

## Part I—Structure and Its Relationship to Acidity

Keep in mind that the **larger** the  $K_a$ , the **stronger** the acid.  
However, the **smaller** the  $pK_a$ , ( $-\log$  of  $K_a$ ), the **stronger** the acid.  
(The text book uses  $K_a$  but the video uses  $pK_a$ .)

Read pages 691-694 in the text and watch the video.

### Binary Acids

Moving **across a period** on the periodic table, the elements have increasingly higher electronegativity. Example:  $Li < Mg < B < C < N < O < F$ .

Electronegativity increases the atom's "pull" on the electrons as well as the electrons in the bond of a binary acid such as HF. This increases electronegativity causes more dispersion over the electron cloud and causes the "anion" to be more stable.

For instance: **CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, HF** all have Hydrogen attached to the non-metal. Each molecule has the potential of being an acid since they can all donate a proton ( $H^+$ ).

As for electronegativity, we have already seen that  $C < N < O < F$ . Since F is the most electronegative, its **acid, HF**, will be the **strongest** of the four molecules. These are **binary acids** since they only contain two different atoms, one of which is H.

So for acid strength across a period,  $HF > H_2O > NH_3 > CH_4$ .

Likewise:  $HCl > H_2O > PH_3 > SiH_4$

Moving **down a group**, on the other hand is quite different, electronegativity decreases which would lead us to think the acidity decreases, but it's not what happens. As we go **down a group** like the halogens (Fluorine group), the electronegativity decreases but the **acidity increases**. Moving down a group, we see that the atomic radius increases for each element. As the radius gets larger, the charge gets more dispersed stabilizing the anion, and the H is held more and more loosely making it easier to donate a proton. This ease to donate a proton makes the **binary acid stronger**.  $HI > HBr > HCl > HF$ . Likewise,  $H_2Se > H_2S > H_2O$ .

### Oxyacids

Oxyacids are acids in which **H** is attached to an **O** which is, in turn, attached to a **central atom** that is **not O**.  $H-O-X$

Oxyacids with a **common central atom**: These are oxyacids in which X is the same for all in the group. For example: ( $HNO_3$  and  $HNO_2$ ), or ( $H_2SO_4$  and  $H_2SO_3$ ), or ( $HClO$ ,  $HClO_2$ ,  $HClO_3$ , and  $HClO_4$ ).

For Oxyacids with a common central atom, the **more oxygens** (O) attached to the central atom, the **stronger the acid**. This is because the oxygens, not attached to the hydrogen, pulls the electronegativity away from the central atom and away from the oxygen attached to the hydrogen. This makes it easier to remove (donate) the proton ( $H^+$ ) and thus making the acid

Example:  $H-O-Cl < H-O-Cl-O < H-O-Cl-O-O$  (See p.692)

Oxyacids with a **different central atom**: These are oxyacids in which X differs between the oxyacids in the group. For example: (HOCl and HOBr) or (HIO<sub>3</sub> and HBrO<sub>3</sub>). The number of oxygens are the same but the central atom is different. The **Central atom** that would be the **stronger acid** if it did not have Oxygens attached (if it were binary) would be stronger oxyacid of the group.

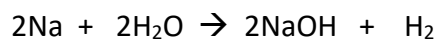
HOCl and HOBr have the same number of oxygens but in a binary acid HBr is stronger so **HOBr** would be the **stronger** of the two acids.

HIO<sub>3</sub> and HBrO<sub>3</sub> both have the same number of oxygens but in a binary acid **HI** would be stronger so **HIO<sub>3</sub>** is the **stronger** oxyacid.

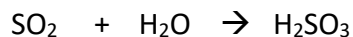
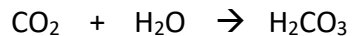
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### Metal Oxides vs Non-metal Oxides (p.693)

**Metal Oxides** when reacted with **H<sub>2</sub>O** will produce **bases** or Hydroxides and hydrogen gas.



**Non-metal Oxides** when reacted with **H<sub>2</sub>O** will produce acids.



## Part II                      Titrations and Buffers

(Read p. 715-723) for buffers, (Read p. 727-735) for titrations.

### Acid-Base Titration of Strong Acids and Strong Bases (Watch video minutes 7-12)

An acid-base titration is also known as **Neutralization** in which equal amounts of  $H^+$  ions are titrated with equal amounts of  $OH^-$  ions resulting in a neutral solution.

This is always true for A/B titrations of strong acids and strong bases. This is why we discuss this type of a titration first.

When **equal amounts of  $H^+$  and  $OH^-$**  are titrated together in a solution, we say the solution has reached **equivalency**.

Starting with a given amount of a particular concentration of strong acid, we titrate a given concentration of a strong base, part by part, until we reach equivalency.

We can plot the pH of the acid (y-axis) versus the volume of the base (x-axis) to get the titration graph. (see p.728-730) and video (min 7-12). At the point of equivalency (equal amounts of  $H^+$  and  $OH^-$ ) there will be a sharp spike in the graph moving straight up. At equivalency the pH should show 7.

Note: The video, for simplicity effect, does not use volume of titrant or solution. We will be using volume and I will show you how so we can calculate concentration and pH from the concentration.

Starting with 30.0 mL of 0.200M HCl is titrated with 0.150M KOH. Calculate the pH of the acid after the following volumes of base is added to the acid. Strong acid and base so  $[H^+] = [HCl]$

- a) 30.0 mL  $[OH^-]=[KOH]$   
b) 39.5 mL  
c) 40.0 mL  
d) 40.1 mL

#### Titration Table for a Strong Acid and Strong Base:

	mol $H^+$	-	mol $OH^-$	$\rightarrow$ mol $H^+$ / total Vol	$[H^+]$	pH
a)	(.030)(.20)	-	(.030)(.15)			
	.006 mol	-	.0045 mol	0.0015mol/.06 L	.075	1.1
b)	.006 mol	-	(.0395)(.15)	0.00075mol/.0695L	.0695	1.2
c)	.006 mol	-	(.040)(.15)	0 (all $H_2O$ )	$1 \times 10^{-7}$	7
d)	.006 mol		(.0401)(.15)	.00002 mol/.0701L	.000285	pOH=3.5 pH=10.5

If you plot this graph it will start at a very low pH and volume. I will increase only slightly in pH until very close to equivalency (pH should jump to 7) at which point it will shoot up to about pH of 10 then increase slightly and level off. The graph will resemble an "S". (See p.730 lower left).

Problem #58 of the HW problems in Ch. 15 is a strong Acid-Base titration similar to this one.

## Weak Acid & Strong Base Titrations or Weak Base & Strong Acid Titrations

Please re-watch Video (Acid/Base Reactions and Buffers) (min. 12-21)

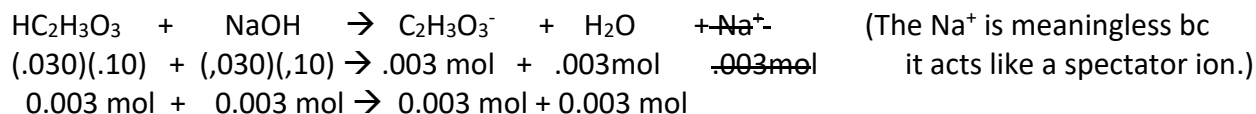
Acid/Base Titration of a Weak acid and a Strong Base or visa verse is a little different than the titrations with both acid and base being strong. The reason for this is that, at **equivalency**, the pH is not 7 as it is with a strong A/B titration. When all the H<sup>+</sup> ion has been neutralized by OH<sup>-</sup> ion the conjugate of either the weak acid or weak base will act like the salt of that acid or base and reverse itself to make either more H<sup>+</sup> ion if it's the conjugate of a weak base or more OH<sup>-</sup> ion if it's the conjugate of a weak acid. This will make the solution of the titration slightly acidic (titration of strong acid and weak base) or slightly basic (titration of a weak acid and strong base.)

We will look at an example:

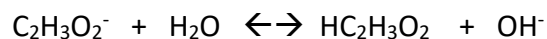
Let's look at a titration at the equivalency point.

If I have 30.0 mL of 0.10 M acetic acid and I titrated it with 30.0 mL of 0.10 M NaOH, this is a titration of a weak acid with a strong base. The strong conj base of the weak acid should cause the solution to be slightly basic at equivalency.

The Ka for acetic acid is  $1.8 \times 10^{-5}$ . Since it is the conjugate base, I need the  $K_b = X^2/[\text{salt formed}]$



The acetic acid and sodium hydroxide completely neutralize to make the water and acetate ion. We now have 0.003 mol of acetate ion in 0.06 L of solution. The concentration of the acetate ion is  $.003/.06 = 0.05\text{M}$  C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>



The acetate ion is acting as a base producing hydroxide ion. The Ka of acetic acid is  $1.8 \times 10^{-5}$ .

$$\begin{array}{l} K_b = \frac{X^2}{[\text{C}_2\text{H}_3\text{O}_2^-]} \quad X = [\text{OH}^-] \quad K_b = 1 \times 10^{-14} / 1.8 \times 10^{-5} = 5.56 \times 10^{-10} \\ 5.56 \times 10^{-10} = \frac{X^2}{.05\text{M}} \\ X = 5.3 \times 10^{-6} \text{ M} \quad \text{pOH} = -\log(5.3 \times 10^{-6}) = 5.3 \quad \text{pH} = 8.7 \end{array}$$

The pH of the equivalency point titration of this weak acid with a strong base is basic pH = 8.7,

Now we will do a titration of a weak acid and strong base like we did for the strong acid and strong base and see how the graph of this titration is different.

**Weak acid and Strong base titration:**

Consider the titration of 30.0 mL of 0.100 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> with 0.15 M KOH.

Calculate the pH after the following volumes of base is added to acetic acid.

- a) 0 mL
- b) 10.0 mL
- c) 19.5 mL
- d) 20.0 mL
- e) 20.5 mL

This titration would require several equations used to solve for X then convert to pOH and then to pH.

Instead of using the method we used to find the pH of the neutralized solution, there is another equation we can use to calculate the pH or pOH very quickly. It is known as the **Henderson-Hasselbalch Equation**. This equation is used to calculate pH of buffer solution which we will discuss next. However, it can also be used to calculate the pH of a weak acid or base being titrated by a strong base or acid.

(Watch video on A/B Reactions and Buffers, min. 13-21)

The Equation has several forms. I would suggest you use one of the following:

$$\text{pH} = \text{pKa} + \log \left( \frac{[\text{conj base}]}{[\text{acid}]} \right) \quad \text{pOH} = \text{pKb} + \log \left( \frac{[\text{conj acid}]}{[\text{base}]} \right) \quad (\text{pKa} = -\log \text{Ka}, \text{ and } \text{pKb} = -\log \text{Kb})$$

Let's proceed to the problem above.

Before any KOH is titrated,  $1.8 \times 10^{-5} = X^2/0.10$      $X = 1.3 \times 10^{-3} \text{ M}$  (this is [C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>])

	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> mol	KOH mol	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup> mol formed	[HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ]	[H <sup>+</sup> ] [C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup> ]
a)	(0.030)(0.10) 0.003	0 0		0.10 M	1.3 x 10 <sup>-3</sup> M
b)	0.003 mol .003-.0015 ,0015 mol	(.010)(.15) .0015	.0015 .0015 mol	.0015/.04 .0375 M	.0015/.04 .0375 M
c)	.003 mol .003-.00293 ,00007	(.0195)(.15) .00293 .00203	.00293	.00007/.0495 .0014	.00293/.0495 .059
d)	.003	,003	Equivalency—pH calculated in the notes above.		
e)	0	(.0205)(.15) .003075mol/.0505L = .061 M KOH			

So, for a) the **pH**  $-\log 1.3 \times 10^{-3} = \mathbf{2.89}$

For b) **pH** = pKa + log [conj base]/[acid] = 4.74 + log (.0375/.0375) = **4.74**

For c) **pH** = 4.74 + log (.059/.0014) = **6.36** (Almost at equivalency)

For d) **pH** = **8.7** (At equivalency)

For e) pOH = -log .061 = 1.21    **pH** = **12.8**

Parts a, b, c are pre-equivalency. Part d is at equivalency, and Part e is post-equivalency.

**Buffers** (Re-watch video min 21-25) and pages 715-723 in the text)

Buffers are solutions that help keep the pH of a solution constant.

**By using a weak acid and the salt of its conjugate base, we can keep the pH of the solution constant. The same is true for the weak base and its salt of the conjugate acid.**

We calculate the pH or pOH of these solutions using the **Henderson-Hasselbalch** equation.

If a small amount of acid or base enters the systems, the pH stays fairly constant.

Remember the equations.

For an acid buffer:  $\text{pH} = \text{pK}_a + \log \left( \frac{[\text{conj base}]}{[\text{acid}]} \right)$

For a basic buffer:  $\text{pOH} = \text{pK}_b + \log \left( \frac{[\text{conj acid}]}{[\text{base}]} \right)$

Remember to convert the pOH of the basic buffer to pH if you are asked for the pH.