
c. $\mathrm{NH}_{4} \mathrm{Cl}$
d. $\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
16. In order to change the pH of a solution from 2.0 to 4.0 the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$must
a. increase by a factor of 2
c. increase by a factor of 100
b. decrease by a factor of 2
d. decrease by a factor of 100
17. A buffer solution may contain equal moles of
a. a weak acid with its conjugate base
c. a weak acid and a strong base
b. a strong acid with its conjugate base
d. a strong acid and a strong base
18. What is the conjugate acid and the conjugate base of $\mathrm{HPO}_{4}{ }^{2-}$ ?

## Conjugate Acid

a. $\mathrm{PO}_{4}{ }^{3-}$
b. $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$
c. $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$
d. $\mathrm{H}_{3} \mathrm{PO}_{4}$

## Conjugate Base

$\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$
$\mathrm{PO}_{4}{ }^{3-}$
$\mathrm{H}_{3} \mathrm{PO}_{4}$
$\mathrm{PO}_{4}{ }^{3-}$
19. When comparing 1.0 M solutions of bases, the base with the lowest $\left[\mathrm{OH}^{-}\right]$is the
a. weakest base and it has the largest $\mathrm{K}_{\mathrm{b}}$ value.
b. strongest base and it has the largest $K_{b}$ value.
c. weakest base and it has the smallest $K_{b}$ value.
d. strongest base and it has the smallest $K_{b}$ value.
20. What is the concentration of $\operatorname{Sr}(\mathrm{OH})_{2}$ in a solution with a $\mathrm{pH}=11.00$ ?
a. $2.0 \times 10^{-11} \mathrm{M}$
b. $\quad 1.0 \times 10^{-11} \mathrm{M}$
c. $\quad 5.0 \times 10^{-4} \mathrm{M}$
d. $\quad 1.0 \times 10^{-3} \mathrm{M}$
21. Which of the following pairs of substances would make a good buffer solution?
a. $\mathrm{H}_{2} \mathrm{SO}_{4}$ and LiOH
b. HCl and KCl
c. $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ and $\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
d. HF and $\mathrm{NaH}_{3}$
22. Consider the neutralization reactions between the following acid-base pairs in dilute aqueous solutions:
(1) $\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{NaOH} \rightarrow$
(2) $\mathrm{HNO}_{3}+\mathrm{KOH} \rightarrow$
(3) $\mathrm{H}_{3} \mathrm{PO}_{4}+\mathrm{Ba}(\mathrm{OH})_{2} \rightarrow$
(4) $\mathrm{HCl}+\mathrm{KOH} \rightarrow$
(5) $\mathrm{H}_{2} \mathrm{SO}_{4}+\mathrm{NH}_{3} \rightarrow$

For which of the reactions above is the net ionic equation $\mathrm{H}^{+}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}$ ?
a. 1,3
b. $2,4,5$
c. 2,4
d. 3,5

1. Nitrogen monoxide, $\mathrm{NO}(\mathrm{g})$, can undergo reactions to produce acids such as $\mathrm{HNO}_{2}$, a weak acid with a $\mathrm{K}_{\mathrm{a}}$ of $4.0 \times 10^{-4}$ and a $\mathrm{pK}_{\mathrm{a}}$ of 3.40.
a. A student is asked to make a buffer solution with a pH of 3.40 by using $0.100 \mathrm{M} \mathrm{HNO}_{2}(\mathrm{aq})$ and 0.100 M $\mathrm{NaOH}(\mathrm{aq})$.
i. Explain why the addition of $0.100 \mathrm{M} \mathrm{NaOH}(\mathrm{aq})$ to $0.100 \mathrm{M} \mathrm{HNO}_{2}(\mathrm{aq})$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $\mathrm{NaOH}(\mathrm{aq})$ to the $\mathrm{HNO}_{2}(\mathrm{aq})$. (2 points)
ii. Determine the volume, in mL , of $0.100 \mathrm{M} \mathrm{NaOH}(\mathrm{aq})$ the student should add to 100 . mL of $0.100 \mathrm{M} \mathrm{HNO}_{2}(\mathrm{aq})$. to make a buffer solution with a pH of 3.40 . Justify your answer. (2 points)
b. A second student makes a buffer by dissolving 0.100 mol of $\mathrm{NaNO}_{2}(\mathrm{~s})$ in $100 . \mathrm{mL}$ of $1.00 \mathrm{M} \mathrm{HNO}_{2}(\mathrm{aq})$. Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (a)? Justify your answer. (1 point)

$$
\mathrm{HF}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \leftrightarrow \mathrm{F}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})
$$

2. The ionization of $\mathrm{HF}(\mathrm{aq})$ in water is represented by the equation above. In a $0.0350 \mathrm{M} \mathrm{HF}(\mathrm{aq})$ solution, the percent ionization of HF is 13.0 percent.
a. Two particulate representations of the ionization of HF molecules in the $0.0350 \mathrm{M} \mathrm{HF}(\mathrm{aq})$ solution are shown below in Figure 1 and Figure 2. Water molecules are not shown. Explain why the representation of ionization of HF molecules in water in Figure 1 is more accurate than the representation in Figure 2. (1 point)
(The key below identifies the particles in the representations.)



Figure 1


Figure 2
b. Use the percent ionization data above to calculate the value of $\mathrm{K}_{\mathrm{a}}$ for HF . (2 points)
c. If 50.0 mL of distilled water is added to 50.0 mL of $0.0350 \mathrm{M} \mathrm{HF}(\mathrm{aq})$, will the percent ionization of $\mathrm{HF}(\mathrm{aq})$ in the solution increase, decrease, or remain the same? Justify your answer with an explanation or a calculation. (1 point)

$$
\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q) \quad K_{a}=1.12 \times 10^{-10}
$$

3. Phenol is a weak acid that partially dissociates in water according to the equation above.
a. What is the pH of a $0.75 \mathrm{M} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}(\mathrm{aq})$ solution? (2 points)
b. For a certain reaction involving $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}(\mathrm{aq})$ to proceed at a significant rate, the phenol must be primarily in its deprotonated form, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{-}(\mathrm{aq})$. In order to ensure that the $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}(\mathrm{aq})$ is deprotonated, the reaction must be conducted in a buffered solution. On the number scale below, circle each pH for which more than 50 percent of the phenol molecules are in the deprotonated form, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{-}(\mathrm{aq})$. Justify your answer. (2 points)
$\begin{array}{llllllllllllll}1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 13 & 14\end{array}$

A pure 14.85 g sample of the weak base ethylamine, $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{2}$, is dissolved in enough distilled water to make 500 . mL of solution.
(a) Calculate the molar concentration of the $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{2}$ in the solution. (2 points)
(b) Write an equation showing how the aqueous ethylamine reacts with water. (1 point)
(c) Write the equilibrium-constant expression for the reaction between $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{2}(\mathrm{aq})$ and water. (1 point)
(d) Of $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{2}(\mathrm{aq})$ and $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}^{+}(\mathrm{aq})$, which is present in the solution at the higher concentration at equilibrium? Justify your answer. (1 point)

2. Each of three beakers contains 25.0 mL of a 0.100 M solution of $\mathrm{HCl}, \mathrm{NH}_{3}$, or $\mathrm{NH}_{4} \mathrm{Cl}$, as shown above. Each solution is at $25^{\circ} \mathrm{C}$.
a. Determine the pH of the solution in beaker 1 . Justify your answer. (1 point)
b. In beaker 2, the reaction $\mathrm{NH}_{3}(a q)+\mathrm{H}_{2} \mathrm{O}(I) \leftrightarrow \mathrm{NH}_{4}{ }^{+}(a q)+\mathrm{OH}^{-}(a q)$ occurs. The value of $K_{b}$ for $\mathrm{NH}_{3}(a q)$ is 1.8 $\times 10^{-5}$ at $25^{\circ} \mathrm{C}$.
i. Write the $K_{b}$ expression for the reaction of $\mathrm{NH}_{3}(a q)$ with $\mathrm{H}_{2} \mathrm{O}(/)$. (1 point)
ii. Calculate the $\left[\mathrm{OH}^{-}\right]$in the solution in beaker 2. (2 points)
c. In beaker 3, the reaction $\mathrm{NH}_{4}^{+}(a q)+\mathrm{H}_{2} \mathrm{O}(I) \leftrightarrow \mathrm{NH}_{3}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ occurs.
i. Calculate the value of $K_{a}$ for $\mathrm{NH}_{4}{ }^{+}(a q)$ at $25^{\circ} \mathrm{C}$. (1 point)
ii. The contents of beaker 2 are poured into beaker 3 and the resulting solution is stirred. Assume that volumes are additive. Calculate the pH of the resulting solution. ( 2 points)
d. The contents of beaker 1 are poured into the solution made in part (c)(ii). The resulting solution is stirred. Assume that volumes are additive. Is the resulting solution an effective buffer? Justify your answer. (1 point)

## AP Chemistry FTW:



## Unit 9: Titrations

## Unit 9 Objectives: Acids, Bases \& Buffers (Titrations)

BIG IDEA 3 - Changes in matter involve the rearrangement and/or the reorganization of atoms and /or the transfer of electrons.

- Enduring Understanding 3.A: Chemical changes are represented by a balanced chemical equation that identifies the ratios with which reactants react and products form.
- Enduring Understanding 3.B: Chemical reactions can be classified by considering what the reactants are, what the products are, or how they change from one into the other. Classes of chemical reactions include synthesis, decomposition, acid-base, and oxidation-reduction reactions.

BIG IDEA 6 - Any bond or intermolecular attraction that can be formed can be broken. These processes are in a dynamic competition, sensitive to initial conditions and external perturbations.

- Enduring Understanding 6.A: Chemical equilibrium is a dynamic, reversible state in which rates of opposing processes are equal.
- Enduring Understanding 6.B: Systems at equilibrium are responsive to external perturbations, with the response leading to a change in the composition of the system.
- Enduring Understanding 6.C: Chemical equilibrium plays an important role in acid-base chemistry and solubility.
- Enduring Understanding 6.D: The equilibrium constant is related to temperature and the difference in Gibbs free energy between reactants and products.


## Neutralization Reactions: Acid/Base Stoichiometry FTW!

Neutralization reaction: when an Arrhenius acid and base react to produce a salt and water

- These reactions will go to $\qquad$ if the acid and/or the base is $\qquad$ .
- Thus, these are $\qquad$ equilibrium calculations: no RICE needed!

Acid/base titrations are neutralization reactions: at the $\qquad$ point, the moles of acid and base are stoichiometrically equal, and thus have completely neutralized each other!

```
                    Monoprotic Neutralization Reactions: 1:1 Stoich (Oh Happy Days!)
```

There are $\qquad$ methods to solve calculations of this type;

1. Stoichiometry Method (especially useful if acid and/or base is given as a $\qquad$ _)
2. Shortcut (easily used when both acid and base are $\qquad$ solutions, like during a titration!)

$$
M_{a} V_{a}=M_{b} V_{b}
$$

Why does this shortcut work? Because when an acid and base have completely neutralized each other,

$$
M_{a} V_{a}=\operatorname{moles}(\operatorname{acid})=\operatorname{moles}\left(\mathrm{H}^{+}\right)=\operatorname{moles}\left(\mathrm{OH}^{-}\right)=\operatorname{moles}(\text { base })=M_{b} V_{b}
$$

Let's Practice!

1. Calculate the volume in milliliters of a 5.0 M solution of HF needed to neutralize 6.2 g of NaOH .
a. Which method is most useful here?
b. Solve the problem.
2. In a titration, the equivalence point is reached when 45.2 mL of HBr with a pH of 1.47 is added to a 25.0 mL sample of LiOH solution. What is the initial concentration of the LiOH solution?
a. Which method is most useful here?
b. Solve the problem.

Now you try! Choose your favorite method. ())
3. In a titration, what volume of $4.65 \mathrm{M} \mathrm{NH}_{3}$ is needed to neutralize 90.7 mL of $1.80 \mathrm{M}_{\mathrm{HNO}}^{3}$ ?
4. If 29.9 mL of a solution of RbOH requires 16.1 mL of a 2.3 M solution of $\mathrm{HClO}_{4}$ for complete titration, what is the initial molarity of the RbOH solution?

## Multiple Choice Practice

1. $0.60 \mathrm{M} \mathrm{HNO}_{3}$ was used to neutralize 15 mL of 0.30 M KOH . What volume of $\mathrm{HNO}_{3}$ was needed?
a. 7.5 mL
b. $\quad 15.0 \mathrm{~mL}$
c. $\quad 22.5 \mathrm{~mL}$
d. $\quad 30.0 \mathrm{~mL}$
2. The complete neutralization of 15.0 mL of KOH requires $0.030 \mathrm{~mol} \mathrm{HNO}_{2}$. The $[\mathrm{KOH}]$ was:
a. $\quad 0.0020 \mathrm{M}$
b. $\quad 0.50 \mathrm{M}$
c. $\quad 2.0 \mathrm{M}$
d. $\quad 5.0 \mathrm{M}$
3. During a titration, what volume of 1.00 M KOH is necessary to completely neutralize 10.0 mL of $2.00 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ ?
a. $\quad 10.0 \mathrm{~mL}$
b. $\quad 20.0 \mathrm{~mL}$
c. $\quad 25.0 \mathrm{~mL}$
d. $\quad 40.0 \mathrm{~mL}$


Figure 1: Titration Setup

A substance in a solution of $\qquad$ concentration (the $\qquad$ usually in a buret) is reacted with another substance in a solution of unknown concentration (the analyte, usually in a flask or beaker)

- Equivalence point: the point at which the moles of each reactant are stoichiometrically equal to each other in solution: $\operatorname{moles}\left(\mathrm{H}^{+}\right)=\operatorname{moles}\left(\mathrm{OH}^{-}\right)$ because the acid and base have completely neutralized.
- End point: the point of the titration where an $\qquad$ changes color


## How to Choose an Indicator

o Choose an indicator with $\qquad$ $=\mathrm{pH}$ at the equivalence point
$0 \quad \mathrm{~K}_{\mathrm{a}}$ of the indicator $\approx 1 \times 10^{-\mathrm{pH} @ \text { eq } \mathrm{pt}}$
o Indicator is a weak $\qquad$ where HA and $\mathrm{A}^{-}$are different colors!
0 If $\mathrm{pH} \leq \mathrm{pK}_{\mathrm{a}}$ mostly HA (one color), if $\mathrm{pH}>\mathrm{pK}_{\mathrm{a}}$ mostly $\mathrm{A}^{-}$(different color)

## Quick Reminder: How to Read a Buret

Burets, unlike most glassware, are read from the $\qquad$ down, not the bottom up!

Example: The image to the left shows a buret of NaOH before titration begins (leftmost) and at the end point (rightmost).

Beginning of Titration


End of Titration


1. What volume of solution was initially present in the buret? $\qquad$
2. What volume was present at the end point of the titration? $\qquad$
3. How much NaOH solution was added to the flask?

Potential Titration Lab Errors

| Error | Cause | Effect |
| :--- | :--- | :--- | :--- |
| 1. Over-titration | Going past equivalence point by adding <br> too much titrant | Calculated moles of titrant and thus calculated <br> moles of analyte are too large. |
| 2. Under-titration | Not reaching equivalence point by <br> adding too little titrant | Calculated moles of titrant and thus calculated <br> moles of analyte are too small. |
| 3. Water added to <br> titrant (buret) | Buret still wet from rinsing when it is <br> filled with titrant | Actual concentration of titrant is lower than <br> marked, so more volume was added, thus <br> calculated moles of analyte are too large. |
| 4. Water added to <br> analyte (flask) | Flask or beaker is still wet from rinsing <br> when analyte is added | Moles of analyte don't change, so no effect on <br> calculated moles of analyte. |

## Titrations Types to Know, Part I: Strong/ Strong

Strong Acid Titrated w/ Strong Base


Strong Base Titrated w/ Strong Acid


Strong Acid + Strong Base (in either direction)

- At equivalence point, pH $\qquad$ 7
- Net ionic will always be: $\qquad$ $(a q)+$ $\qquad$ $(a q) \rightarrow$ $\qquad$ (l)
- Use $M_{a} V_{a}=M_{b} V_{b}$ to calculate volume needed to reach equivalence point


## Titrations Types to Know, Part II: Weak/ Strong

## Weak Acid Titrated with Strong Base



Weak Base Titrated with Strong Acid


## pH at Equivalence point

- Weak acid + strong base: pH $\qquad$ 7
- Weak base + strong acid: pH $\qquad$ 7


## $\underline{1 / 2}$ Equivalence point (midpoint). A perfect buffer!

- Weak acid + strong base: $[\mathrm{HA}]=\left[\mathrm{A}^{-}\right]$, thus $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{K}_{\mathrm{a}}$ and $\qquad$ $=$ $\qquad$
- Weak base + strong acid: $[\mathrm{B}]=\left[\mathrm{BH}^{+}\right]$, thus $\left[\mathrm{OH}^{-}\right]=\mathrm{K}_{\mathrm{b}}$ and $\qquad$ $=$ $\qquad$

[^0]
## How Increasing $K_{a}$ Affects the Titration Curve

Notice the effect of increasing the $K_{a}$ value of the titrated acid on the titration curve in the image to the right.

Things to note:

1. The equivalence point volume does $\qquad$ change, regardless of the $\qquad$ of the acid (always $V_{A} M_{A}=V_{B} M_{B}$ ).
2. Equivalence point $\qquad$ does change.
3. The initial steep increase (at the very beginning of the titration curve) decreases and ultimately disappears as the strength of the acid increases.


## How to Determine $\mathrm{pK}_{\mathrm{a}} / \mathrm{pK}_{\mathrm{b}}$ of Weak Acid or Base from Titration Data

1. Calculate location of $\qquad$ -equivalence point by dividing volume at equivalence point in half! ()-
2. Use titration curve to determine the $\qquad$ at the half-equivalence point.
a. Analyte a weak acid? $\mathrm{pH}=$ $\qquad$ ,$K_{a}=1 \times 10^{-\mathrm{pH}}$
b. Analyte a weak base? $\mathrm{pH}=$ $\qquad$ (of $\mathrm{BH}^{+}$), so $\mathrm{pK}_{\mathrm{b}}=14-\mathrm{pH}, \mathrm{K}_{\mathrm{b}}=1 \times 10^{-(14-\mathrm{pH})}$

Let's Practice! Assume the acid and base solutions for each of the following graphs are equimolar.

| Graph 1 | Graph 2 | Graph 3 | Graph 4 |
| :---: | :---: | :---: | :---: |
| 1) What type of titration? | 4) What type of titration? | 7) What type of titration? | 10) What type of titration? |
| 2) At equivalence point, $\mathrm{pH} \approx$ $\qquad$ <br> 3) If possible, determine the $\mathrm{pK}_{\mathrm{a}}$ or $\mathrm{pK} \mathrm{K}_{\mathrm{b}}$ of the analyte (and identify if value is $\mathrm{pK}_{\mathrm{a}}$ or $\mathrm{pK}_{\mathrm{b}}$ ). | 5) At equivalence point, $\mathrm{pH} \approx$ $\qquad$ <br> 6) If possible, determine the $\mathrm{pK}_{\mathrm{a}}$ or $\mathrm{pK}_{\mathrm{b}}$ of the analyte (and identify if value is $\mathrm{pK}_{\mathrm{a}}$ or $\mathrm{pK}_{\mathrm{b}}$ ). | 8) At equivalence point, $\mathrm{pH} \approx$ $\qquad$ <br> 9) If possible, determine the $\mathrm{pK}_{\mathrm{a}}$ or $\mathrm{pK} \mathrm{K}_{\mathrm{b}}$ of the analyte (and identify if value is $\mathrm{pK}_{\mathrm{a}}$ or $\mathrm{pK}_{\mathrm{b}}$ ). | 11) At equivalence point, $\mathrm{pH} \approx$ $\qquad$ <br> 12) If possible, determine the $\mathrm{pK}_{\mathrm{a}}$ or $\mathrm{pK}_{\mathrm{b}}$ of the analyte (and identify if value is $p K_{a}$ or $p K_{b}$ ). |

## Multiple Choice Practice

Use the following information to answer questions 1-5.
The following curve is obtained during the titration of 30.0 mL of $1.0 \mathrm{M} \mathrm{NH}_{3}$, a weak base, with a strong acid.


1. Why is the solution acidic at the equivalence point?
a. The strong acid dissociates fully, leaving excess $\left[\mathrm{H}^{+}\right]$in solution.
b. The conjugate acid of $\mathrm{NH}_{3}$ is the only ion present at the equivalence point.
c. The water which is being created during the titration acts as an acid.
d. The acid is diprotic, donating two protons for every unit dissociated.
2. What is the concentration of the acid?
a. $\quad 0.50 \mathrm{M}$
b. $\quad 1.0 \mathrm{M}$
c. $\quad 1.5 \mathrm{M}$
d. $\quad 2.0 \mathrm{M}$
3. What ions are present in significant amounts during the buffer region?
a. $\mathrm{NH}_{3}$ and $\mathrm{NH}_{4}^{+}$
b. $\mathrm{NH}_{3}$ and $\mathrm{H}^{+}$
c. $\mathrm{NH}_{4}{ }^{+}$and $\mathrm{OH}^{-}$
d. $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{NH}_{3}$
4. Which volume on the titration curve corresponds with the region of maximum buffer efficacy?
a. 0 mL
b. $\quad 7.5 \mathrm{~mL}$
c. $\quad 15 \mathrm{~mL}$
d. 22.5 mL
5. The titration is completed using an indicator which changes color at the exact equivalence point of the titration. The protonated form of the indicator is HIn , and the deprotonated form is $\mathrm{In}^{-}$. At the equivalence point of the reaction:
a. $[\mathrm{HIn}]=\left[\mathrm{In}^{-}\right]$
b. $\quad[\mathrm{HIn}]=1 /\left[\mathrm{In}^{-}\right]$
c. $[\mathrm{HIn}]=2\left[\mathrm{In}^{-}\right]$
d. $[\mathrm{HIn}]=\left[\mathrm{In}^{-}\right]^{2}$

## How to Sketch A Titration Curve

1. Shape of curve
a. Acid titrated with a base (i.e. base added to acid, [acid] unknown): start $\qquad$ and end $\qquad$
b. Base titrated with an acid (i.e. acid added to base, [base] unknown): start $\qquad$ and end $\qquad$
2. Starting $\mathbf{p H}$ (initial plateau)
a. Starting pH $\qquad$ 7 if acid titrated with a base
b. Starting pH $\qquad$ 7 if base titrated with an acid
3. Equivalence point $\qquad$ ( mL ): steepest part (inflection point)
a. Make sure you are using the volume of the solution being added (your $\qquad$ _)
b. Use $V_{A} M_{A}=V_{B} M_{B}$
4. Equivalence point $\qquad$
a. Strong acid + strong base: pH $\qquad$ 7
b. Strong acid + weak base: pH $\qquad$ 7
c. Weak acid + strong base: pH $\qquad$ 7
5. Ending pH (final plateau)
a. Ending pH $\qquad$ 7 if acid titrated with a base
b. Ending pH $\qquad$ 7 if base titrated with an acid

## Let's Practice!

6. A 30.0 mL sample of 0.215 M hydroiodic acid completely neutralized 21.2 mL of aqueous rubidium hydroxide solution in a titration experiment.
a. Calculate the molarity of the initial rubidium hydroxide solution.
b. Sketch the curve that would result from this titration experiment on the grid below.

7. It is found that 24.68 mL of 0.1165 M NaOH is needed to titrate 0.2931 g of a solid, unknown, weak monoprotic acid to the end point. Calculate the molar mass of the acid.
a. Calculate the moles of unknown acid in your sample.
b. Determine the molar mass of the unknown acid.
c. Sketch the curve that would result from this titration experiment on the grid below.

d. The following acid-base indicators are available to follow the titration.

| Color Change |  |  |  |
| :---: | :---: | :---: | :---: |
| Indicator | Acid Form | Base Form | pH Transition Interval |
| Bromocresol purple | yellow | purple | $5.2-6.8$ |
| Bromthymol blue | yellow | blue | $6.0-7.6$ |
| Phenolphthalein | clear | pink | $8.3-10.0$ |

i. Which of them would be most appropriate for signaling the endpoint of the titration?
ii. Why?

## Multiple Choice Practice:

7. Examine the data and titration curve below for the titration of a weak acid with NaOH .

| Volume NaOH <br> added (mL) | 0.00 | 5.00 | 10.00 | 12.50 | 15.00 | 20.00 | 24.00 | 24.90 | 25.00 | 26.00 | 30.00 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{p H}$ | 2.88 | 4.15 | 4.58 | 4.76 | 4.93 | 5.36 | 6.14 | 7.15 | 8.73 | 11.29 | 11.96 |



What is the approximate value of the $\mathrm{K}_{\mathrm{a}}$ for this acid?
a. $1 \times 10^{-3}$
b. $1 \times 10^{-5}$
c. $1 \times 10^{-9}$
d. $1 \times 10^{-11}$

Use the following information to answer questions 8-10.
A student titrates 20.0 mL of 1.0 M NaOH with 2.0 M formic acid, $\mathrm{HCO}_{2} \mathrm{H}\left(\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-4}\right)$. Formic acid is a monoprotic acid.
8. How much formic acid is necessary to reach the equivalence point?
b. $\quad 10.0 \mathrm{~mL}$
b. $\quad 20.0 \mathrm{~mL}$
c. $\quad 30.0 \mathrm{~mL}$
d. $\quad 40.0 \mathrm{~mL}$
9. At the equivalence point, is the solution acidic, basic, or neutral? Why?
a. Acidic; the strong acid dissociates more than the weak base.
b. Basic; the only ion present at equilibrium is the conjugate base.
c. Basic; the higher concentration of the base is the determining factor.
d. Neutral; equal moles of both acid and base are present.
10. If the formic acid were replaced with a strong acid such as HCl at the same concentration ( 2.0 M ), how would that change the volume needed to reach the equivalence point?
a. The change would reduce the amount as the acid now fully dissociates.
b. The change would reduce the amount because the base will be more strongly attracted to the acid.
c. The change would increase the amount because the reaction will now go to completion instead of equilibrium.
d. Changing the strength of the acid will not change the volume needed to reach equivalence point.

## Lab: Identification of an Unknown Weak Acid

Introduction: A common question chemists have to answer is how much of something is present in a sample or a product. If the product contains an acid or base, this question is usually answered by a titration. Acid-base titrations can be used to measure the concentration of an acid or base in solution, to calculate the molar mass of an unknown acid or base, and to determine the equilibrium constant of a weak acid $\left(K_{a}\right)$ or weak base $\left(K_{b}\right)$.

Objective: In this lab, you will titrate an unknown weak acid with a strong base. In doing so, you will be able to identify the molar mass and $\mathrm{pK}_{\mathrm{a}}$ value of the unknown weak acid, and by comparing your values to a table of known weak acids, you be able to determine the identity of your unknown weak acid.

Table of Known Weak Acids

| Name | Formula of Most <br> Common Form | Molar Mass <br> (g/mol) | $\mathbf{K}_{\mathbf{a}}$ | pKa |
| :---: | :---: | :---: | :---: | :---: |
| glycolic <br> acid | $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{3}$ | 76.05 | $1.6 \times 10^{-4}$ | 3.80 |
| potassium dihydrogen <br> phosphate | $\mathrm{KH}_{2} \mathrm{PO}_{4}$ | 136.09 | $\mathrm{~K}_{\mathrm{a} 2}$ of $\mathrm{H}_{3} \mathrm{PO}_{4}=6.2 \times 10^{-8}$ | 7.21 |
| potassium hydrogen <br> sulfate | $\mathrm{KHSO}_{4}$ | 136.17 | $\mathrm{~K}_{\mathrm{a} 2}$ of $\mathrm{H}_{2} \mathrm{SO}_{4}=1.2 \times 10^{-2}$ | 1.92 |
| potassium hydrogen <br> sulfite | $\mathrm{KHSO}_{3}$ | 120.16 | $\mathrm{~K}_{\mathrm{a} 2}$ of $\mathrm{H}_{2} \mathrm{SO}_{3}=6.4 \times 10^{-8}$ | 7.19 |
| sodium hydrogen <br> sulfate | $\mathrm{NaHSO}_{4} \bullet \mathrm{H}_{2} \mathrm{O}$ | 138.08 | $\mathrm{~K}_{\mathrm{a} 2}$ of $\mathrm{H}_{2} \mathrm{SO}_{4}=1.2 \times 10^{-2}$ | 1.92 |
| sodium hydrogen <br> sulfite | $\mathrm{NaHSO}_{3}$ | $\mathrm{~K}_{\mathrm{a} 2}$ of $\mathrm{H}_{2} \mathrm{SO}_{3}=6.4 \times 10^{-8}$ | 7.19 |  |
| sodium hydrogen <br> tartrate | $\mathrm{NaHC}_{4} \mathrm{H}_{4} \mathrm{O}_{6} \bullet \mathrm{H}_{2} \mathrm{O}$ | 190.09 | $\mathrm{~K}_{\mathrm{a} 2}$ of $\mathrm{H}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6}=4.6 \times$ | 4.34 |

## Materials

## Chemicals

Phenolphthalein (indicator), $1.0 \%, 1 \mathrm{~mL}$
Sodium hydroxide solution, $\mathrm{NaOH}, 0.100 \mathrm{M}$
Unknown weak acid, dried
Distilled Water

## Equipment

Balance, Funnel, pH probe, Wash Bottle
Beaker ( 250 mL ), Buret ( 50 mL )
Magnetic Stirrer and Stir Bar
Data Collection Device

IT IS IMPORTANT THAT YOU ARE CAREFUL WITH THE TIP OF THE pH PROBE! THEY EASILY BREAK!! Carefully unscrew the container of storage solution at the tip of the pH probe and set the container in a safe place where it will not tip over. When you are not using the pH probe, gently rest it in a beaker of tap water.

Be sure to rinse the pH probe with distilled water EACH TIME before using!

## Procedure:

1. Prepare for data collection by connecting your pH probe to the data collection device as directed by your instructor.
2. The burets have been prepared for you. However, you will need to check two things:
a. Check the buret tip and make sure it is full of liquid and has NO air bubbles.
b. Make sure the initial volume of solution in your buret is at or below 0 mL .
c. If one or the other of these things is not ready, you will need to open the buret stopcock and drain a small amount of liquid. Be certain to place a container underneath the buret BEFORE opening it!
3. Mass about 0.1 grams of the unknown acid into a clean 250 mL beaker. Record the precise mass in the appropriate data table.
4. Add about 50 mL of distilled water to the beaker and swirl until all of the unknown acid is dissolved.

Question: Do you need to add precisely 50.0 mL of distilled $\mathrm{H}_{2} \mathrm{O}$ ?
**Does adding distilled water change the number of moles of acid in your beaker?**
5. Add three drops of phenolphthalein indicator to the unknown acid solution.
6. If available, carefully add a magnetic stir bar to the beaker.
7. Rinse the pH probe with distilled water and insert the pH probe into the flask. Clamp the pH electrode so it is submerged in the acid solution (see figure to the right). BE SURE THE STIR BAR DOES NOT HIT THE ELECTRODE. Set the stir bar gently spinning (solution should not be splashing up on the sides of the beaker).
8. When the pH reading has (pretty much) stabilized, record the initial pH of your unknown acid solution in the appropriate Data Table.
9. Measure the precise volume in the buret and record this value in the appropriate data table as "initial volume."
10. You are now ready to begin titration. This process goes faster if one person manipulates and reads the buret while another person operates the data
 collection device and records volume measurements.
a. Begin the titration by adding approximately 0.50 mL of the NaOH solution to the beaker. Record the exact volume added to the hundredths place in the appropriate data table. When the pH reading has stabilized, record the pH value as well.
b. Continue adding NaOH in 0.50 mL mL increments. Be sure to stir the solution thoroughly and record the pH value and the exact volume of NaOH added after EACH addition.
c. You will know that you are approaching the equivalence point when it takes longer for the phenolphthalein color to fade. You can decrease the amount of NaOH
d. Record the volume of NaOH in the buret when the indicator changes to a faint pink and remains that color for at least $\mathbf{3 0}$ seconds.
e. Once you've reached equivalence point (as determined by your indicator), resume adding the sodium hydroxide in 0.5 mL increments. Be sure to record the exact volume of NaOH added after EACH addition.
f. Continue adding NaOH in 0.5 mL increments until the pH levels off in the distinctly basic range to complete your titration curve.
11. If time permits or your instructor indicates it is necessary, repeat steps $3-10$ with a second trial. This time, however, try to more closely determine the equivalence point by adding the NaOH solution in one-drop increments when you are close to the equivalence point.
12. Clean up and dispose of chemicals as directed by your instructor.

Final Clean-up: (last period to perform titration)
13. Empty extra NaOH from buret into the beaker with analyte and add it to the waste beaker.
14. Rinse the buret 3 times with distilled water, and clamp it upside down (with stopcock open) to dry.

Trial 1
Initial Mass of Unknown Acid:
Initial Volume of Buret:
Volume NaOH added when indicator changes color:

| Volume <br> NaOH <br> Added <br> (mL) | pH | Volume <br> $\mathbf{N a O H}$ <br> Added <br> Continued <br> $(\mathrm{mL})$ | pH <br> continued |
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Trial 2
Initial Mass of Unknown Acid:
Initial Volume of Buret:
Volume NaOH added when indicator changes color:

| Volume <br> NaOH <br> Added <br> (mL) | pH | Volume <br> NaOH <br> Added <br> Continued <br> (mL) | pH <br> continued |
| :---: | :--- | :--- | :--- |
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## Graphical Analysis:

1. Open a new Google Sheet or Excel file.
2. In the top left cell ( A 1 ), put the header " NaOH added ( mL )". Enter your volume values down the rest of the column: enter all of the volume measurements that you have, in order.
3. In the top cell of column $\mathrm{B}(\mathrm{B} 1)$, put the header " pH ". Enter your pH values down the rest of the column and be sure each pH matches the volume it is next to.
4. When all of your data is entered, select the entire area containing your headers and data. Select "Insert" in the menu bar, then select "Chart".
5. Use the dropdown menu to change chart type to "Line". X-Axis should already be set to NaOH added ( mL ). If not, fix it. Series should already be set to pH . If not, fix it.
6. Go to "Customize" tab and expand the "Chart style" menu. Check off the "Smooth" box.

Calculations: Use your titration curve to answer the following questions.

1. From the titration curve of pH versus volume of NaOH added, determine the following.
a. What is the pH at the equivalence point?
b. What is the pH at the $1 / 2$-equivalence point?
c. What is the value of $\mathrm{pK} \mathrm{K}_{\mathrm{a}}$ for this acid?
d. What is the value of the $K_{a}$ for this acid? (Show your work below!)
2. Using the data from your best trial (if you were able to perform more than one trial),
a. calculate the number of moles of weak acid in your sample.
b. calculate the molar mass of your weak acid.
3. Use your experimentally determined values of the molar mass and $\mathrm{pK}_{\mathrm{a}}$ of your unknown acid (and consult the table of known weak acids on page 1 of this lab) to identify your unknown acid.

Experimentally Determined
Weak Acid Name: $\qquad$ Formula: $\qquad$
Molar Mass: $\qquad$ $\mathrm{K}_{\mathrm{a}}$ : $\qquad$ $\mathrm{pK}_{\mathrm{a}}$ : $\qquad$
4. Speak to your instructor to determine the true identity of your unknown acid.

## Accepted

Weak Acid Name: $\qquad$ Formula: $\qquad$
Molar Mass: $\qquad$ $\mathrm{K}_{\mathrm{a}}$ : $\qquad$ $\mathrm{pK}_{\mathrm{a}}$ : $\qquad$
5. Calculate the following:
a. Percent error of your experimentally determined $\mathrm{pK}_{\mathrm{a}}\left(\boldsymbol{N O T} \mathrm{K}_{\mathrm{a}}\right)$ value.
b. Percent error of your experimentally determined molar mass.

## Analysis:

6. List the measurements that you collected in this lab that gave you enough data to calculate the molar mass of the unknown acid.
7. List the calculations/equations that you did with your data to determine the molar mass of the unknown acid.
8. If a pH probe was unavailable for use in this experiment, what chemical method could be used to indicate when the equivalence point was reached? Explain how this method works.
9. Your unknown acid sample was dried in an oven (on low heat) before your titration was performed, and then kept in a desiccator until the time of titration.
a. What was the purpose of drying the sample?
b. What error might you have seen with the calculated molar mass of the acid if your sample had not been dried? Justify your response.
10. What effect would over-titration have on your calculated molar mass? Explain.

## pHun with Titration Calculations

## Strong Acid + Strong Base = 3 Situations to Determine pH

1. Initial acid concentration:
a. only strong acid
b. $\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log [$ acid $]$
2. Equivalence point:
a. moles of $\mathrm{H}^{+}=$moles of $\mathrm{OH}^{-}$
b. $\mathrm{pH}=7$
c. Use $V_{A} M_{A}=V_{B} M_{B}$ to calculate volume needed to reach equivalence point.
3. Before or after equivalence point: use stoich (BCA table) to calculate excess moles of $\mathrm{H}^{+}$or $\mathrm{OH}^{-}$, divide by total volume, and calculate the pH based on this value.

Titration Curve of 50.0 mL of 0.200 M HCl with 0.100 M NaOH


Example:
a. $\quad 100.0 \mathrm{~mL}$ of 1.00 M HCl is titrated with 0.500 M NaOH . Calculate the pH after 50.0 mL of base has been added.
b. Calculate the pH after 200.0 mL of base has been added.
c. Calculate the pH after 300.0 mL of base has been added.

1. The pH before the titration begins: $\qquad$ weak acid.
2. During titration but before equivalence point: this is a $\qquad$ problem!!!

- Once the titration begins, weak acid has reacted with the strong base to produce salt (the conjugate base of the weak acid).

3. $1 / 2$ Equivalence point (midpoint). A perfect buffer!

- $[\mathrm{HA}]=\left[\mathrm{A}^{-}\right]$, thus $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{K}_{\mathrm{a}}$ and $\qquad$ $=$ $\qquad$

4. Equivalence point. All acid and base neutralized: only species left are $\qquad$ and $\qquad$ .

- pH is based on $\qquad$ properties of the salt (conjugate $\qquad$ of weak acid.) ()-

5. Beyond the equivalence point: all about the $\qquad$ $!$

- Calculate the amount of excess strong base added beyond the equivalence point.

The pH Curve for the Titration of 50.0 mL of $0.100 \mathrm{M} \mathrm{H}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ with 0.100 M NaOH


The pH Curve for the Titration of 100.0 mL of $0.050 \mathrm{M} \mathrm{NH}_{3}$ with 0.10 M HCl


## The half-way point is important!

After you have determined the equivalence point (endpoint) of the titration, go to half that value. The pH at the half-titration point is equal to the $\mathrm{p} K_{\mathrm{a}}$ of the weak acid, $\mathrm{BH}^{+}$. To get the $\mathrm{p} K_{\mathrm{b}}$ of the base (B) you MUST subtract the $\mathrm{p} K_{\mathrm{a}}$ from 14 . The reason for this is that the pOH is actually what equals the $\mathrm{p} K_{\mathrm{b}}$.

$$
\mathrm{p} K_{\mathrm{b}}=14-\mathrm{p} K_{\mathrm{a}}
$$



Examples:

1. Consider the titration of 100.0 mL of 0.200 M acetic acid $\left(\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}\right)$ by 0.100 M KOH . Calculate the pH of the resulting solution after the following volumes of KOH have been added.
a. $\quad 0.0 \mathrm{~mL}$
b. $\quad 100.0 \mathrm{~mL}$
c. $\quad 150.0 \mathrm{~mL}$
d. $\quad 200.0 \mathrm{~mL}$
e. 250.0 mL
2. Consider the titration of 100.0 mL of $0.100 \mathrm{M} \mathrm{H}_{2} \mathrm{NNH}_{2}\left(\mathrm{~K}_{\mathrm{b}}=3.0 \times 10^{-6}\right)$ by $0.200 \mathrm{M} \mathrm{HNO}_{3}$. Calculate the pH of the resulting solution after the following volumes of $\mathrm{HNO}_{3}$ have been added.
a. 0.0 mL
b. 20.0 mL
c. $\quad 25.0 \mathrm{~mL}$
d. 50.0 mL
e. $\quad 100.0 \mathrm{~mL}$

Both methods of solving (stoichiometry AND the shortcut) still work! There's just a slight twist. ©)

Example: What volume, in mL , of $4.65 \mathrm{M} \mathrm{Ba}(\mathrm{OH})_{2}$ is needed to neutralize 91 mL of 1.80 M HBr ?

1. Stoichiometry:
2. Shortcut: Now your equation looks like

$$
\boldsymbol{M}_{\boldsymbol{H}^{+}} \boldsymbol{V}_{\boldsymbol{a}}=\boldsymbol{M}_{\boldsymbol{O H}}{ }^{-} \boldsymbol{V}_{\boldsymbol{b}}
$$

Why the change? If an acid and/or base are polyprotic,

$$
\operatorname{moles}(\text { acid }) \neq \operatorname{moles}\left(\mathrm{H}^{+}\right)=\operatorname{moles}\left(\mathrm{OH}^{-}\right) \neq \operatorname{moles}(\text { base })
$$

Note: If either the base or acid is monoprotic, you can keep that calculation the same as the original shortcut.

Now you try! Choose your favorite method. ()-)

1. Calculate the molarity of an $\mathrm{Al}(\mathrm{OH})_{3}$ solution if 32.5 mL of it is needed to neutralize 21 mL of $3.5 \mathrm{M} \mathrm{HClO}{ }_{4}$.
2. Calculate the volume, in mL , of $1.20 \mathrm{M} \mathrm{H}_{3} \mathrm{PO}_{4}$ solution needed to neutralize 250 mL of $0.75 \mathrm{M} \mathrm{Ca}(\mathrm{OH})_{2}$.

## Multiple Choice Practice

1. $0.60 \mathrm{M} \mathrm{HNO}_{3}$ was used to neutralize 15 mL of $0.30 \mathrm{M} \mathrm{Sr}(\mathrm{OH})_{2}$. What volume of $\mathrm{HNO}_{3}$ was needed?
a. 7.5 mL
b. $\quad 15.0 \mathrm{~mL}$
c. $\quad 22.5 \mathrm{~mL}$
d. $\quad 30.0 \mathrm{~mL}$
2. The complete neutralization of 15.0 mL of KOH requires $0.025 \mathrm{~mol} \mathrm{H}_{2} \mathrm{SO}_{4}$. The $[\mathrm{KOH}]$ was:
a. $\quad 1.50 \mathrm{M}$
b. $\quad 1.67 \mathrm{M}$
c. $\quad 3.33 \mathrm{M}$
d. $\quad 6.67 \mathrm{M}$
3. During a titration, what volume of 0.500 M KOH is necessary to completely neutralize 10.0 mL of $2.00 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ ?
a. $\quad 10.0 \mathrm{~mL}$
b. $\quad 20.0 \mathrm{~mL}$
c. $\quad 25.0 \mathrm{~mL}$
d. $\quad 40.0 \mathrm{~mL}$

## Polyprotic Limiting and Excess Calculations

A fun type of limiting excess problem is determining which conjugate of a polyprotic acid is left over in solution after incomplete neutralization with a base!

If you add strong base in a $1: 1$ mole ratio with a polyprotic acid, one $\mathrm{H}^{+}$will be removed:
10. $\mathrm{mL} 1.0 \mathrm{M} \mathrm{NaOH}+10 . \mathrm{mL} 1.0 \mathrm{M} \mathrm{H}_{3} \mathrm{PO}_{4} \rightarrow$ $\qquad$ $+$ $\qquad$

If you add strong base in a 2:1 mole ratio with a polyprotic acid, two $\mathrm{H}^{+} \mathrm{s}$ will be removed:
20. $\mathrm{mL} 1.0 \mathrm{M} \mathrm{NaOH}+10 . \mathrm{mL} 1.0 \mathrm{M} \mathrm{H}_{3} \mathrm{PO}_{4} \rightarrow$ $\qquad$ $+$ $\qquad$
If you add strong base in a $3: 1$ mole ratio with a polyprotic acid, three $\mathrm{H}^{+}$' s will be removed:
30. mL $1.0 \mathrm{M} \mathrm{NaOH}+10 . \mathrm{mL} 1.0 \mathrm{M} \mathrm{H}_{3} \mathrm{PO}_{4} \rightarrow$ $\qquad$ $+$ $\qquad$
4. Equal volumes of equimolar $\mathrm{NaOH}(\mathrm{aq})$ and $\mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq})$ are mixed. Which of the following best shows the relative concentrations of ions in solution?
a. $\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]=\left[\mathrm{HCO}_{3}^{-}\right]>\left[\mathrm{CO}_{3}{ }^{2-}\right]>[\mathrm{NaOH}]$
b. $\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]>\left[\mathrm{HCO}_{3}^{-}\right]=\left[\mathrm{CO}_{3}{ }^{2-}\right]>[\mathrm{NaOH}]$
c. $\left[\mathrm{HCO}_{3}{ }^{-}\right]>\left[\mathrm{CO}_{3}{ }^{2-}\right]>\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]>[\mathrm{NaOH}]$
d. $\left[\mathrm{CO}_{3}{ }^{2-}\right]>[\mathrm{NaOH}]>\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]=\left[\mathrm{HCO}_{3}{ }^{-}\right]$
5. What volume of 0.50 M LiOH would you need to add to $100 . \mathrm{mL}$ solution of $1.0 \mathrm{M} \mathrm{H}_{3} \mathrm{PO}_{4}$ to ensure $\mathrm{PO}_{4}{ }^{3-}$ is the predominant anion in solution?
a. $\quad 150 . \mathrm{mL}$
b. $300 . \mathrm{mL}$
c. $600 . \mathrm{mL}$
d. $1000 . \mathrm{mL}$

## Polyprotic Acid Titration

When titrating a polyprotic acid, each acidic hydrogen will have its $\qquad$ equivalence point!

$$
\begin{array}{ll}
\mathrm{H}_{3} \mathrm{~A}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{H}_{2} \mathrm{~A}^{-} & K_{a 1}= \\
\mathrm{H}_{2} \mathrm{~A}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{HA}^{2-} & K_{a 2}= \\
\mathrm{HA}^{2-}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}^{3-} & K_{a 3}=
\end{array}
$$



Acids, Bases \& Buffers Cheat Sheet: The 6 Ways to Determine pH

## 1) Strong Acids/ Strong Bases

## You MUST memorize:

Strong Acids: $\mathrm{HCl}, \mathrm{HBr}, \mathrm{HI}, \mathrm{HNO}_{3}, \mathrm{HClO}_{4}, \mathrm{H}_{2} \mathrm{SO}_{4}$
Strong Bases: Groups IA and IIA metal hydroxides
100\% Dissociation! Easy life:

$$
\begin{gathered}
p H=-\log \left[H^{+}\right]=-\log [H A]_{o} \\
p O H=-\log \left[O H^{-}\right]=-\log [B]_{o} \\
p H+p O H=14
\end{gathered}
$$

## 2) Weak Acids/ Weak Bases

If it's not strong, it's weak!

## $<1 \%$ Dissociation $\rightarrow$ Equilibrium!

Time saver!! Since acids ionize $1 \mathrm{H}^{+}$at a time, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=$ $\left[\mathrm{A}^{-}\right]$, and $\left[\mathrm{OH}^{-}\right]=\left[\mathrm{BH}^{+}\right]$. For weak acids and bases, make the assumption $[\mathrm{HA}]_{0}-\boldsymbol{x} \approx[\mathrm{HA}]_{0}$ and $[\mathrm{B}]_{0}-\boldsymbol{x} \approx[\mathrm{B}]_{0}$.

## Weak Acids:

$K_{a}=\frac{[x][x]}{[H A]_{o}-x} \approx \frac{[x][x]}{[H A]_{o}}$ where $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{x} \ll[\mathrm{HA}]_{\circ}$

## Weak Bases:

$K_{b}=\frac{[x][x]}{[B]_{o}-x} \approx \frac{[x][x]}{[B]_{o}}$ where $\left[\mathrm{OH}^{-}\right]=\mathrm{x} \ll[\mathrm{B}]_{\circ}$

## 3) Salty Salts

To know if a salt will affect pH , determine: $\quad \rightarrow$ Will the salt ions will hydrolyze (or split) water?
Conjugates of Strong Acids/Bases: do NOT hydrolyze water, and thus don't affect pH
Conjugates of Weak Acids/Bases: DO hydrolyze water, and thus do affect pH !

## How to Determine the pH of a Salt

1. Dissociate your salt.

Make the cation into a base: is it strong or weak?
2. Make the anion into an acid: is it strong or weak?
3. Strong wins!
4. If either is weak, write the hydrolysis reaction:

Conjugate base of WA: $\quad \mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{OH}^{-}+\mathrm{HA}$
Conjugate acid of WB: $\quad \mathrm{BH}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{B}$

Example

$$
\mathrm{CaSO}_{3} \rightarrow \mathrm{Ca}^{2+}+\mathrm{SO}_{3}^{2-}
$$

$\mathrm{Ca}^{2+}+2 \mathrm{OH}^{-} \rightarrow \mathrm{Ca}(\mathrm{OH})_{2}$ Strong base
$\mathrm{H}^{+}+\mathrm{SO}_{3}^{-} \rightarrow \mathrm{HSO}_{3}^{-} \quad$ Weak acid
$\mathrm{SB}+\mathrm{WA}$, so this salt is basic!
$\mathrm{SO}_{3}{ }^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{OH}^{-}+\mathrm{HSO}_{3}{ }^{-}$
5. Use your hydrolysis equation to calculate the pH using the Weak Acids/Bases method.
6. Be careful. Did the problem give you $K_{a}$, or $K_{b}$ instead? Do you need to convert based on your hydrolysis reaction? Remember: $\quad \mathrm{K}_{\mathrm{w}}=\mathrm{K}_{\mathrm{a}} \times \mathrm{K}_{\mathrm{b}}=1.0 \times 10^{-14}$

## 4) Adding Strong Acids + Strong Bases (Yes, this includes titrations!)

These are really just stoichiometry problems with a limiting reagent! ©)

- What is "excess" determines the $\mathbf{p H}$ (since all strong/strong combos neutralize)
- Beware the change in volume if multiple solutions are being added! (calculate moles of either $\mathrm{H}^{+}$or $\mathrm{OH}^{-}$in excess, and divide by total volume to determine concentration of $\left[\mathrm{H}^{+}\right]$or $\left[\mathrm{OH}^{-}\right]$, and go from there)


## 5) Buffers

Whenever a weak acid or base is present with its conjugate salt - YOU HAVE A BUFFER!!! Four ways to get a buffer:

1. Weak acid and its conjugate base (HA and $\mathrm{A}^{-}$OR HA and NaA ) $1: 1$ mole ratio
2. Weak base and its conjugate acid ( $B$ and $B H^{+} O R B$ and $B H C l$ ) 1:1 mole ratio
3. Weak base with strong acid (titration) $1 \mathrm{WB}: 0.5 \mathrm{SA}$ mole ratio
$\rightarrow$ strong acid reacts with weak base, producing conjugate acid
4. Weak acid with strong base (titration) $\mathbf{1} \mathrm{WA}: \mathbf{0 . 5} \mathrm{SB}$ mole ratio
$\rightarrow$ strong base reacts with weak acid, producing conjugate base
The best buffer has: 1) High capacity (lots of acid and base), 2) [HA] =[ $\left.\mathrm{A}^{-}\right], 3$ ) pH (of buffer) $=\mathrm{pK}_{\mathrm{a}}$ (of acid form)
Two calculation options: $\quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=K_{a} \frac{[H A]}{\left[A^{-}\right]} \quad$ or $\quad \mathrm{pH}=\mathrm{pKa}+\log \left(\frac{\left[A^{-}\right]}{[H A]}\right)$
[HA] = Weak acid or salt ot conjugate base or added strong base (in a WB/SA titration)
$\left[A^{-}\right]=$Weak base or salt of conjugate acid or added strong acid (in a WA/SB titration)
Shortcut!!! Since $\frac{[\text { AAcid }]}{[\text { Base }]}$ is a ratio in the equations, the amount of moles may be substituted in place of concentration because the final volumes will be the same, and thus cancel out.
6) Adding Strong Acids/Bases + Weak Bases/Acids (Yes, this includes titrations!)

Buffers make the titration curve "flat" at the region where buffering occurs. On a titration curve, this is the point of inflection (buffer arrow) = maximum buffering capacity!

Weak Acid Titrated with Strong Base


Weak Base Titrated with Strong Acid


There are 4 zones of interest along a titration curve for a Weak Acid/Base and Strong Base/Acid:

1. Initial pH : simply a weak acid or weak base problem!
2. During titration, before equivalence point: BUFFER! The amount of conjugate formed = the amount of strong acid or base added. (Amount of weak left $=\mathrm{HA}_{\mathrm{o}}$ - strong added)
3. Equivalence point: only salt and water are left; salt is either a weak base (if a weak acid was titrated) or a weak acid (if a weak base was titrated); remember to convert $K_{a}$ to $K_{b}$ or vice versa! (Use $M_{A} V_{A}=M_{B} V_{B}$ )
4. Beyond the equivalence point: Stoichiometry! Calculate how much STRONG (acid or base) is left after equivalence, recalculate its molarity (remember, volume increased during titration), and calculate using the strong acid/base method.

Best Indicator: Choose indicator with $\mathrm{pK}_{\mathrm{a}}$ (of indicator) $\approx \mathrm{pH}$ (at equivalence point of titration). This means that $\mathrm{K}_{\mathrm{a}}$ of the indicator $\approx 1 \times 10^{-\mathrm{pH}}$ @ eq pt $)$

Remember: if $\mathrm{pH} \leq \mathrm{pK}_{\mathrm{a}}$ the acid form (HA) predominates, if $\mathrm{pH}>\mathrm{pK}_{\mathrm{a}}$ the conjugate base form ( $\mathrm{A}^{-}$) predominates

## Unit 9 Multiple Choice Practice

Use the following information to answer questions 1-4.

A student titrates some 1.0 M HCl into 20.0 mL of methylamine $\left(\mathrm{CH}_{3} \mathrm{NH}_{2}\right)$, a weak base which only accepts a single proton. The following titration curve results:


1. What is the concentration of the methylamine?
a. $\quad 0.50 \mathrm{M}$
b. $\quad 0.75 \mathrm{M}$
c. $\quad 1.0 \mathrm{M}$
d. $\quad 1.25 \mathrm{M}$
2. What is the approximate $\mathrm{pK}_{\mathrm{b}}$ for methylamine?
a. 3.5
b. 5.5
c. 10.5
d. $\quad 12.5$
3. What buffer region of this titration is located:
a. Below 3.0 mL
c. Between 14.0 mL and 16.0 mL
b. Between 3.0 mL and 14.0 mL
d. Above 16.0 mL
4. The methylamine is replaced by 20.0 mL of sodium hydroxide of an identical concentration. If the sodium hydroxide is titrated with the 1.0 M HCl , which of the following options accurately describes the pH levels at various points during the titration when compared to the pH levels at the same point in the $\mathrm{HCl} /$ methylamine titration?

Initial pH Equivalence pH Ending pH
a. lower
b. higher
c. same
d. higher
same
higher
higher
lower
higher
same
same
lower
5. What volume of 0.300 M KOH would be needed to completely neutralize 60.0 mL of $0.200 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}$ ?
a. $\quad 40.0 \mathrm{~mL}$
b. $\quad 60.0 \mathrm{~mL}$
c. $\quad 80.0 \mathrm{~mL}$
d. $100 . \mathrm{mL}$
6. Which of the following indicators would be most suitable for the titration of 0.10 M lactic acid $\left(\mathrm{pK}_{\mathrm{a}}=3.08\right)$ with 0.10 $\mathrm{M} \mathrm{KOH}(\mathrm{aq})$ ?
a. phenol red $\left(\mathrm{pK}_{\mathrm{a}}=6.9\right)$
c. thymol blue $\left(\mathrm{pK}_{\mathrm{a}}=1.7\right)$
b. alizarin red $\left(\mathrm{pK}_{\mathrm{a}}=4.5\right)$
d. methyl orange $\left(\mathrm{pK}_{\mathrm{a}}=3.4\right)$
7. What is the pH of the solution formed when 0.040 moles of $\mathrm{NaOH}(\mathrm{s})$ is added to 1.00 L of 0.050 M HCl ?
a. $\quad 1.00$
b. $\quad 2.00$
c. $\quad 7.00$
d. 12.00
8. What volume of $0.25 \mathrm{M} \mathrm{HClO}_{4}$ would be needed to completely neutralize 30.0 mL of $0.20 \mathrm{M} \mathrm{Ca}(\mathrm{OH})_{2}$ ?
a. $\quad 12 \mathrm{~mL}$
b. $\quad 24 \mathrm{~mL}$
c. $\quad 36 \mathrm{~mL}$
d. $\quad 48 \mathrm{~mL}$
9. Equal volumes of $0.50 \mathrm{M} \mathrm{Mg}(\mathrm{OH})_{2}(\mathrm{aq})$ and $1.0 \mathrm{M} \mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{aq})$ are mixed. Which of the following ions is found in the highest concentration?
a. $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$
b. $\mathrm{HPO}_{4}{ }^{2-}$
c. $\mathrm{PO}_{4}{ }^{3-}$
d. $\mathrm{OH}^{-}$
10. What volume of 0.100 M NaOH is required to completely neutralize 15.00 mL of $0.100 \mathrm{M} \mathrm{H}_{3} \mathrm{PO}_{4}$ ?
a. $\quad 5.00 \mathrm{~mL}$
b. $\quad 15.00 \mathrm{~mL}$
c. $\quad 30.00 \mathrm{~mL}$
d. $\quad 45.00 \mathrm{~mL}$
11. The complete neutralization of 15.0 mL of KOH requires $0.025 \mathrm{~mol} \mathrm{H}_{2} \mathrm{SO}_{4}$. The [ KOH ] was:
a. $\quad 1.50 \mathrm{M}$
b. $\quad 1.67 \mathrm{M}$
c. $\quad 3.33 \mathrm{M}$
d. $\quad 6.67 \mathrm{M}$
12. During a titration, what volume of 0.500 M KOH is necessary to completely neutralize 10.0 mL of $2.00 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ ?
a. $\quad 10.0 \mathrm{~mL}$
b. $\quad 20.0 \mathrm{~mL}$
c. $\quad 25.0 \mathrm{~mL}$
d. $\quad 40.0 \mathrm{~mL}$
13. What is the pH of the solution formed when 0.060 moles of NaOH is added to 1.00 L of 0.050 M HCl ?
a. $\quad 2.00$
b. $\quad 7.00$
c. $\quad 12.00$
d. 12.78
14. Which of the following titrations will always have an equivalence point at a $\mathrm{pH}>7.00$ ?
a. weak acid with a weak base
c. weak acid with a strong base
b. strong acid with a weak base
d. strong acid with a strong base
$\qquad$ Period $\qquad$ Favorite cartoon character: $\qquad$

## Unit 9 Quiz Free Response Practice (5 points)

1. A solution of 0.080 M HCl , hydrochloric acid, is prepared to determine the concentration of 40.0 mL of a solution of methylamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$, a weak base $\left(\mathrm{K}_{\mathrm{b}}=4.38 \times 10^{-4}\right)$. The 40.0 mL of $\mathrm{CH}_{3} \mathrm{NH}_{2}$ is placed in an Erlenmeyer flask. A pH probe is used to obtain pH readings throughout the titration experiment. To reach the equivalence point, 25.0 mL of hydrochloric acid is added to the Erlenmeyer flask. Assume all data is collected at $25^{\circ} \mathrm{C}$.

The neutralization reaction is shown below:

$$
\mathrm{HCl}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{NH}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})
$$

a. What concentration of $\mathrm{CH}_{3} \mathrm{NH}_{2}$ was initially present in solution? Justify your answer with a calculation. [1 pt]
b. When the moles of added HCl are equal to the initial moles of $\mathrm{CH}_{3} \mathrm{NH}_{2}$ present in solution, will the pH of the solution be less than 7, equal to 7, or greater than 7? Justify your answer. [2 pt]
c. On the axis below, sketch the general shape of the titration curve when 40.0 mL of $\mathrm{CH}_{3} \mathrm{NH}_{2}$ is titrated with 60.0 mL of HCl over time. [2 pts]



1. A solution of 0.100 M HCl and a solution of 0.100 M NaOH are prepared. A 40.0 mL sample of one of the solutions is added to a beaker and then titrated with the other solution. A pH electrode is used to obtain the data that are plotted in the titration curve shown above.
a. Write the net ionic equation for the reaction of $\mathrm{HCl}(\mathrm{aq})$ and $\mathrm{NaOH}(\mathrm{aq})$. (1 point)
b. Identify the solution that was initially added to the beaker. Explain your reasoning. (1 point)
c. On the titration curve above, circle the point that corresponds to the equivalence point. (1 point)
d. At the equivalence point, how many moles of titrant have been added? (1 point)
e. The same titration is to be performed again, this time using an indicator. Use the information in the table below to select the best indicator for the titration. Explain your choice. (2 points)

| Indicator | pH Range of <br> Color Change |
| :---: | :---: |
| Methyl violet | $0-1.6$ |
| Methyl red | $4-6$ |
| Alizarin yellow | $10-12$ |

f. What is the difference between the equivalence point of a titration and the end point of a titration? (1 point)
g. On the grid provided on the next page, sketch the titration curve that would result if the solutions in the beaker and buret were reversed (i.e., if 40.0 mL of the solution used in the buret in the previous titration were titrated with the solution that was in the beaker). (3 points)

2. A 1.22 g sample of a pure monoprotic acid, HA, was dissolved in distilled water. The HA solution was then titrated with 0.250 M NaOH . The pH was measured throughout the titration, and the equivalence point was reached when 40.0 mL of the NaOH solution had been added. The data from the titration are recorded in the table below.

| Volume of 0.250 MNaOH <br> Added $(\mathrm{mL})$ | pH of Titrated <br> Solution |
| :---: | :---: |
| 0.00 | $?$ |
| 10.0 | 3.72 |
| 20.0 | 4.20 |
| 30.0 | $?$ |
| 40.0 | 8.62 |
| 50.0 | 12.40 |

a. Explain how the data in the table above provide evidence that HA is a weak acid rather than a strong acid. (1 point)
b. Write the balanced net-ionic equation for the reaction that occurs when the solution of NaOH is added to the solution of HA. (1 point)
c. Calculate the number of moles of HA that were titrated. (1 point)
d. Calculate the molar mass of HA. (1 point)

The equation for the dissociation reaction of HA in water is shown below.

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \leftrightarrow \mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})
$$

e. Assume that the initial concentration of the HA solution (before any NaOH solution was added) is 0.200 $M$. Determine the pH of the initial HA solution. (3 points)
3. To produce an aqueous solution of $\mathrm{HNO}_{2}$, a student bubbles $\mathrm{N}_{2} \mathrm{O}_{3}(\mathrm{~g})$ into distilled water. Assume that the reaction goes to completion and that $\mathrm{HNO}_{2}$ is the only species produced. To determine the concentration of $\mathrm{HNO}_{2}(\mathrm{aq})$ in the resulting solution, the student titrates a $100 . \mathrm{mL}$ sample of the solution with $0.100 \mathrm{M} \mathrm{KOH}(\mathrm{aq})$. The neutralization reaction is represented below.

$$
\mathrm{HNO}_{2}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{NO}_{2}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

The following titration curve shows the change in pH of the solution during the titration.

a. Use the titration curve and the information above to
i. determine the initial concentration of the $\mathrm{HNO}_{2}(\mathrm{aq})$ solution (1 point)
ii. estimate the value of the $\mathrm{pK}_{\mathrm{a}}$ for $\mathrm{HNO}_{2}(\mathrm{aq})$ (1 point)
b. During the titration, after a volume of 15 mL of $0.100 \mathrm{M} \mathrm{KOH}(\mathrm{aq})$ has been added, which species, $\mathrm{HNO}_{2}(\mathrm{aq})$ or $\mathrm{NO}_{2}^{-}(\mathrm{aq})$, is present at a higher concentration in the solution? Justify your answer. (1 point)

## Polyatomic Ions

## 1st six-weeks



## $2^{\text {nd }}$ six-weeks

| $\mathrm{ClO}_{4}^{-}$ | perchlorate | $\mathrm{IO}^{-}$ | hypoiodite |
| :--- | :--- | :--- | :--- |
| $\mathrm{ClO}^{-}$ | hypochlorite | $\mathrm{BrO}_{4}^{-}$ | perbromate |
| $\mathrm{IO}_{4}^{-}$ | periodate | $\mathrm{BrO}^{-}$ | hypobromite |


|  | Difference in <br> Oxygen from ATE |
| :---: | :---: |
| Per____ate | +1 |
| Ate | 0 |
| Ite | -1 |
| Hypo___ite | -2 |

## $3^{\text {rd }}$ six-weeks

| $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$ | dihydrogen phosphate | $\mathrm{HCO}_{3}^{-}$ | hydrogen carbonate or bicarbonate |
| :--- | :--- | :--- | :--- |
| $\mathrm{HPO}_{4}{ }^{2-}$ | hydrogen phosphate | $\mathrm{HSO}_{4}^{-}$ | hydrogen sulfate |

## $4^{\text {th }}$ six-weeks

| $\mathrm{NH}_{4}{ }^{+}$ | ammonium | $\mathrm{OH}^{-}$ |
| :--- | :--- | :--- |
| $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$or $\mathrm{CH}_{3} \mathrm{COO}^{-}$ | acetate | $\mathrm{H}_{3} \mathrm{O}^{+}$ |

## $5^{\text {th }}$ six-weeks

| $\mathrm{MnO}_{4}^{-}$ | permanganate | $\mathrm{CrO}_{4}{ }^{2-}$ | chromate |
| :--- | :--- | :--- | :--- |
| $\mathrm{CN}^{-}$ | cyanide | $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ | dichromate |

## $6^{\text {th }}$ six-weeks

| $\mathrm{O}_{2}{ }^{2-}$ | peroxide | $\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6}{ }^{2-}$ | tartrate |
| :--- | :--- | :--- | :--- |
| $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ | thiosulfate | $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}$ | oxalate |


| Acid Nomenclature |  |
| :---: | :---: |
| Binary | Hydro_____ ic |
| ate | ic |
| ite | ous |

## Polyatomic lons

## Br-Based Ions

$\mathrm{BrO}^{-}$hypobromite
$\mathrm{BrO}_{2}{ }^{-} \quad$ bromite
$\mathrm{BrO}_{3}{ }^{-}$bromate
$\mathrm{BrO}_{4}^{-}$perbromate

## Cr-Based Ions

$$
\mathrm{CrO}_{4}{ }^{2-} \quad \text { chromate }
$$

$\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ dichromate

I-Based Ions
$\mathrm{IO}^{-}$hypoiodite
$\mathrm{IO}_{2}{ }^{-} \quad$ iodite
$\mathrm{IO}_{3}{ }^{-} \quad$ iodate
$\mathrm{IO}_{4}{ }^{-}$periodate

## P-Based Ions

$\mathrm{PO}_{3}{ }^{3-} \quad$ phosphite
$\mathrm{PO}_{4}{ }^{3-} \quad$ phosphate
$\mathrm{HPO}_{4}{ }^{2-} \quad$ hydrogen phosphate
$\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \quad$ dihydrogen phosphate

## Other Ions

$\mathrm{CN}^{-}$cyanide
$\mathrm{O}_{2}{ }^{2-} \quad$ peroxide
$\mathrm{MnO}_{4}{ }^{-} \quad$ permanganate

C-Based Ions
$\mathrm{CO}_{3}{ }^{2-}$
$\mathrm{HCO}_{3}{ }^{-}$
$\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}$or $\mathrm{CH}_{3} \mathrm{COO}^{-}$ $\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6}{ }^{2-} \quad$ tartrate $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-} \quad$ oxalate

Cl-Based Ions
$\mathrm{ClO}^{-}$
$\mathrm{ClO}_{2}{ }^{-}$
$\mathrm{ClO}_{3}^{-}$
$\mathrm{ClO}_{4}{ }^{-}$

## N -Based Ions

$\mathrm{NO}_{2}{ }^{-} \quad$ nitrite
$\mathrm{NO}_{3}{ }^{-}$nitrate
$\mathrm{NH}_{4}{ }^{+}$

S-Based Ions

| $\mathrm{SO}_{3}{ }^{2-}$ | sulfite |
| :--- | :--- |
| $\mathrm{SO}_{4}{ }^{2-}$ | sulfate |
| $\mathrm{HSO}_{4}{ }^{-}$ | hydrogen sulfate |
| $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ | thiosulfate |

Acid \& Base Ions
$\begin{array}{cc}\mathrm{H}_{3} \mathrm{O}^{+} & \text {hydronium } \\ \mathrm{OH}^{-} & \text {hydroxide }\end{array}$
PERIODIC TABLE OF THE ELEMENTS


| ex | $\begin{array}{\|c\|c} \substack{59 \\ \text { Pr } \\ 14090} \end{array}$ | $\begin{array}{\|c\|} \hline 60 \\ \mathrm{Nd} \end{array}$ |  |  | $\begin{gathered} 63 \\ \text { ciun } \\ \hline 1592 \end{gathered}$ |  | $\begin{gathered} \text { C5b } \\ \hline 159 \end{gathered}$ | $\begin{gathered} 66 \\ \text { Dyy } \\ \text { Di625 } \end{gathered}$ | $\begin{gathered} 67 \\ \text { Ho } \end{gathered}$ | $\substack{68 \\ \hline \text { Er } \\ \hline 6)^{6}}$ | $\begin{aligned} & \frac{69}{\mathrm{Tm}} \end{aligned}$ | $\begin{aligned} & 70 \\ & \hline 130 \\ & \hline \text { Yb } \end{aligned}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | ${ }_{\text {Pa }}^{\text {Pa }}$ | ${ }^{92}$ | Np | ${ }_{\text {Pu }}^{\text {Pu }}$ | 95 <br>  <br> 18 <br> 123 | cm | ${ }_{\text {Bk }}$ | cf | ${ }_{\text {Es }}$ | F $\begin{aligned} & 100 \\ & \text { Fm }\end{aligned}$ | cos | - | 边 |
| ${ }_{22204}$ | ${ }_{23} 23.10$ | ${ }_{23,03}$ |  | $\xrightarrow{\text { Pu }}$ | ${ }_{\text {am }}$ | $\xrightarrow{\text { cma }}$ | ${ }_{(247)}^{125}$ | $\substack { \text { cis } \\ \begin{subarray}{c}{\text { cis } \\ \text { cmid }{ \text { cis } \\ \begin{subarray} { c } { \text { cis } \\ \text { cmid } } } \end{subarray}$ |  | ${ }_{\text {(25) }}$ | (125) | ${ }_{\text {(159) }}$ | ${ }_{2}$ |

## AP ${ }^{\circledR}$ CHEMISTRY EQUATIONS AND CONSTANTS

Throughout the exam the following symbols have the definitions specified unless otherwise noted.

```
L, mL = liter(s), milliliter(s) mm Hg = millimeters of mercury
g = gram(s) J, kJ = joule(s), kilojoule(s)
nm = nanometer(s) V = volt(s)
atm = atmosphere(s) mol = mole(s)
```


## ATOMIC STRUCTURE

$$
\begin{aligned}
& E=h v \\
& c=\lambda v
\end{aligned}
$$

$$
\begin{aligned}
E & =\text { energy } \\
\nu & =\text { frequency } \\
\lambda & =\text { wavelength }
\end{aligned}
$$

Planck's constant, $h=6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}$
Speed of light, $c=2.998 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$
Avogadro's number $=6.022 \times 10^{23} \mathrm{~mol}^{-1}$
Electron charge, $e=-1.602 \times 10^{-19}$ coulomb

## EQUILIBRIUM

$$
\begin{aligned}
K_{c} & =\frac{[\mathrm{C}]^{c}[\mathrm{D}]^{d}}{[\mathrm{~A}]^{a}[\mathrm{~B}]^{b}}, \text { where } a \mathrm{~A}+b \mathrm{~B} \rightleftarrows c \mathrm{C}+d \mathrm{D} \\
K_{p} & =\frac{\left(P_{\mathrm{C}}\right)^{c}\left(P_{\mathrm{D}}\right)^{d}}{\left(P_{\mathrm{A}}\right)^{a}\left(P_{\mathrm{B}}\right)^{b}} \\
K_{a} & =\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]} \\
K_{b} & =\frac{\left[\mathrm{OH}^{-}\right]\left[\mathrm{HB}^{+}\right]}{[\mathrm{B}]} \\
K_{w} & =\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} \text { at } 25^{\circ} \mathrm{C} \\
& =K_{a} \times K_{b} \\
\mathrm{pH} & =-\log \left[\mathrm{H}^{+}\right], \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] \\
14 & =\mathrm{pH}+\mathrm{pOH} \\
\mathrm{pH} & =\mathrm{p} K_{a}+\log \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]} \\
\mathrm{p} K_{a} & =-\log K_{a}, \mathrm{p} K_{b}=-\log K_{b}
\end{aligned}
$$

## Equilibrium Constants

$K_{c}$ (molar concentrations)
$K_{p}$ (gas pressures)
$K_{a}$ (weak acid)
$K_{b}$ (weak base)
$K_{w}$ (water)

## KINETICS

$$
\begin{aligned}
\ln [\mathrm{A}]_{t}-\ln [\mathrm{A}]_{0} & =-k t \\
\frac{1}{[\mathrm{~A}]_{t}}-\frac{1}{[\mathrm{~A}]_{0}} & =k t \\
t_{1 / 2} & =\frac{0.693}{k}
\end{aligned}
$$

$$
\begin{aligned}
k & =\text { rate constant } \\
t & =\text { time } \\
t_{1 / 2} & =\text { half-life }
\end{aligned}
$$

## GASES, LIQUIDS, AND SOLUTIONS

$$
\begin{aligned}
P V & =n R T \\
P_{A} & =P_{\text {total }} \times X_{\mathrm{A}}, \text { where } X_{\mathrm{A}}=\frac{\text { moles A }}{\text { total moles }} \\
P_{\text {total }} & =P_{\mathrm{A}}+P_{\mathrm{B}}+P_{\mathrm{C}}+\ldots \\
n & =\frac{m}{M} \\
\mathrm{~K} & ={ }^{\circ} \mathrm{C}+273 \\
D & =\frac{m}{V}
\end{aligned}
$$

$K E$ per molecule $=\frac{1}{2} m v^{2}$
Molarity, $M=$ moles of solute per liter of solution

$$
A=a b c
$$

$P=$ pressure
$V=$ volume
$T=$ temperature
$n=$ number of moles
$m=$ mass
$\boldsymbol{M}=$ molar mass
$D=$ density
$K E=$ kinetic energy
$v=$ velocity
$A=$ absorbance
$a=$ molar absorptivity
$b=$ path length
$c=$ concentration
Gas constant, $R=8.314 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ $=0.08206 \mathrm{~L} \mathrm{~atm} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ $=62.36 \mathrm{~L}^{\text {torr } \mathrm{mol}^{-1} \mathrm{~K}^{-1}}$
$1 \mathrm{~atm}=760 \mathrm{~mm} \mathrm{Hg}=760$ torr
STP $=273.15 \mathrm{~K}$ and 1.0 atm
Ideal gas at $\mathrm{STP}=22.4 \mathrm{~L} \mathrm{~mol}^{-1}$

## THERMODYNAMICS / ELECTROCHEMISTRY

$$
\begin{aligned}
q & =m c \Delta T \\
\Delta S^{\circ} & =\sum S^{\circ} \text { products }-\sum S^{\circ} \text { reactants } \\
\Delta H^{\circ} & =\sum \Delta H_{f}^{\circ} \text { products }-\sum \Delta H_{f}^{\circ} \text { reactants } \\
\Delta G^{\circ} & =\sum \Delta G_{f}^{\circ} \text { products }-\sum \Delta G_{f}^{\circ} \text { reactants } \\
\Delta G^{\circ} & =\Delta H^{\circ}-T \Delta S^{\circ} \\
& =-R T \ln K \\
& =-n F E^{\circ} \\
I & =\frac{q}{t}
\end{aligned}
$$

$$
\begin{aligned}
q & =\text { heat } \\
m & =\text { mass } \\
c & =\text { specific heat capacity } \\
T & =\text { temperature } \\
S^{\circ} & =\text { standard entropy } \\
H^{\circ} & =\text { standard enthalpy } \\
G^{\circ} & =\text { standard Gibbs free energy } \\
n & =\text { number of moles } \\
E^{\circ} & =\text { standard reduction potential } \\
I & =\text { current (amperes) } \\
q & =\text { charge (coulombs) } \\
t & =\text { time (seconds) }
\end{aligned}
$$

Faraday's constant, $F=96,485$ coulombs per mole of electrons
1 volt $=\frac{1 \text { joule }}{1 \text { coulomb }}$
PERIODIC TABLE OF THE ELEMENTS

| 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 18 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| H | 2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | He |
| ${ }_{\text {coid }}^{3}$ | 2 |  |  |  |  |  |  |  |  |  |  |  | 14 | 15 |  | 17 | 400 |
| Li | Be |  |  |  |  |  |  |  |  |  |  | B | c | N | 0 | F | Ne |
| ${ }_{694}^{11}$ | ${ }^{909}$ |  |  |  |  |  |  |  |  |  |  | ${ }^{1089}$ | ${ }_{1201}^{14}$ | ${ }^{1401}$ | ${ }_{1600}^{16}$ | ${ }^{1990} 17$ | ${ }^{2018}$ |
| Na | Mg |  |  |  |  |  |  |  |  |  |  | Al | Si | P | s | Cl | Ar |
| $\frac{29}{19}$ | ${ }^{2430}$ | ${ }^{21}$ | ${ }^{42}$ | ${ }^{23}$ | ${ }^{24}$ | ${ }^{25}$ | ${ }^{26}$ | ${ }^{27}$ | ${ }^{28}$ | ${ }^{29}$ | 12 | ${ }^{2098}$ | ${ }^{32}$ | ${ }^{33}$ | ${ }^{34}$ | ${ }^{35}$ | ${ }^{36}$ |
| K | Ca | Sc | Ti | v | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 年10 | ${ }_{\text {4098 }}$ | ${ }^{499}{ }^{\text {49，}}$ | $4{ }_{4}^{490}$ | $\frac{5094}{44}$ | 5200 | ${ }_{4}^{594}$ | ${ }^{44}$ | ${ }_{\text {cisa }}^{45}$ | ${ }_{4} 46$ | ${ }^{47}$ | ${ }_{6}^{639}$ | ${ }^{49}$ | ${ }_{7250}$ | ${ }_{\text {7492 }}^{51}$ | ${ }_{\text {\％}}^{5} 5$ | ${ }^{53}$ | ${ }_{5}^{54}$ |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | 1 | Xe |
| $8{ }^{854}$ | ${ }^{8,62}$ | ${ }_{89} 8$ | ${ }^{1122}$ | 2291 | 9599 | （199） | 0110 | 1027 | 1064 | ${ }_{1088}$ | 12.4 | 4， | ， |  |  |  |  |
| Cs | Ba | ${ }^{\text {＊}}$ a | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | TI | Pb | Bi | Po | At | Rn |
|  | ${ }^{\frac{1737}{88}}$ | ${ }_{\text {13991 }}^{118}$ | ${ }_{\text {cras }}^{\frac{1784}{104}}$ | ${ }_{\text {18095 }}^{105}$ | ${ }_{1835}^{1105}$ | ${ }_{\text {18621 }}^{107}$ | ${ }^{1902}$ |  | ${ }^{19508}$ |  |  |  |  |  |  |  |  |
| Fr | Ra | $\dagger$ †c | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg |  |  |  |  |  |  |  |


|  | \％ |
| :---: | :---: |
| $\bigcirc \bigcirc$ | N |
| $\left\|\begin{array}{lll} \boldsymbol{E} & 0 \\ 0 & \underset{[ }{6} & 0 \\ 0 \end{array}\right\|$ | $\underset{\sim}{2} \text { N }$ |
|  | 읏 圃 |
| $\left\|\begin{array}{ccc} \hat{0} & 0 & 0 \\ \hline \end{array}\right\|$ | の 또 N |
| $\left\|\begin{array}{lll} \circ & \underset{\sim}{\mathrm{N}} \end{array}\right\|$ | $\cdots$～ |
| $\left\|\begin{array}{lll} 1 & 0 & 0 \\ 0 & E & 0 \\ 0 \end{array}\right\|$ | 内 |
|  | $\bigcirc$ 오＊ |
| （lll |  |
| $\left\|\right\|$ | サ $\square^{\text {a }}$ |
|  | $\cdots \underset{\sim}{2} \underset{\sim}{0}$ |
|  | N $\square$ ¢ |
| $\left\|\begin{array}{lll} \mathfrak{n} & \dot{y} \\ \mathfrak{n} & \vdots \\ j \end{array}\right\|$ |  |
| $\infty$ |  |

＊Lanthanide Series



[^0]:    *Note: We can still use $M_{a} V_{a}=M_{b} V_{b}$ to calculate volume needed to reach equivalence point!

