

Lecture Notes for AP Chemistry

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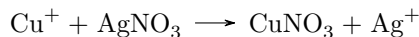
1 Acids and Bases

1.1 Identifying Acids and Bases

Differences: acids taste sour while bases are bitter. This is an evolutionary response as most bases are toxic. In touch, bases are slippery while dilute acids feel like water. Concentrated acids will hurt. Concentrated bases don't hurt when touched, but attacks fat tissue.

1.2 Reactions

Most acids react with most metals. Consider the reaction



The copper is more active than the silver, so it bonds to the nitrate in a single replacement reaction. It will not go backwards.

1.3 Conductivity

Both acids and bases conduct electricity.

1.4 Acid and Base Definitions

Arrhenius Definition: an Arrhenius acid dissolves in water with H^+ as its only ion. an Arrhenius base dissolves in water with only OH^- as an ion.

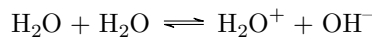
Bronstead-Lowry: Acids are proton donors, bases are proton acceptors.

Lewis: Acids are electron pair donors, bases are electron pair acceptors.

1.5 Strong Acids and Bases

Amphoteric molecules can act as both acids and bases. e.g. water

Consider the auto-ionization of water,

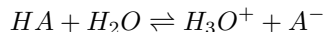


$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \rightarrow [\text{H}^+] = 10^{-7} M$$

$$\text{pH} = -\log [\text{H}^+] = 7$$

This is why pH of water is 7. Because it's an equilibrium expression, it is temperature dependent. At higher temperatures, neutral pH is lower than 7.

A strong acid completely dissociates in water. The relative strength of an acid can be measured with



where A is some acid. The K of this equilibrium is given by

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

If K is high, then the acid is strong because it dissociates a lot.

The list of strong acids: HCl, HNO₃, H₂SO₄, HBr, HI, HClO₄, HClO₃

Strong bases are group 1 and 2 hydroxides which are soluble.

1.6 Finding pH

Consider a sample of 0.001M HBr, take the negative log of the molarity.

$$pH = -\log_{10} .001 = 3$$

Now take a more complicated example: .025M HNO₃. Do the same thing; $-\log .025 = 1.6$

Problem 1: Find [H⁺] of a 2.8pH HClO₄ solution.

Solution: Take the antilog; [H⁺] = $10^{-2.8} = \boxed{.0016}$

Problem 2: Find the pH of a solution made to be [HClO₃] = $2.8 \times 10^{-10} M$

Solution: The math says $pH = 9.6$, but that doesn't make sense given the molarity of the HClO₃. This is because it doesn't take into account the equilibrium of the water, $2H_2O \rightleftharpoons H_3O^+ + OH^-$. This is the overwhelming equilibrium, and the addition of [HClO₃] doesn't matter. The answer is just $\boxed{7}$.

Now, consider a problem with equilibrium put in.

Problem: Find the pH of a 0.15M HClO₂ solution with $K_a = 1.2 \times 10^{-2}$.

Solution: The equilibrium expression is $HClO_2 \rightleftharpoons H^+ + ClO_2^-$.

$$K_a = \frac{[H^+][ClO_2^-]}{[HClO_2]} = \frac{x^2}{.15 - x}$$

Now solve, $1.2 \times 10^{-2} = \frac{x^2}{.15 - x}$, we get $x = .04$, so [H⁺] = .04. Then taking the antilog, the pH is $\boxed{1.4}$.

Problem: Find the pH of a solution that is 0.5M HF and 1.00M HOCl, given that $K_a(HF) = 7.2 \times 10^{-4}$ and $K_a(HOCl) = 3.5 \times 10^{-8}$,

Solution: Note that the K of HF 2000 times the K of HOCl. Then the HF will flood into the system and "bully" the equilibrium of HOCl $\rightleftharpoons OCl^- + H^+$. It will go in full reverse, and HOCl basically remains undissociated. The only one that matters is .5M HF. Solve for it with K, and we are done.

1.7 Percent Dissociation

$$D = \frac{[\text{dissociated}]}{[\text{initial}]} \times 100\%$$

Problem: Find the % dissociation of a 0.1M HC₂H₃O₂ solution, $K_a = 1.8 \times 10^{-5}$

Solution:

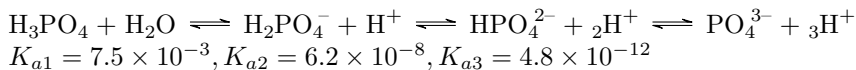
$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{x^2}{.1 - x}$$

which yields $x = .013M$. Then the percent dissociation is $\frac{.013}{.1} \times 100\% = \boxed{1.3\%}$.

1.8 Polyprotic Acids

Polyprotic acids have more than 1 acidic proton. e.g. H₃PO₄

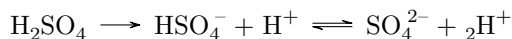
There can be many states of equilibrium for this acid. How do we calculate pH?



We can observe that K_{a1} is much more than any of the other K values, so the equilibria that aren't for the monoprotic equilibrium are "washed out". We can treat H₃PO₄ as monoprotic.

Solution: To find the pH of .5M H₃PO₄, $7.5 \times 10^{-3} = \frac{x^2}{.5 - x} \Rightarrow x = .06$, the pH is $-\log .06 = \boxed{1.2}$.

Consider sulfuric acid, H₂SO₄. It is a strong acid, so the reaction with water completes itself. However, the second deprotonation is an equilibrium.



$K_a(HSO_4^-) = 1.2 \times 10^{-2}$. Find the pH of a .05M H₂SO₄ solution.

Solution: The equation for K is $K_a = \frac{[SO_4^{2-}][H^+]}{[HSO_4^-]}$, $1.2 \times 10^{-2} = \frac{x(.05+x)}{.05-x} \Rightarrow x = 8.5 \times 10^{-3}$. [H⁺] = .0585, the pH is $\boxed{1.2}$.

1.9 Conjugate Acids and Bases

Consider the reaction $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$. Since H_3O^+ accepts a proton it is the conjugate acid, and Cl^- is the conjugate base (**Bronstead-Lowry**).

In $\text{NaOH(s)} \rightarrow \text{Na}^+ + \text{OH}^-$, Na^+ is the conjugate acid and OH^- is the conjugate base (**Lewis Definition**).

It is true for all acid-base reactions that

$$K_a K_b = K_w$$

So the strength of the conjugate acid/base is inversely proportional to the strength of the original.

Take $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$, $K_a(\text{HF}) = 7.2 \times 10^{-4}$, with $K_w = 1 \times 10^{-14}$.

Solution: We can find that $K_b = 1.4 \times 10^{-11}$. Then we can use

$$K_b = \frac{[\text{OH}^-][\text{HF}]}{[\text{F}^-]} \Rightarrow 1.4 \times 10^{-11} = \frac{x^2}{.35 - x}$$

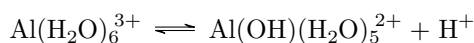
$x = [\text{OH}^-] = 2.21 \times 10^{-6}$, $\text{pOH} = 5.65$. Then the pH is $14 - \text{pOH} \Rightarrow \text{pH} = \boxed{8.345}$.

A niche case: Consider $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, with $K_a(\text{HC}_2\text{H}_3\text{O}_2) = 1.8 \times 10^{-5}$ and $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$. The conjugate acid is the ammonium, the conjugate base is acetic acid. The concentrations of the conjugate acid and base are equal, so the pH is 7.

$K_b(\text{C}_2\text{H}_5\text{NH}_2) = 5.6 \times 10^{-4}$, would a solution of $\text{C}_2\text{H}_5\text{NH}_3\text{C}_2\text{H}_3\text{O}_2$ be basic or acidic?

1.10 Acidity of Metal Ions

All metals, under normal circumstances, are positive ions. Therefore, they are the conjugate acids of some hydroxide. Many metals do not have strong acids attached to them, such as $\text{Al}(\text{OH})_3 \rightarrow \text{Al}^{3+}$, which is a reasonably good acid. What the aluminum does is form a **complex**, $\text{Al}^{3+} + 6 \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{H}_2\text{O})_6^{3+}$, which has $K_a = 1.4 \times 10^{-5}$. This is roughly the same as vinegar. The dissociation is



Calculating pH is the same process as before. Say there was a solution made by adding 210g of AlBr_3 to make a 3.0L solution.

a) Does the $[\text{Br}^-]$ affect pH? No, Br^- is the conjugate base of HBr , a strong acid. Therefore, Br^- is pathetically weak and doesn't affect the equilibrium.

b) Find the pH.

The concentration of AlBr_3 is .26, so from the above equilibrium we can solve.

$$1.4 \times 10^{-5} = \frac{x^2}{.26 - x} \Rightarrow x = 1.9 \times 10^{-3}$$

$\log 1.9 \times 10^{-3} = \boxed{2.72}$

1.11 Structure and Effects on Acidity and Basicity

$\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ in terms of acidity.

$\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$ in terms of bond strength.

The reason for this is that since the bonds hold the atom together with more strength, it will dissociate less in water. In this list, HF is the only weak acid. The stronger the bonds, the weaker the acid.

The Electron Withdrawal Effect

Consider HClO_4 . The central Cl atom has a very strong attraction to all electrons in the molecule. This makes for a very weak O-H bond, and the H^+ dissociates very easily. However, with HClO_3 there are less oxygens so it has less electron withdrawing potential. The O-H bond is less weak, so it is considered a weak acid.

2 Applications of Aqueous Equilibria

Consider HNO_2 , with $K_a = 4.5 \times 10^{-4}$. Calculate the pH of a 0.5M solution.

The equilibrium is $\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$. The pH can be calculated with $4.5 \times 10^{-4} = \frac{x^2}{.5-x}$ which gives $\text{pH}=1.82$.

Now we can modify it; find the pH of a 0.50M HNO_2 solution in 1.0M NaNO_2 .

Solution: This would change the equilibrium concentrations. Doing some analysis gives $4.5 \times 10^{-4} = \frac{x(1.0+x)}{0.5-x} \implies x = 2.2 \times 10^{-4}, \text{pH} = 3.6$.

This is called a **buffered solution**, where if a weak acid or base is placed in a solution with a corresponding salt it is buffered. A buffer acts to **resist a change in pH**.

Problem: Find the pH of a 0.5M acetic acid in 0.5M $\text{NaC}_2\text{H}_3\text{O}_2$, with $K_a = 1.8 \times 10^{-5}$. The pH comes out to be 4.74. However, if .010 mol NaOH is added to 1.0L of this buffer, we attack the problem in 2 steps.

Step 1: Neutralization Reaction. Since they both have one H or OH, it will be a 1-1 neutralization reaction. It follows $\text{HC}_2\text{H}_3\text{O}_2 + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaC}_2\text{H}_3\text{O}_2$. It changes the initial concentrations based on the amount of NaOH added to the buffer, in this case

$$[\text{HC}_2\text{H}_3\text{O}_2]_0 = 0.49\text{M}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-]_0 = 0.51\text{M}$$

Step 2: Proceed with the math as with before. The pH turns out to be 4.76.

We can evaluate the efficacy of the buffer by calculating ΔpH , which in this case is .02. That's not that much of a pH change.

The pH of a 0.01M NaOH solution in pure water is 12 and the pH of neutral water is 7, so $\Delta\text{pH} = 5$. That means the buffer is really good at resisting pH changes.

For the equilibrium of an acid $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$, $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \implies \boxed{[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}}$

This says that if there is a lot of buffer, the slight addition of a base/acid does almost nothing.

2.1 Henderson-Hasselbalch

Define $\text{p}K_a$ as $-\log K_a$. Then $\boxed{\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}}$ which is the **Henderson-Hasselbalch equation**. However, this equation assumes that the 5% estimation works.

2.2 Titrations

During a titration, we can use a modified version of Henderson-Hasselbalch.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{acid}]}{[\text{base}]}$$

Problem: Consider the titration of 100. mL of 1.0M $\text{HC}_2\text{H}_3\text{O}_2$, with $K_a = 1.8 \times 10^{-5}$. 1.0M NaOH will be added.

a) What is the pH before the addition of the base?

Acetic acid is a weak acid, we can use $K_a = \frac{x^2}{1.0-x}$ to get $\text{pH} = 2.4$.

b) What is the pH when 10 mL of base is added?

The neutralization reaction is $\text{NaOH} + \text{HC}_2\text{H}_3\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{NaC}_2\text{H}_3\text{O}_2$. Stoichiometry tells us that there are 0.09 mol $\text{HC}_2\text{H}_3\text{O}_2$ and 0.01 mol $\text{C}_2\text{H}_3\text{O}_2^-$ present at this point. When dividing the concentrations, they exist in the same solution so the total moles cancels out. All we need is the ratio of the moles, so we can use Henderson-Hasselbalch.

$$\text{pH} = \text{p}K_a + \log \frac{.01\text{molHC}_2\text{H}_3\text{O}_2}{.09\text{molC}_2\text{H}_3\text{O}_2^-} = 3.7 \text{ at } 10 \text{ mL base added.}$$

c) Using the same method, the rest of the pH's come out. At the equivalence point, $\text{pH} = \text{p}K_a$ and that allows us to find K_a . At the equivalence point, $\text{pH} = 4.7$. There is 0.1 mol $\text{NaC}_2\text{H}_3\text{O}_2$ present from neutralization, which is the only compound left. $\text{C}_2\text{H}_3\text{O}_2^-$ is the conjugate base, which follows $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^-$. (cont'd on next page)

Using $K_a K_b = K_w$, we get $K_b = 5.56 \times 10^{-10}$, then the equilibrium is

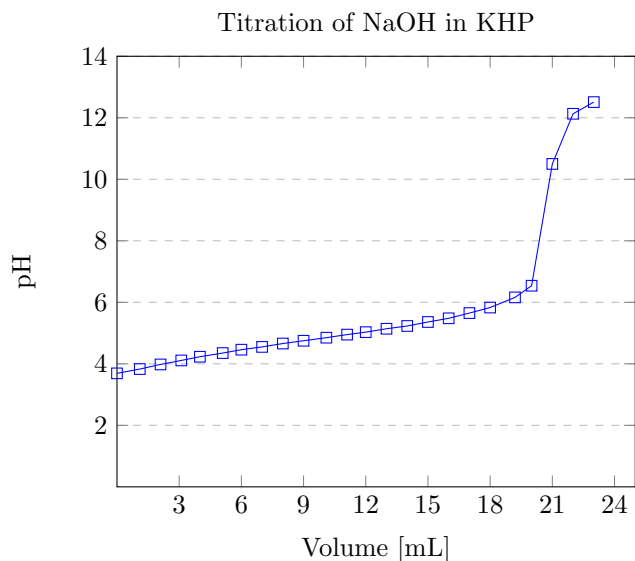
$$K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} \Rightarrow \text{pOH} = 5.8, \boxed{\text{pH} = 9.2}$$

At a concentration of NaOH after the equivalence point, we don't have a base buffer so it just becomes a strong base problem. The pH asymptotically approaches 14.

Titration of a diprotic weak acid in a strong base: the graph shows more humps as you're basically stacking 2 buffer problems on top of one another.

An actual experiment

Consider a solution with 0.47g NaOH in 100mL of water, $M = 0.1175$. It is titrated with 0.46g of $\text{C}_8\text{H}_5\text{KO}_4$ with unknown concentration. The graph:



2.3 Indicators

Indicators by themselves are weak acids or weak bases. To detect a change with an indicator, the color ratio must be 10:1 in an area to be visible. That's why indicators only work visually within certain ranges, usually with ± 1 pH. They're usually used at the equivalence point of a titration, where there is a dramatic spike in pH. Therefore, it doesn't matter that much that it's inaccurate.