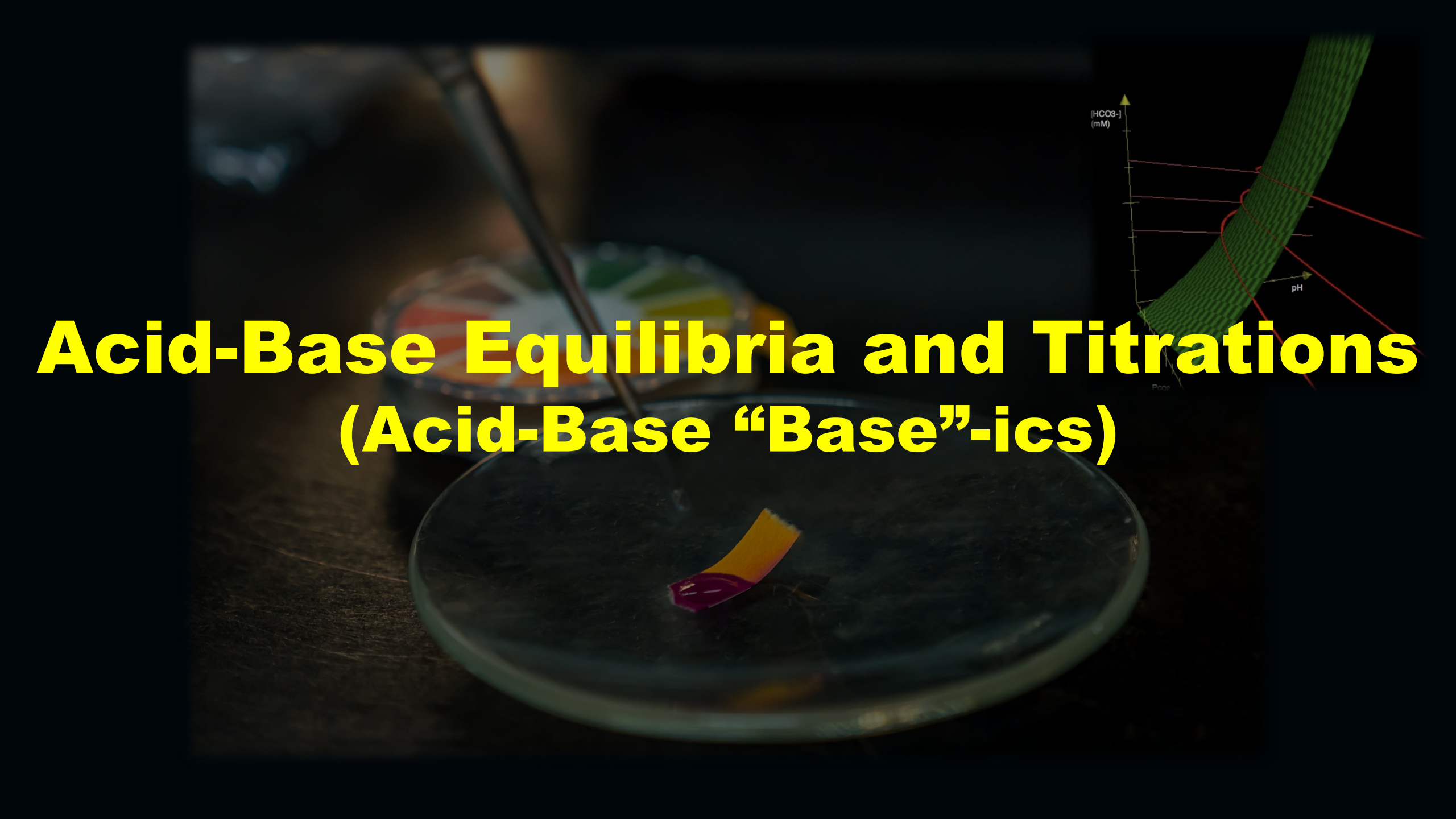
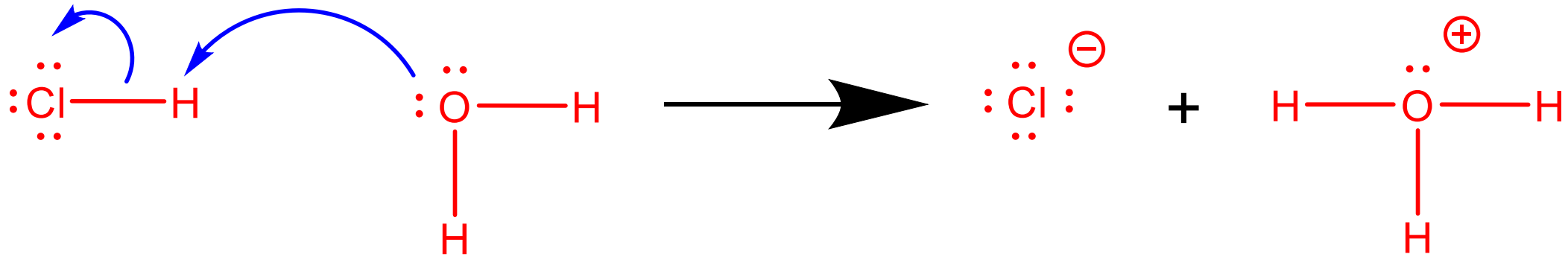


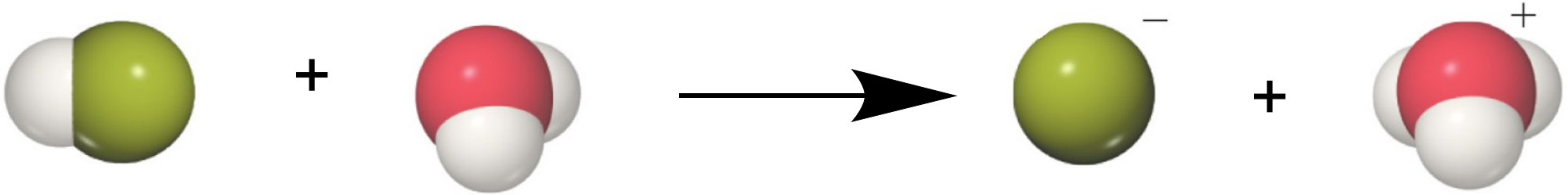
Acid-Base Equilibria and Titrations
(Acid-Base “Base”-ics)

Arrhenius Acids and Bases

An ***Arrhenius acid*** is *a substance that donates H^+ ions (**protons**) in aqueous solution*. For example, here is HCl dissolving in water:

$$HCl_{(g)} + H_2O_{(l)} \rightarrow Cl^-_{(aq)} + H_3O^+_{(aq)}$$

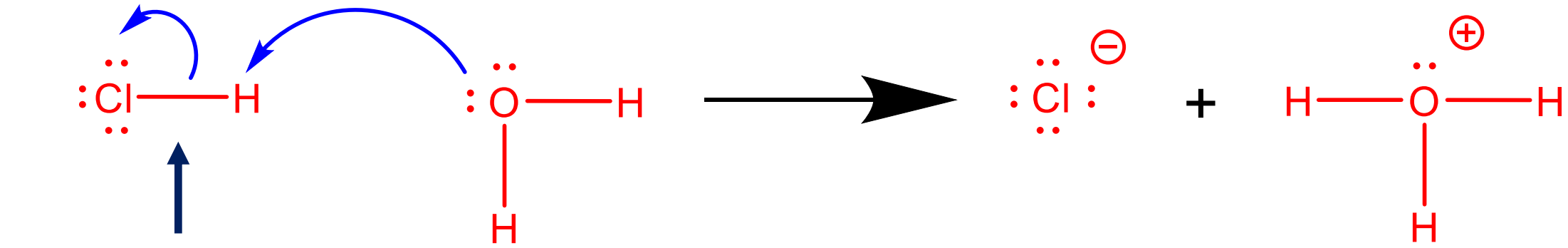




Arrhenius Acids and Bases

An ***Arrhenius acid*** is *a substance that donates H^+ ions (**protons**) in aqueous solution*. For example, here is HCl dissolving in water:

$$HCl_{(g)} + H_2O_{(l)} \rightarrow Cl^-_{(aq)} + H_3O^+_{(aq)}$$

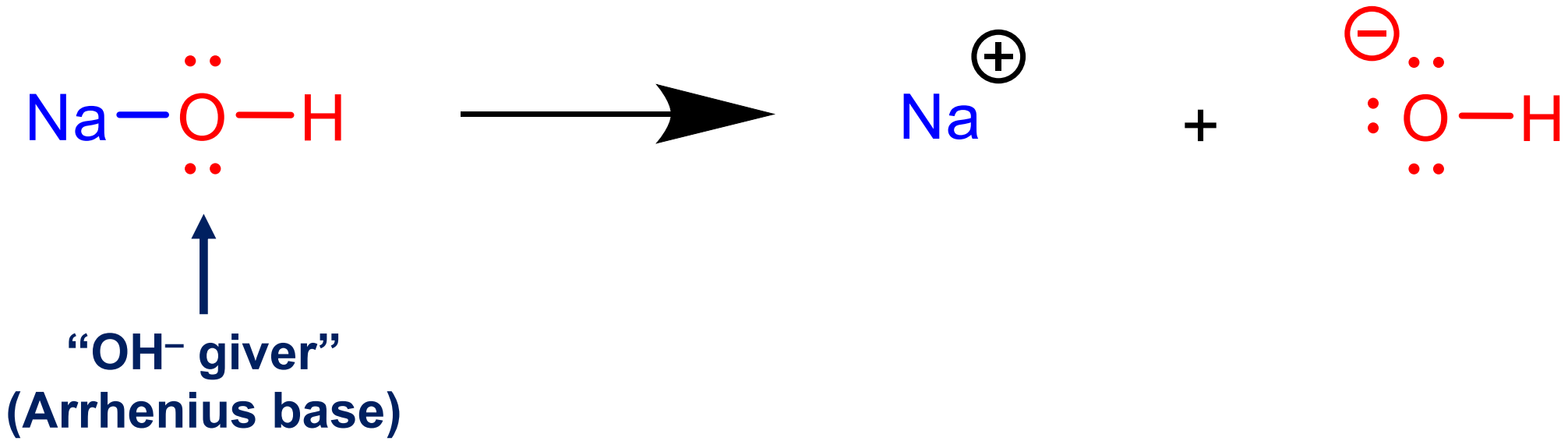


"H^+ giver"
(Arrhenius acid)

Arrhenius Acids and Bases

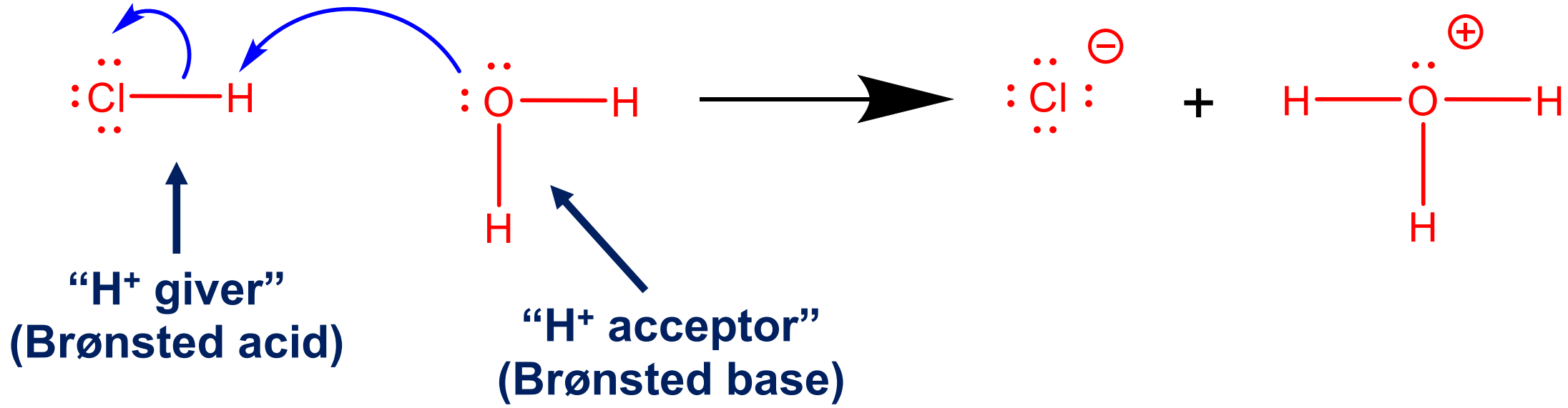
An ***Arrhenius base*** is *a substance that donates OH^- (**hydroxide**) ions in aqueous solution*. For example, here is NaOH dissolving in water:

$$NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$



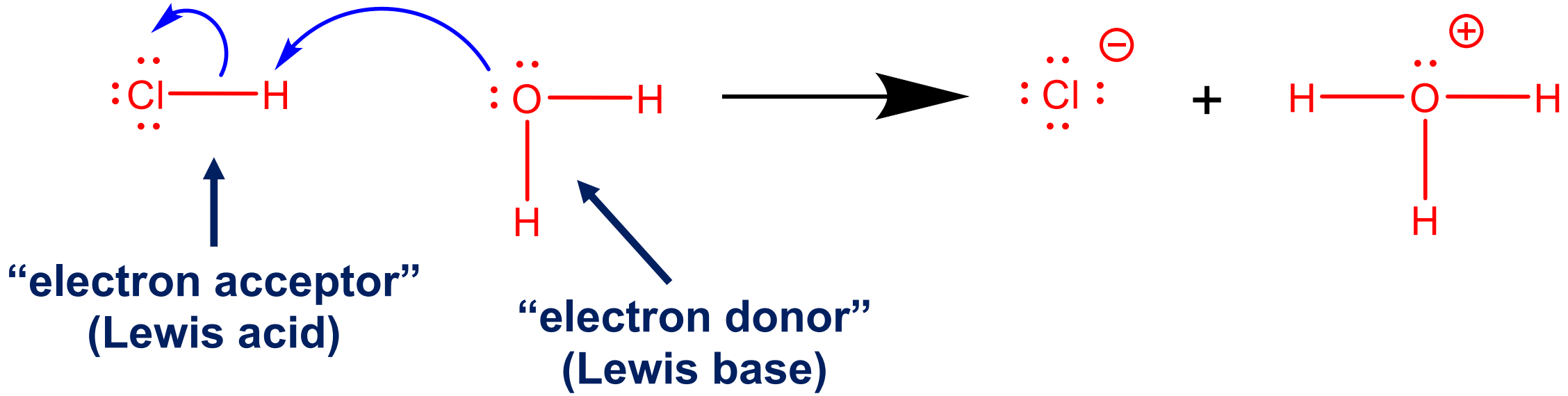
Brønsted Acids and Bases

A ***Brønsted acid*** is *a substance that donates H^+ ions (**protons**)*. A ***Brønsted base*** is *a substance that accepts H^+ ions*. For example, here is HCl dissolving in water:



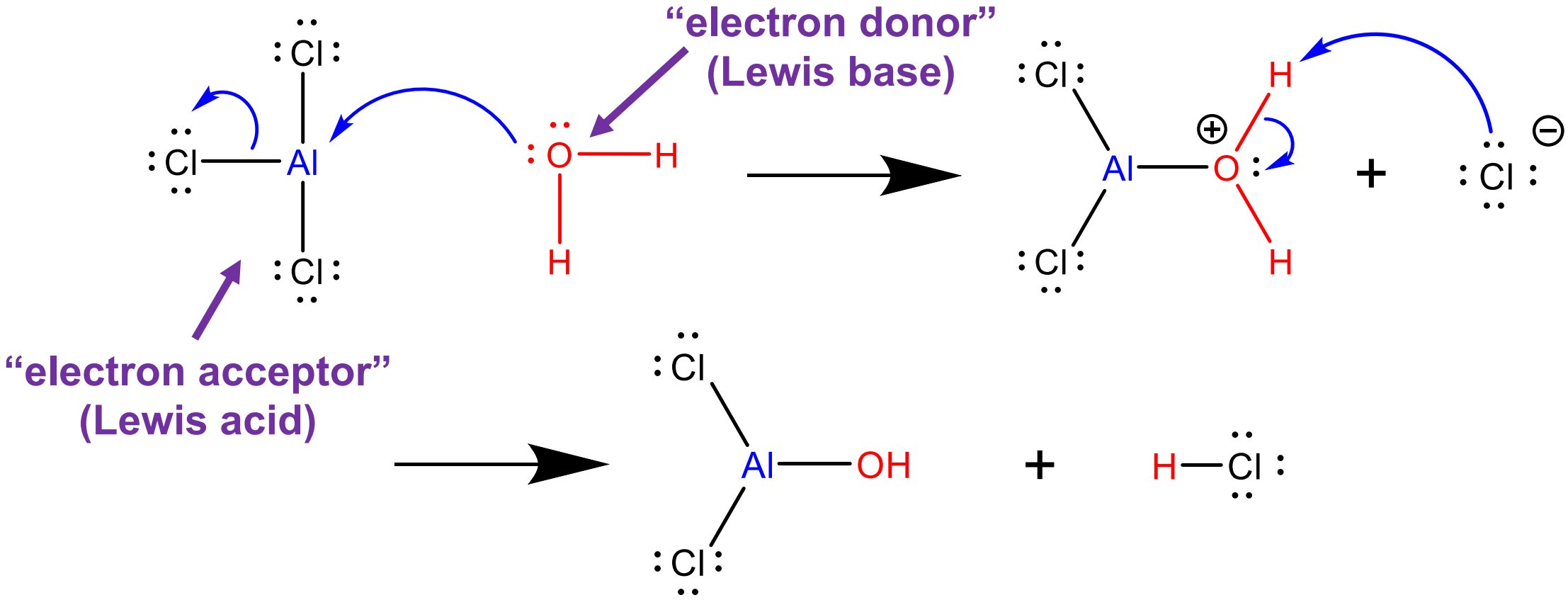
Lewis Acids and Bases

A ***Lewis acid*** is *a substance that accepts* ***electrons***. A ***Lewis base*** is *a substance that donates* ***electrons***.



Lewis Acids and Bases

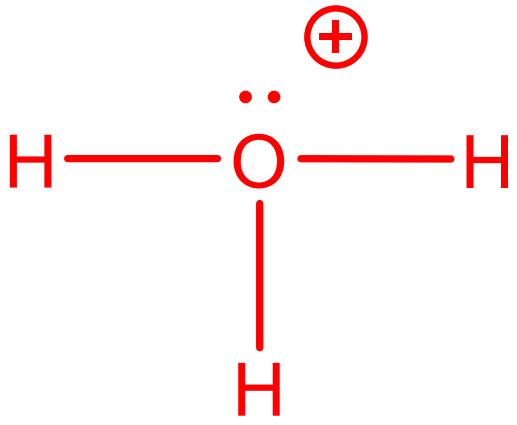
The ***Lewis*** definition of acids and bases is particularly useful for categorizing acids like $AlCl_3$. $AlCl_3$ does NOT donate H^+ ions, so it's not an ***Arrhenius*** or ***Brønsted acid***. Yet, it still makes a solution acidic. How?



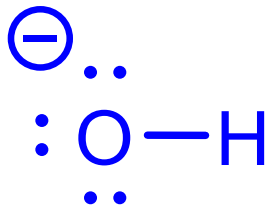
Lewis Acids and Bases

A ***Lewis acid*** is *an electron-acceptor*. A ***Lewis base*** is *an electron-donor*.

It's easy to remember this if you remember acids tend to have positive charges, so they want to accept electrons. Bases tend to have negative charges, so they want to donate electrons.



acids (more +ly charged, accept e^-)



bases (more –ly charged, donate e^-)

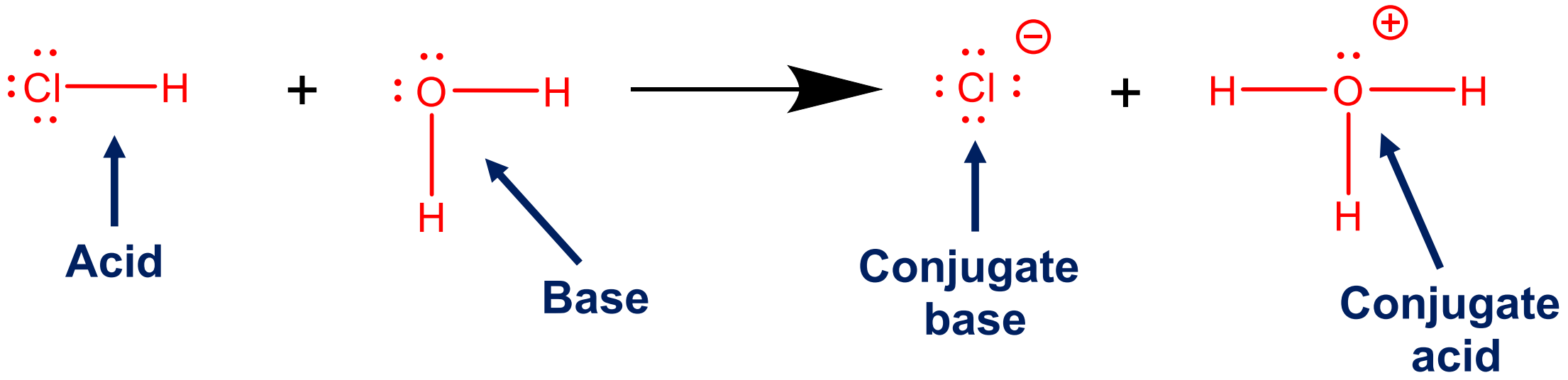
Acid-Base Summary

This table summarizes our three categories of definitions of acids and bases. Please familiarize yourself with these.

	Arrhenius	Bronsted-Lowry	Lewis
Acid	H^+ donor in water	H^+ donor	Electron acceptor
Base	OH^- donor in water	H^+ acceptor	Electron donors

Conjugate Acids and Bases

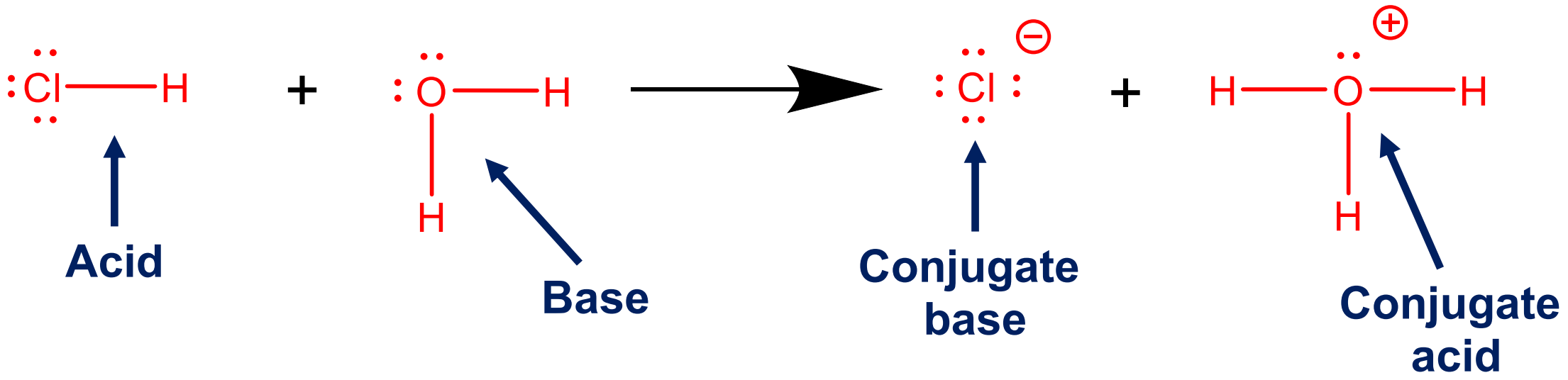
In any **acid-base** reaction, the product that comes from the acid is called that acid's ***conjugate base***. The product that comes from the base is called that base's ***conjugate acid***.



Identifying the ***conjugate base*** is easy: it's the product that looks exactly like the ***acid***, but with a – charge replacing the H. The ***conjugate acid*** is the product that looks exactly like the base, with an H and + added to it.

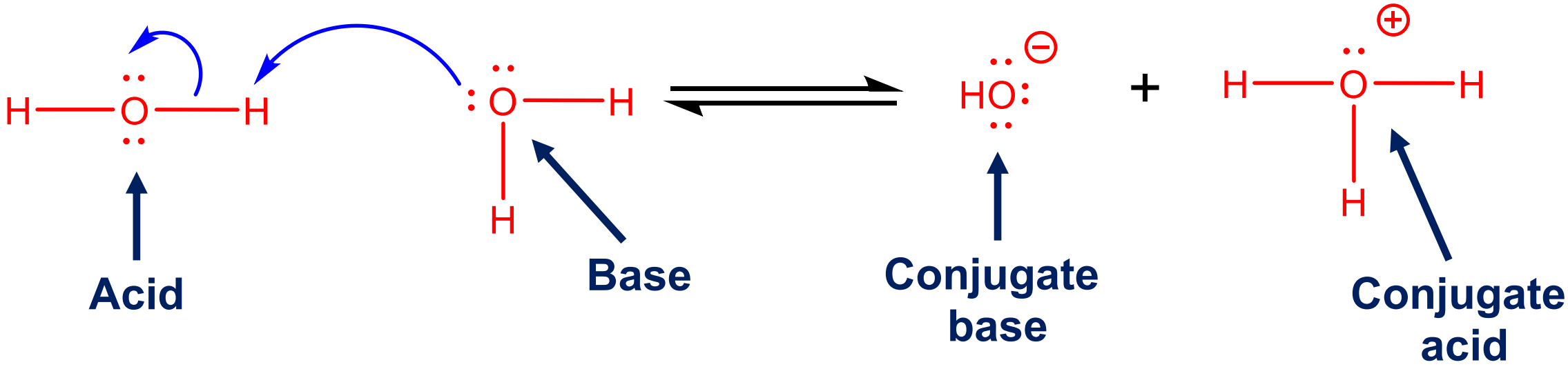
Conjugate Acids and Bases

In any **acid-base** reaction, the product that comes from the acid is call that acid's ***conjugate base***. The product that comes from the base is called that base's ***conjugate acid***.



To draw the ***conjugate base*** of any acid, just remove one proton (an H) from the acid and decrease its charge by +1. To draw the ***conjugate acid*** of any base, just add one proton (an H) to the base and increase its charge by +1.

Autoionization of Water



A substance (such as water) that can behave as either an acid or a base is called ***amphiprotic*** or ***amphoteric***.

Autoionization of Water

Amphiprotic: a substance that can act as both a proton acceptor and/or proton donor. This term is useful if you're talking about ***Arrhenius*** or ***Bronsted-Lowry*** acids and bases.

Amphoteric: a substance that can act as both an acid and a base. This term is useful for describing ***Lewis acids/bases*** that don't have a proton, like $AlCl_3$, and is consequently a more universal definition.

As we just saw water by itself auto-dissociates (autoionizes) to form H_3O^+ and OH^-. Thus, water is both ***amphiprotic*** and ***amphoteric***.

Autoionization of Water

As we just saw, when water is by itself, it auto-dissociates (***autoionizes***) to form H_3O^+ and OH^-, according to this equation:

$$2\ H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

What is the ***equilibrium constant expression*** for the autoionization of water?

$$K_C = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}$$

Remember that liquids, ***(l)***, are not included in ***K expressions***. As it turns out, water's autoionization K_C is called K_W, and K_W is equal to 1.0×10^{-14}.

Autoionization of Water

Because pure water autoionizes to form equal amounts of H_3O^+ and OH^-, the pH of pure water is completely neutral, (7.0).

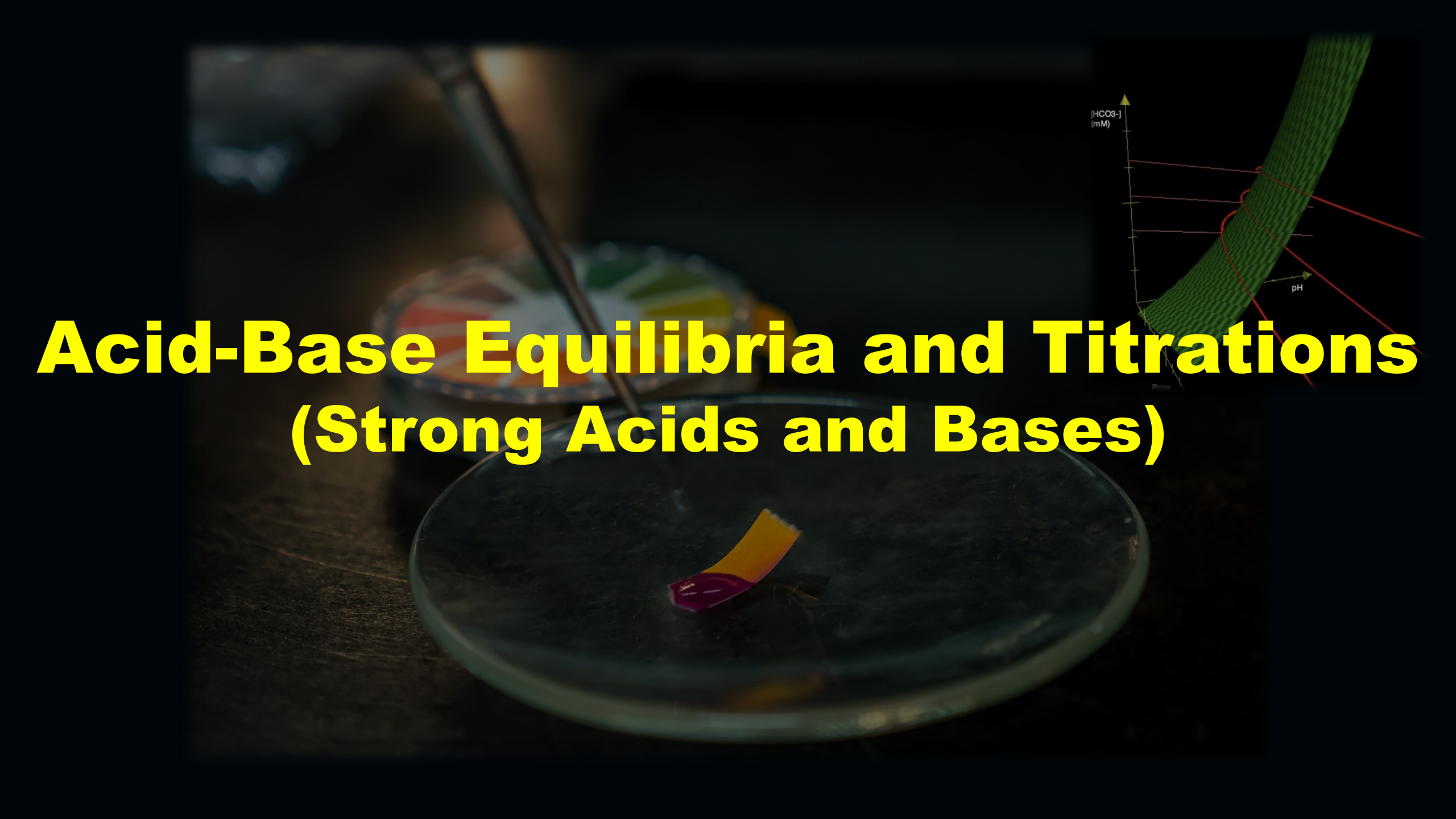
I told you that $K_W = 1.0 \times 10^{-14}$. However, this is only true at 25 °C. If you change the temperature, K_w changes, so pure water's "neutral pH" will be different at different temperatures.

Medical fun fact: because the body's temperature is approximately 37 °C, the "neutral pH" of the human body is actually around 7.4. Thus, a pH of 7.0 is considered slightly acidic when dealing with the human body.

Questions

Fill in the missing ***conjugate acid*** or ***conjugate base:***

Conjugate Acid	Conjugate Base
	HSO_4^{-1}
	NO_3^{-1}
H_3O^+	
HSO_4^{-1}	



Acid-Base Equilibria and Titrations
(Strong Acids and Bases)

Memorize These

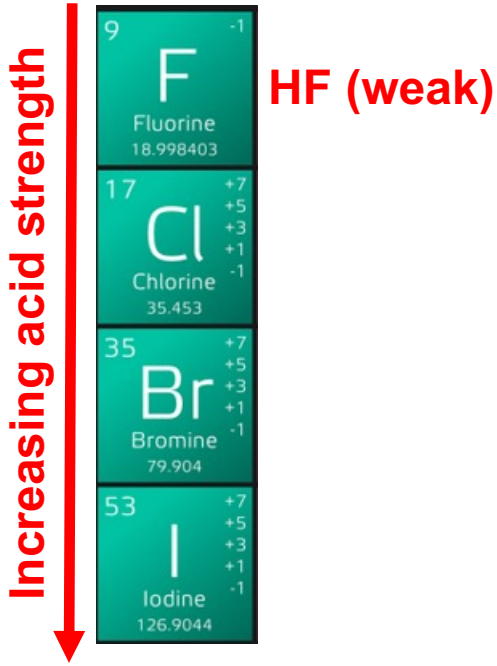
You should definitely memorize the names and formulas of the following ***strong acids*** and ***strong bases***, as well the fact that they ARE ***strong acids*** and ***strong bases***, which means they dissociate in water more-or-less 100%:

Strong Acids
HI
HBr
HCl
$HClO_3$
$HClO_4$
H_2SO_4
HNO_3

Memorize These

You should definitely memorize the names and formulas of the following ***strong acids*** and ***strong bases***, as well the fact that they ARE ***strong acids*** and ***strong bases***, which means they dissociate in water more-or-less 100%:

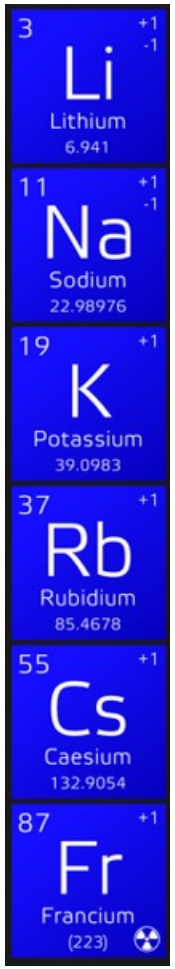
Strong Acids	Strong Bases
binary acids: HI, HBr, HCl	Group 1 metal hydroxides
$HClO_3$	$Mg(OH)_2$
$HClO_4$	$Ca(OH)_2$
H_2SO_4	$Sr(OH)_2$
HNO_3	$Ba(OH)_2$



Memorize These

You should definitely memorize the names and formulas of the following ***strong acids*** and ***strong bases***, as well the fact that they ARE ***strong acids*** and ***strong bases***, which means they dissociate in water more-or-less 100%:

Strong Acids	Strong Bases
HI	
HBr	Group 1 metal hydroxides
HCl	$Mg(OH)_2$
$HClO_3$	$Ca(OH)_2$
$HClO_4$	$Sr(OH)_2$
H_2SO_4	$Ba(OH)_2$
HNO_3	



LiOH

NaOH

KOH

RbOH

CsOH

FrOH

Mono- and Polyprotic Acids

Some acids, like **HI**, only have one H^+ per molecule. These are called ***monoprotic acids:***

$$HI_{(aq)} \rightarrow H^+_{(aq)} + I^-_{(aq)}$$

Because **HI** is a strong ***monoprotic acid***, if you dilute it in water to a concentration of **0.1 M**, for example, then you will end up with 0.1 moles/liter of H^+ and 0.1 moles/liter of I^-.

Mono- and Polyprotic Acids

Other acids, like H_2SO_4, however, have more than one H^+ per molecule. These are called ***polyprotic acids:***

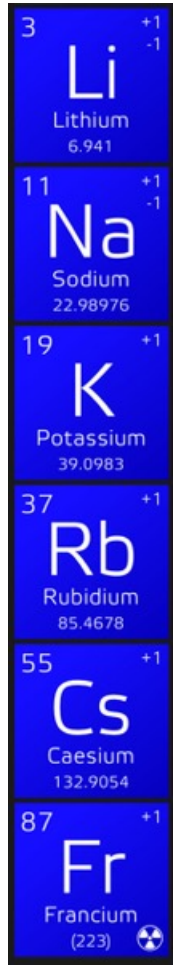
$$H_2SO_4\ (aq) \rightarrow H^+\ (aq) + HSO_4^-\ (aq) \rightleftharpoons H^+\ (aq) + SO_4^{2-}\ (aq)$$

Because H_2SO_4 is <u>also</u> a strong acid, if you dilute it in water to a concentration of **0.1 M**, it will dissolve 100% to give 0.1 moles/liter of H^+ and 0.1 moles/liter of HSO_4^-. However, HSO_4^- is <u>also</u> an acid, which will dissolve further to form H^+ and SO_4^{2-}.

Thus, if you dissolve 0.1 moles/liter of H_2SO_4, you will <u>actually</u> get a little <u>more</u> than 0.1 moles/liter of H^+ (probably around 0.12 moles/liter) because H_2SO_4 is ***diprotic***.

Returning to Our List

Strong Acids	Strong Bases
HI	Group 1 metal hydroxides
HBr	$Mg(OH)_2$
HCl	$Ca(OH)_2$
$HClO_3$	$Sr(OH)_2$
$HClO_4$	$Ba(OH)_2$
H_2SO_4	
HNO_3	



LiOH

NaOH

KOH

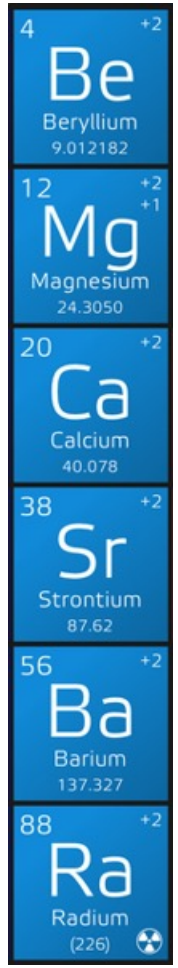
RbOH

CsOH

FrOH

Returning to Our List

Strong Acids	Strong Bases
HI	
HBr	Group 1 metal hydroxides
HCl	$Mg(OH)_2$
$HClO_3$	$Ca(OH)_2$
$HClO_4$	$Sr(OH)_2$
H_2SO_4	$Ba(OH)_2$
HNO_3	



$Be(OH)_2$

$Mg(OH)_2$

$Ca(OH)_2$

$Sr(OH)_2$

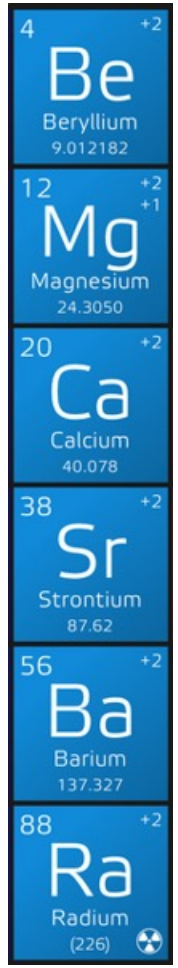
$Ba(OH)_2$

$Ra(OH)_2$

Dihydroxide Bases

Hydroxide bases from metals in Group 2 donate *two* **OH^-**'s per base, even when they aren't very water soluble.

For example, even though **$Ca(OH)_2$** and **$Mg(OH)_2$** are not very soluble in water, they are still considered strong hydroxide bases and *do* release two equivalents of **OH^-** per molecule of base.



$Be(OH)_2$

$Mg(OH)_2$

$Ca(OH)_2$

$Sr(OH)_2$

$Ba(OH)_2$

$Ra(OH)_2$

Dihydroxide Bases

For example, **0.1 M** $Ca(OH)_2$ *does* release **0.2 M** of OH^-, despite $Ca(OH)_2$'s minimal solubility in water:

$$Ca(OH)_{2\,(s)} \rightarrow Ca^{+2}{}_{(aq)} + 2\,OH^-{}_{(aq)}$$

0.1 M 0.1 M 0.2 M

This contrasts with ***diprotic acids*** like H_2SO_4. Even though H_2SO_4 has two H^+'s per molecule, **0.1 M** H_2SO_4 only gives off a *little* more than **0.1 moles/liter** of H^+ (around **0.12 M**).

$$H_2SO_{4\,(aq)} \rightarrow H^+{}_{(aq)} + HSO_4^-{}_{(aq)} \rightarrow H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

0.1 M 0.1 M 0.1 M 0.02 M 0.02 M

Acid-Base Equilibria and Titrations
(Trends in Acid Strength)

Seven Strong Acids You Should Know

There are seven strong acids whose names and formulas you should definitely memorize, as well as the fact that they *are* strong acids:

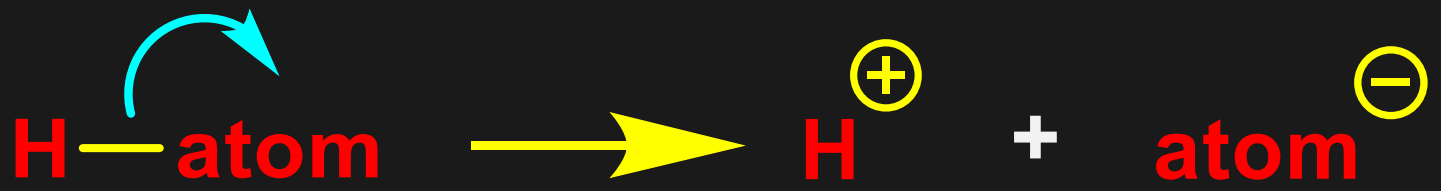
Binary Acids:	Oxyacids:
Hydrochloric acid, HCl Hydrobromic acid, HBr Hydroiodic acid, HI	Chloric acid, $HClO_3$ Perchloric acid, $HClO_4$ Nitric acid, HNO_3 Sulfuric acid, H_2SO_4

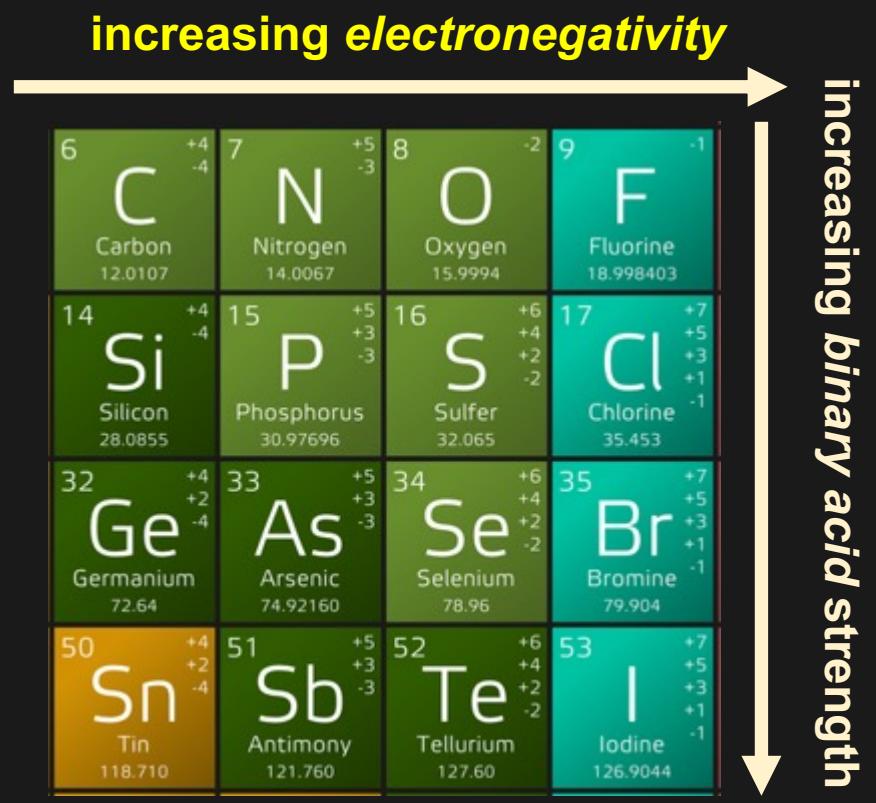
Binary Acid Strengths

For ***binary acids***, whose general formulas are **H-atom**, acid strength increases as the **"atom"** in your formula is located further to the right and down on the periodic table.

Left-to-Right Across a Row

The reason acidity increases as you move to the right across a row is that atoms get more ***electronegative***.





Binary Acid Strengths

For ***binary acids***, whose general formulas are **H-atom**, acid strength increases as the **"atom"** in your formula is located further to the right and down on the periodic table.

increasing *electronegativity*

Left-to-Right Across a Row

The reason acidity increases as you move to the right across a row is that atoms get more ***electronegative***.

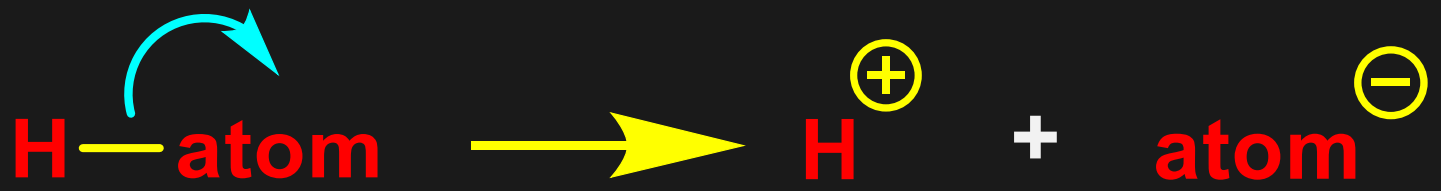
- **HF is a weak acid**
- **H_2O is neutral**
- **H_3N is a base**
- **CH_4 does very little acid-base chemistry**

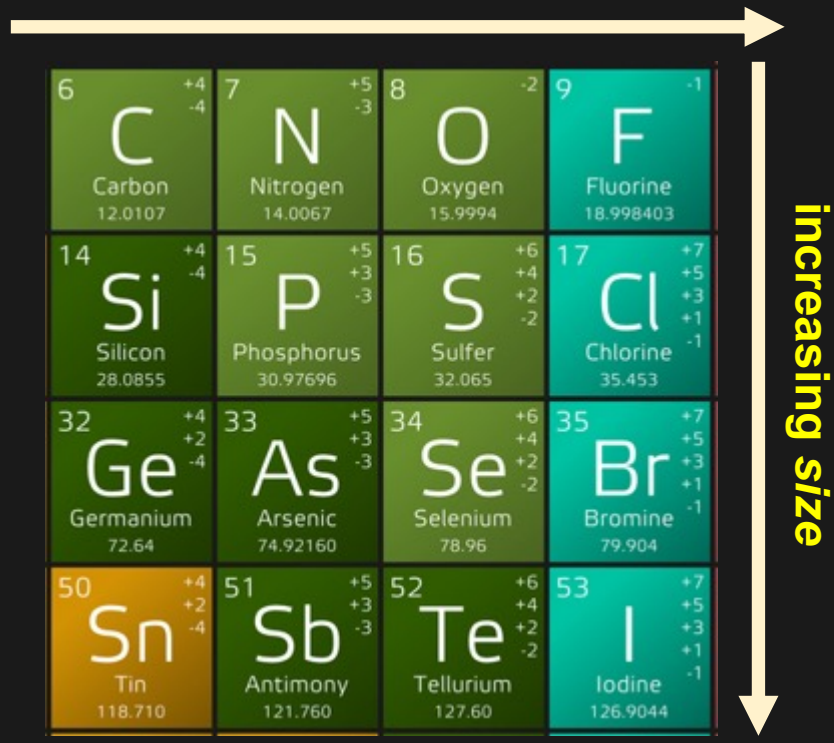
Binary Acid Strengths

For ***binary acids***, whose general formulas are **H-atom**, acid strength increases as the **"atom"** in your formula is located further to the right and down on the periodic table.

Down a Column

The reason acidity increases as you move down a column is that atoms get ***larger***.





Binary Acid Strengths

For ***binary acids***, whose general formulas are **H-atom**, acid strength increases as the **"atom"** in your formula is located further to the right and down on the periodic table.

Down a Column

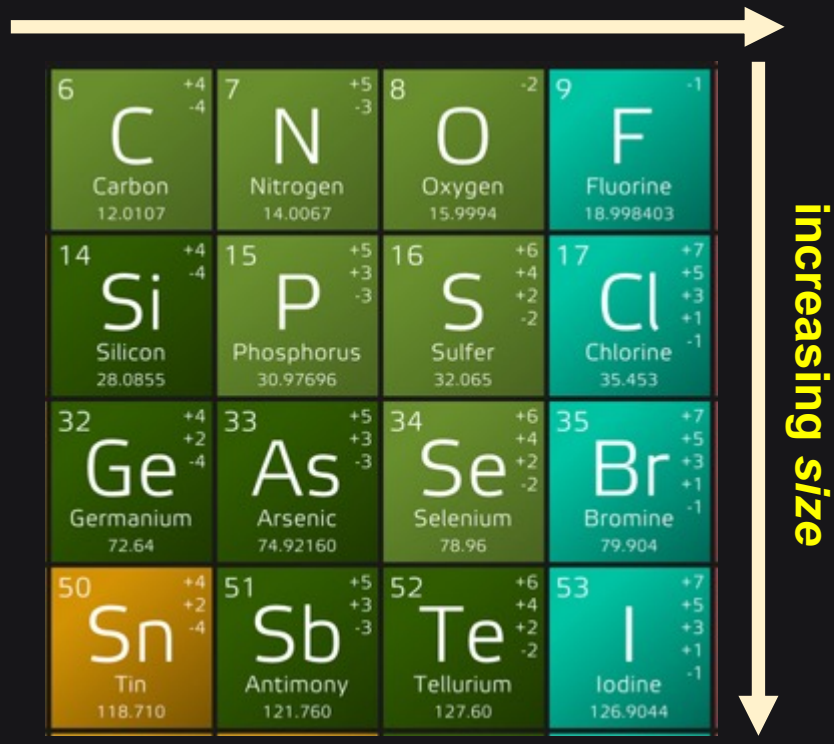
The reason acidity increases as you move down a column is that atoms get ***larger***.

strong

weak

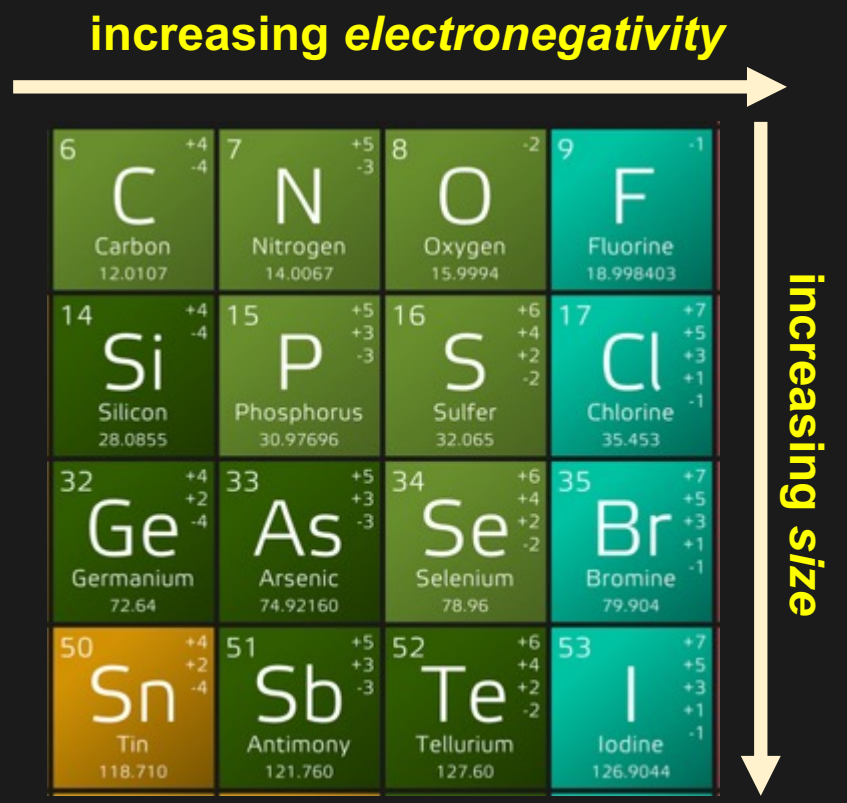
HI > HBr > HCl > HF

increasing *acidity*



Binary Acid Strengths

For ***binary acids***, acid strength increases as the **"atom"** bonded to the **H** in your formula is further down and to the right on the periodic table.



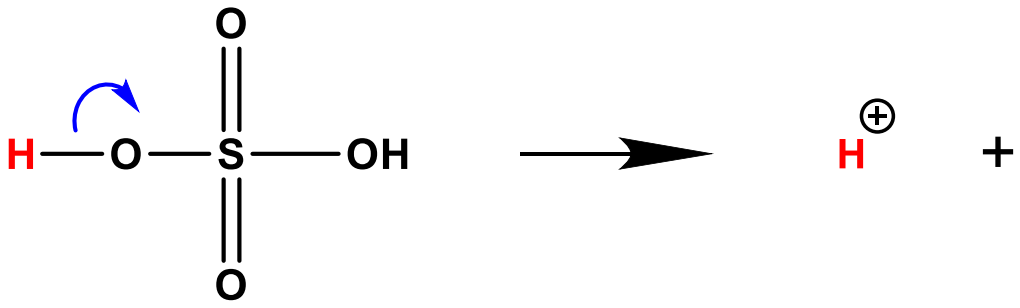
Oxyacid Strengths

Oxyacids are acids that have at least one oxygen and some other element (called the ***heteroatom***) in their formula:

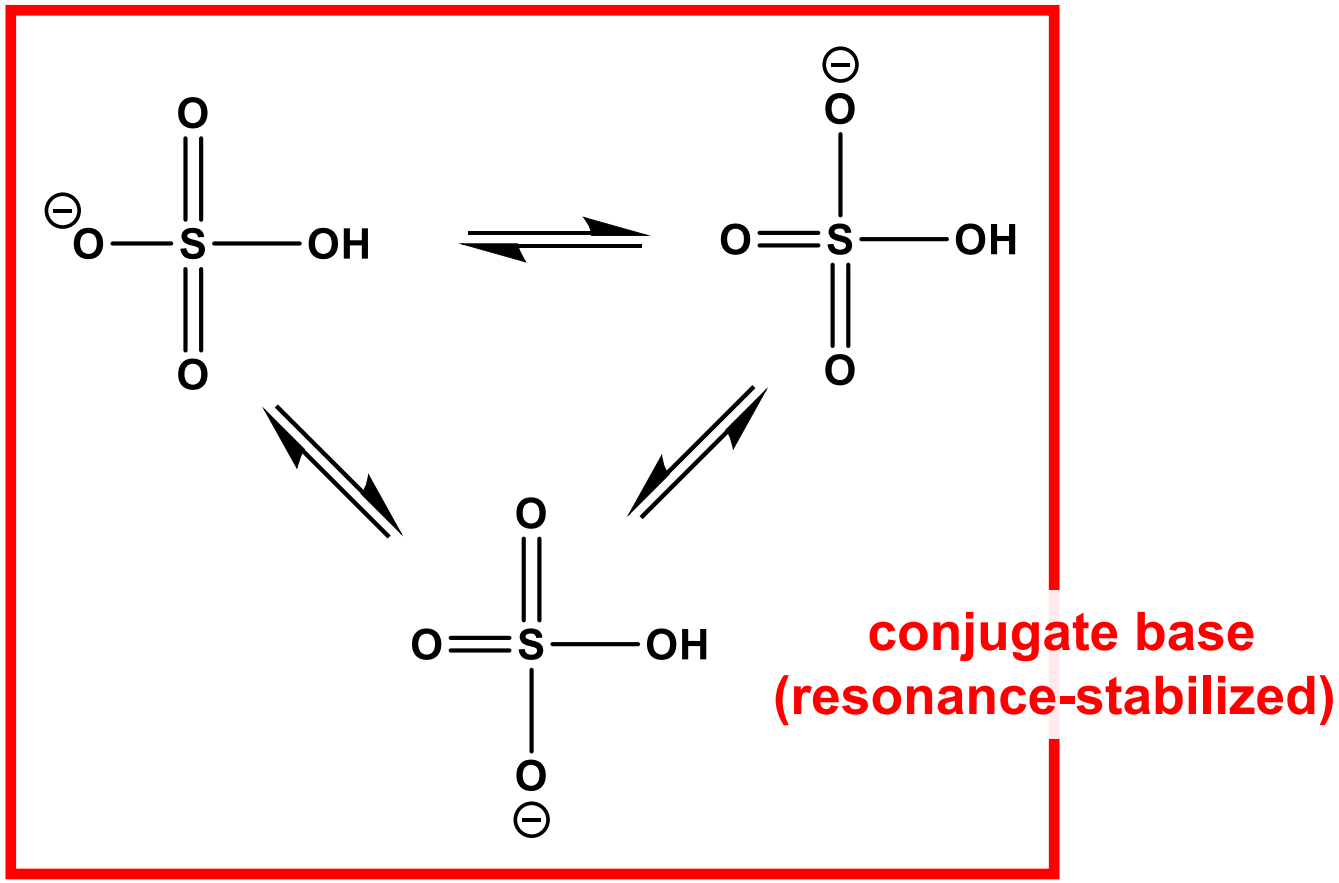
Binary Acids:	Oxyacids:
Hydrochloric acid, HCl Hydrobromic acid, HBr Hydroiodic acid, HI	Chloric acid, $HClO_3$ Perchloric acid, $HClO_4$ Nitric acid, HNO_3 Sulfuric acid, H_2SO_4

Oxyacid Strengths

In general, the more oxygen atoms you have, the more acidic the ***oxyacid*** becomes. The reason is that having more oxygen atoms increases the stability of the acid's ***conjugate base***, which makes it more acidic.

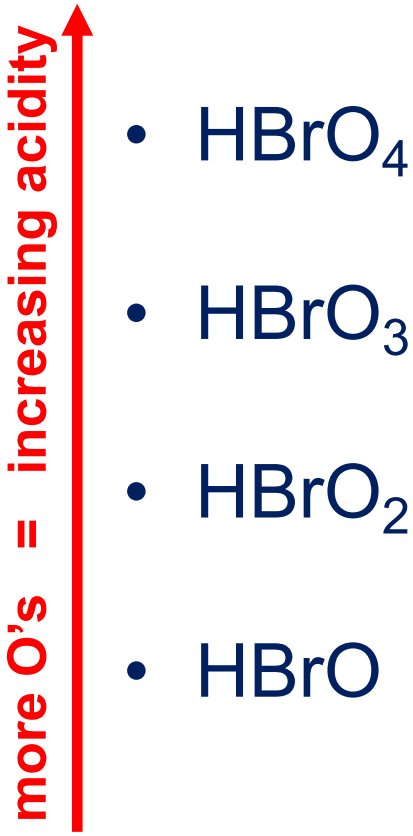


↑ conjugate base stability ≈ ↑ acidity



Oxyacid Strengths

In general, the more oxygen atoms you have, the more acidic the ***oxyacid*** becomes. The reason is that having more oxygen atoms increases the stability of the acid's ***conjugate base***, which makes it more acidic.



- $HBrO_4$
- $HBrO_3$
- $HBrO_2$
- $HBrO$

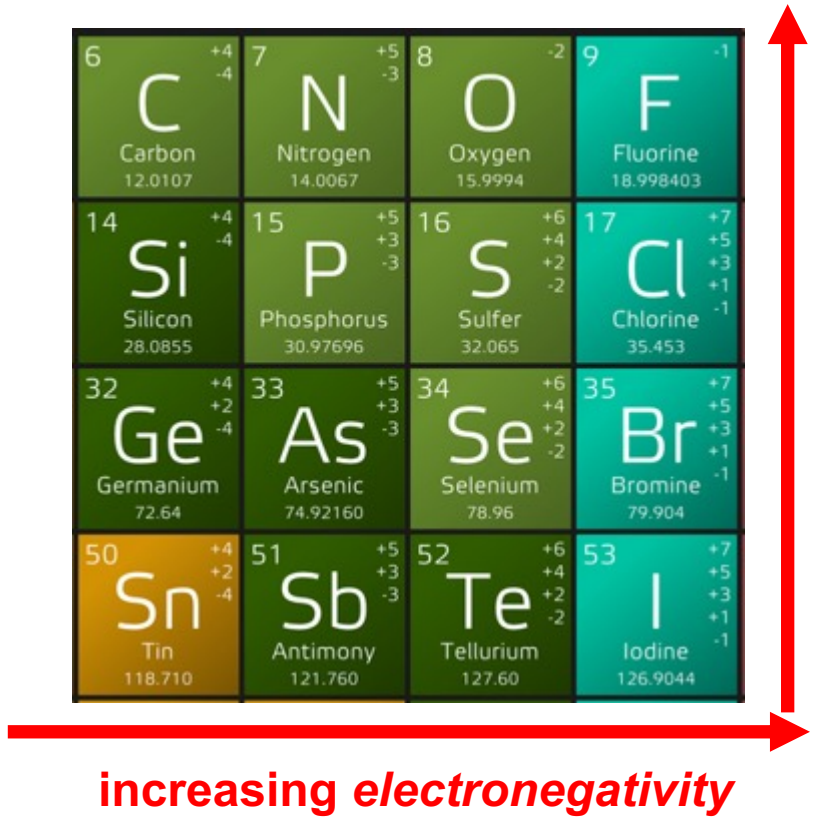
If you draw the ***Lewis structures*** of these compounds, you can see that more oxygen atoms means more resonance. More resonance means more stable conjugate base. More stable conjugate base means more acidic. In general, the more oxygen atoms you have, the more acidic the ***oxyacid*** becomes.

Oxyacid Strengths

When comparing two ***oxyacids*** that have different ***heteroatoms***, if all other things are equal, then in general, the more ***electronegative*** the ***heteroatom***, the more acidic the ***oxyacid***.

Which of the following would be more acidic: **$HClO_4$** of **$HBrO_4$**?

As you can see, these two acids' formulas are identical, except for their ***heteroatoms*** (Cl versus Br). As stated, in this type of situation, the more ***electronegative*** the ***heteroatom***, the more acidic the ***oxyacid***, due to the ***inductive effect***. Thus, **$HClO_4$** is a stronger acid than **$HBrO_4$**.



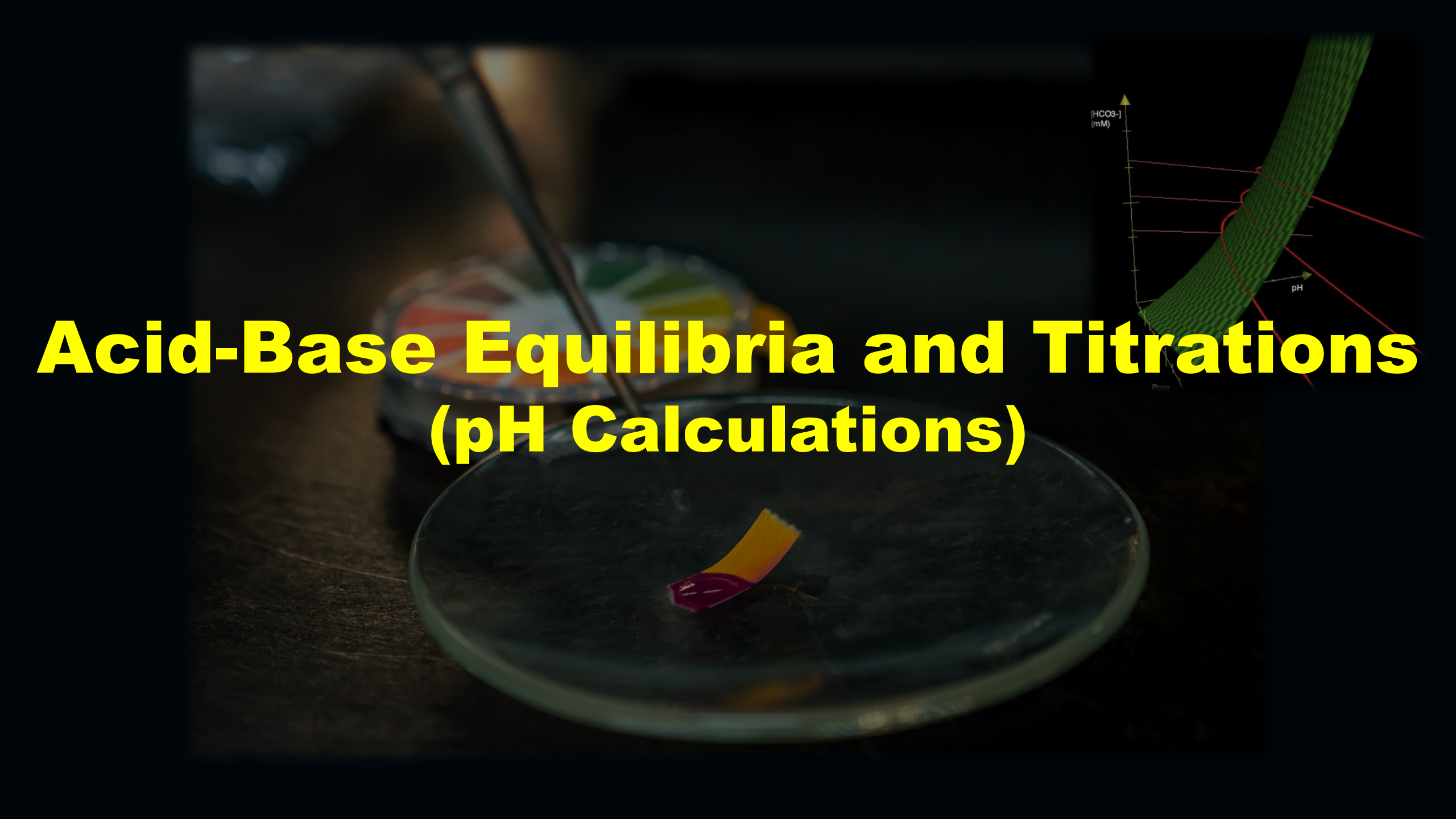
To Summarize

Memorize these seven ***strong acids***' names and formulas, as well as the fact that they *are* strong acids:

Binary Acids:	Oxyacids:
Hydrochloric acid, HCl Hydrobromic acid, HBr Hydroiodic acid, HI	Chloric acid, $HClO_3$ Perchloric acid, $HClO_4$ Nitric acid, HNO_3 Sulfuric acid, H_2SO_4

For ***binary acids*** (**H-atom**), acid strength increases as the **atom** is further to the right and down on the periodic table.

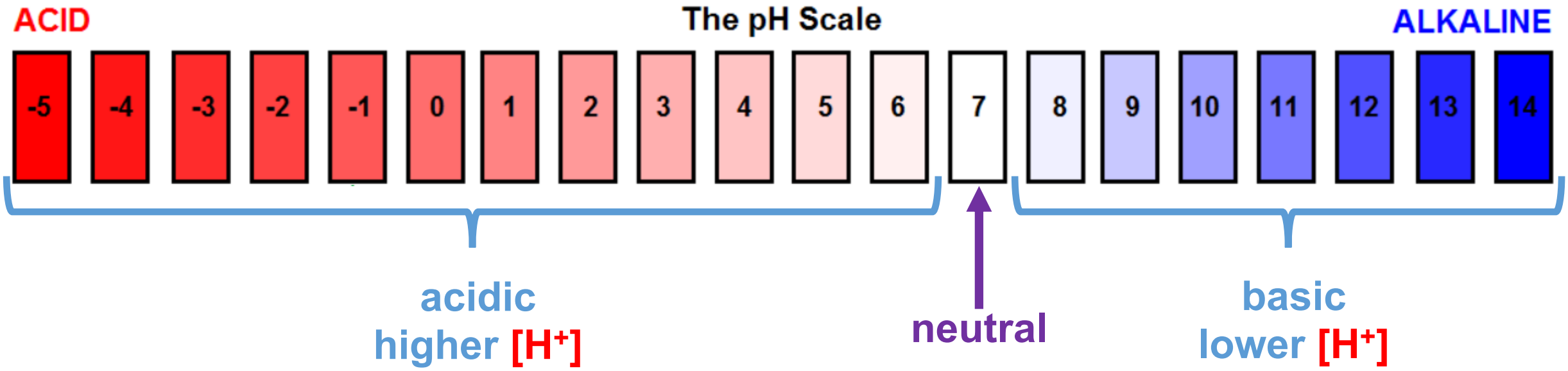
For ***oxyacids***, acid strength increases with an increasing number of oxygens. For ***oxyacids*** whose only difference is their ***heteroatom***, the more ***electronegative*** the ***heteroatom***, the more acidic the ***oxyacid***. Size does NOT matter in ***oxyacids*** like it does in ***binary acids***; for ***oxyacids***, it's about electronegativity and inductive effects.



Acid-Base Equilibria and Titrations
(pH Calculations)

What is pH?

Scientists have developed a simple system for reporting how acidic or basic a solution is. This system is called the ***pH scale***.



What is pH?

Here are some ***pH*** equations you should definitely know:

$$pH = -\log [H^+]$$

Also, for reasons I will now explain on the board:

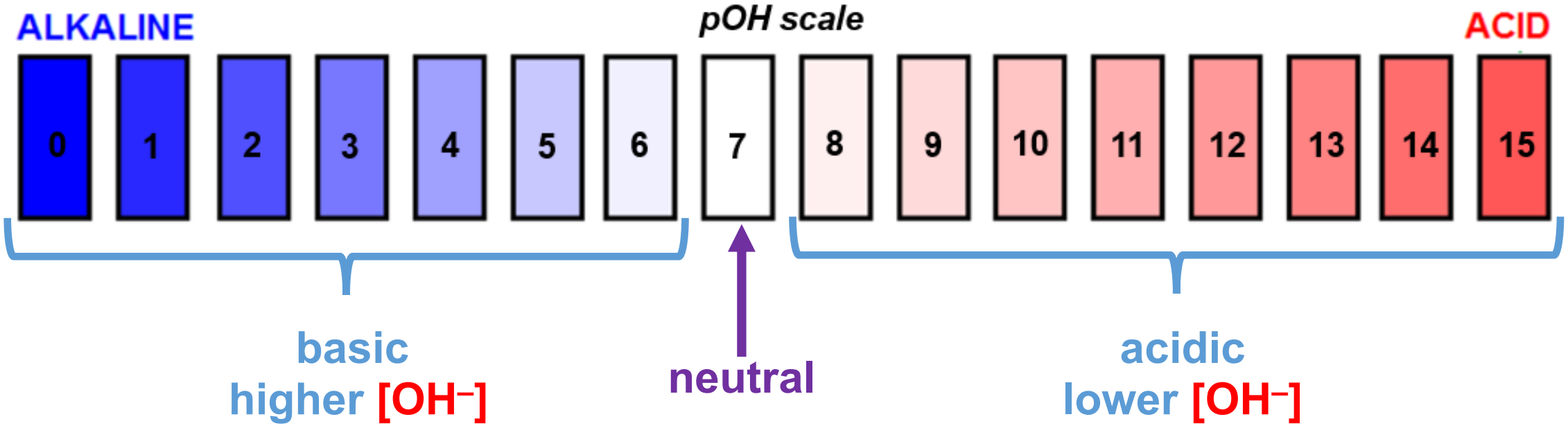
$$[H^+] = 10^{-pH}$$

In aqueous media, $[H^+]$ and $[H_3O^+]$ are interchangeable.

* This formula does not work for very dilute strong acids, $[H^+] < 10^{-7}$, because for such cases, the $[H^+]$ from H_2O is higher than the $[H^+]$ from the acid.

What is pOH?

Possibly for the purpose of being confusing, there also exists something called the ***pOH scale***, which conveys **[OH^-]** and is essentially the inverse of the ***pH scale:***



What is pOH?

Similar to ***pH***:

$$pOH = -\log [OH^-]$$

It should make sense, for the same mathematical reasons I just laid out for ***pH***, that:

$$[OH^-] = 10^{-pOH}$$

Connecting the Two

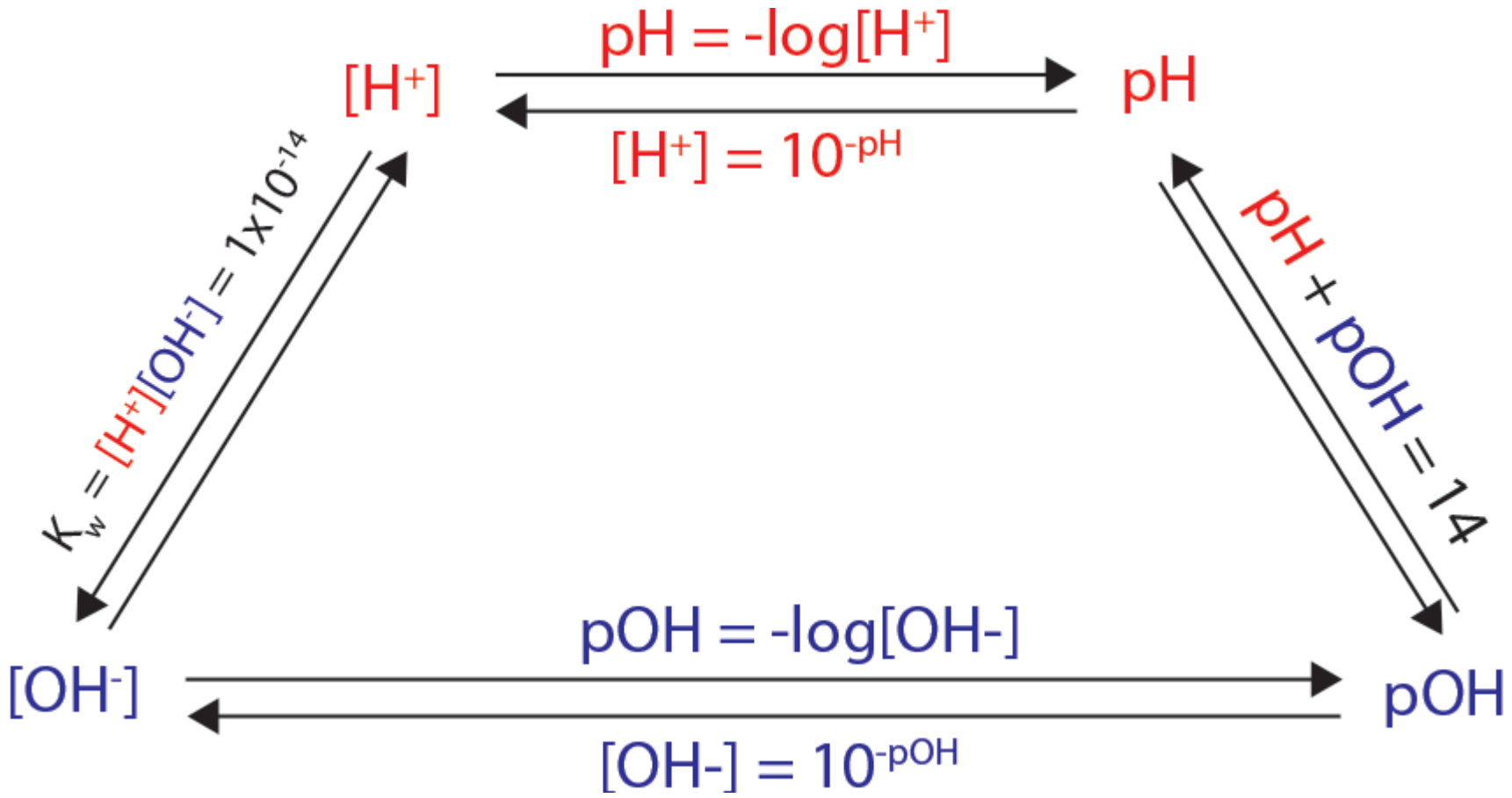
Also, the following equations connect the two:

$$K_W = 1.0 \times 10^{-14} = [H^+] \times [OH^-]$$

$$pH + pOH = 14$$

To Summarize

The following flowchart can help you navigate pH calculation problems using these different equations:



Questions

Please fill in the blanks:

$[H^+]$	pH	$[OH^-]$	pOH
	8		
			3
1.0×10^{-3} M			
		3.5×10^{-4} M	

Questions

What are the approximate pH and pOH values of an aqueous solution of 1.0×10^{-3} M HBr?

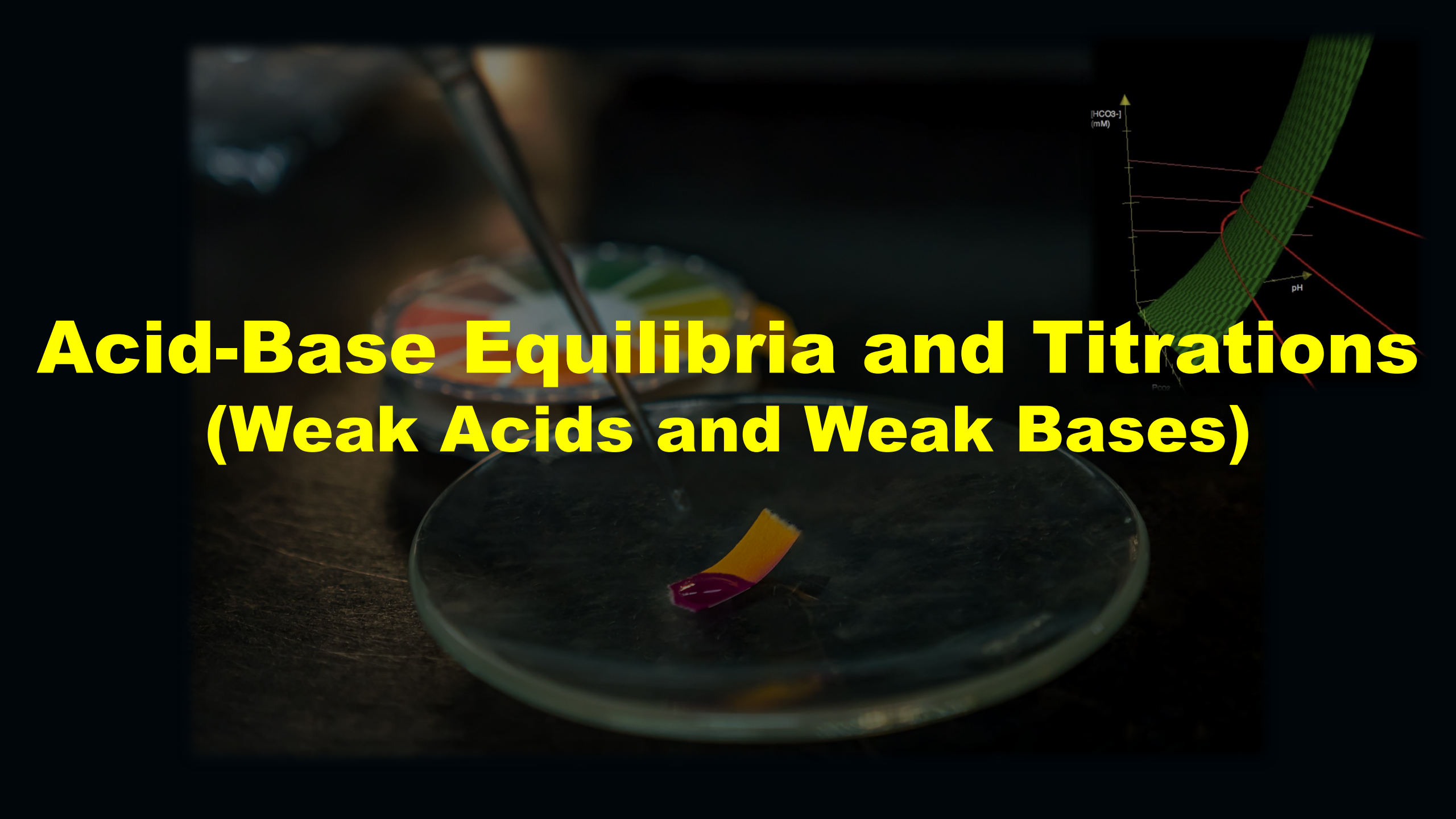
Questions

If a solution has a **pH** of **2.0**, what are **[H^+]** and **[OH^-]**?

Questions

Please approximate the missing ***pH*** values:

$[H^+]$	pH
0.01 M HCl	
0.01 M H_2SO_4	
0.00320 M HNO_3	
1×10^{-11} M HBr	
0.01 M KOH	
0.01 M $Ba(OH)_2$	



Acid-Base Equilibria and Titrations
(Weak Acids and Weak Bases)

Strong Acids

In a prior video, I taught you that ***strong acids*** dissolve virtually 100% in water. Thus, they have one-way arrows, like this:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

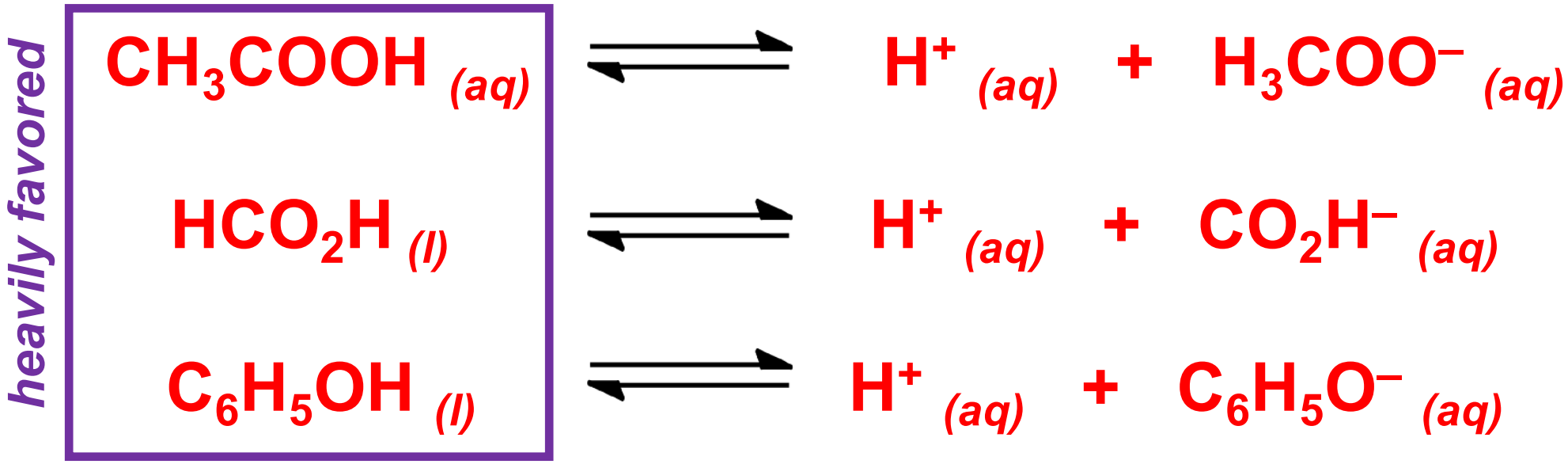
$$H_2SO_{4\ (aq)} \rightarrow H^+_{(aq)} + HSO_4^-{}_{(aq)}$$

$$HClO_{4\ (aq)} \rightarrow H^+_{(aq)} + ClO_4^-{}_{(aq)}$$

In other words, they do NOT form ***equilibrium reactions***.

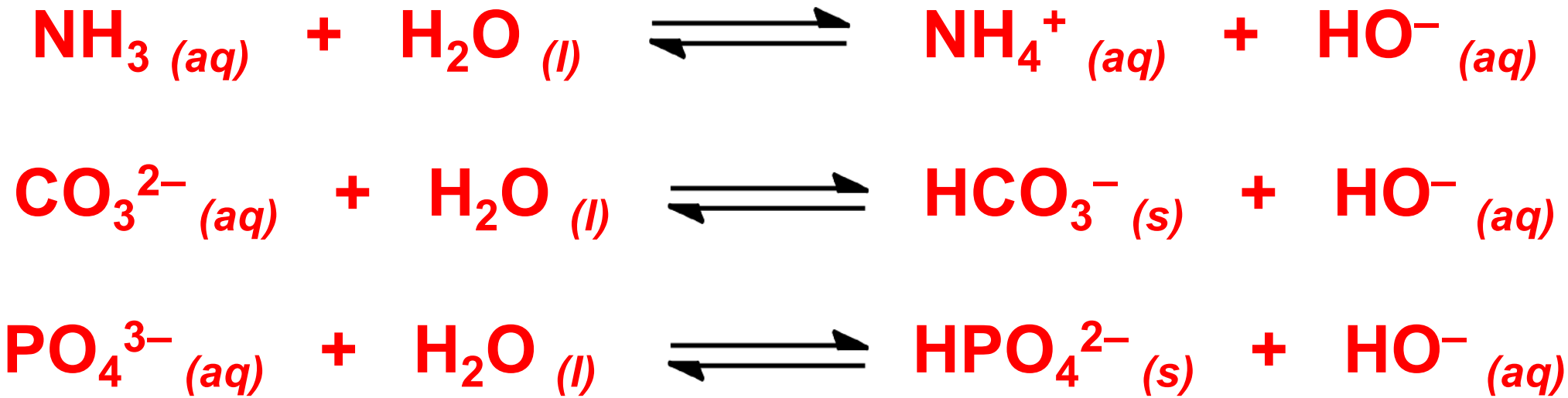
Weak Acids

By comparison, ***weak acids*** do NOT dissolve fully in water and therefore have two-way ***equilibrium-reaction*** arrows, like this:



Weak Bases

The same thing is true of ***weak bases:***



K_A Values

Similar to any <u>other</u> ***equilibrium reaction***, weak acids and bases also have ***dissociation constants***, or ***K*** values, called K_A's (for weak acids) and K_B's (for weak bases). For any generic ***weak acid equilibrium*** reaction:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

. . . . Its ***equilibrium rate constant*** (K_A) is:

$$K_A = \frac{[H_3O^+][A^-]}{[HA]}$$

<u>shortcut</u>

$$[H_3O^+] = \sqrt{Ka[HA]}$$

This works for weak acids in the VAST majority of cases, because **[HA] > > [A⁻]**.

K_B Values

By analogy, for any generic ***weak base equilibrium*** reaction:

$$A^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HA_{(aq)} + OH^-_{(aq)}$$

. . . . Its ***equilibrium rate constant*** (K_B) is:

$$K_B = \frac{[HA][OH^-]}{[A^-]}$$

shortcut

$$[OH^-] = \sqrt{Kb[A-]}$$

This works for weak bases in the VAST majority of cases, because $[A^-] >> [HA]$.

pK_A and pK_B Values

So, K_A and K_B values are often really small numbers, like $\mathbf{1.2 \times 10^{-5}}$. Because dealing with such small values is sometimes mathematically tricky, scientists often use terms called pK_A and pK_B instead of K_A or K_B.

$$pK_A = -\log [K_A] \qquad pK_B = -\log [K_B]$$

This little switcheroo makes it so pK_A and pK_B values become much simpler numbers, like **5**, **10**, or **25**. The point is (and you should *definitely* memorize this):

$\downarrow pK_A = \uparrow K_A = \uparrow$ **acid strength** $\qquad \downarrow pK_B = \uparrow K_B = \uparrow$ **base strength**

Equations

We can now update our list of ***pH*** equations:

$$K_W = 1.0 \times 10^{-14} = [H^+] \times [OH^-] = K_A \times K_B$$

$$pH + pOH = 14 = pK_A + pK_B$$

Larger K_A = smaller pK_A = stronger acid

Larger K_B = smaller pK_B = stronger base

Questions

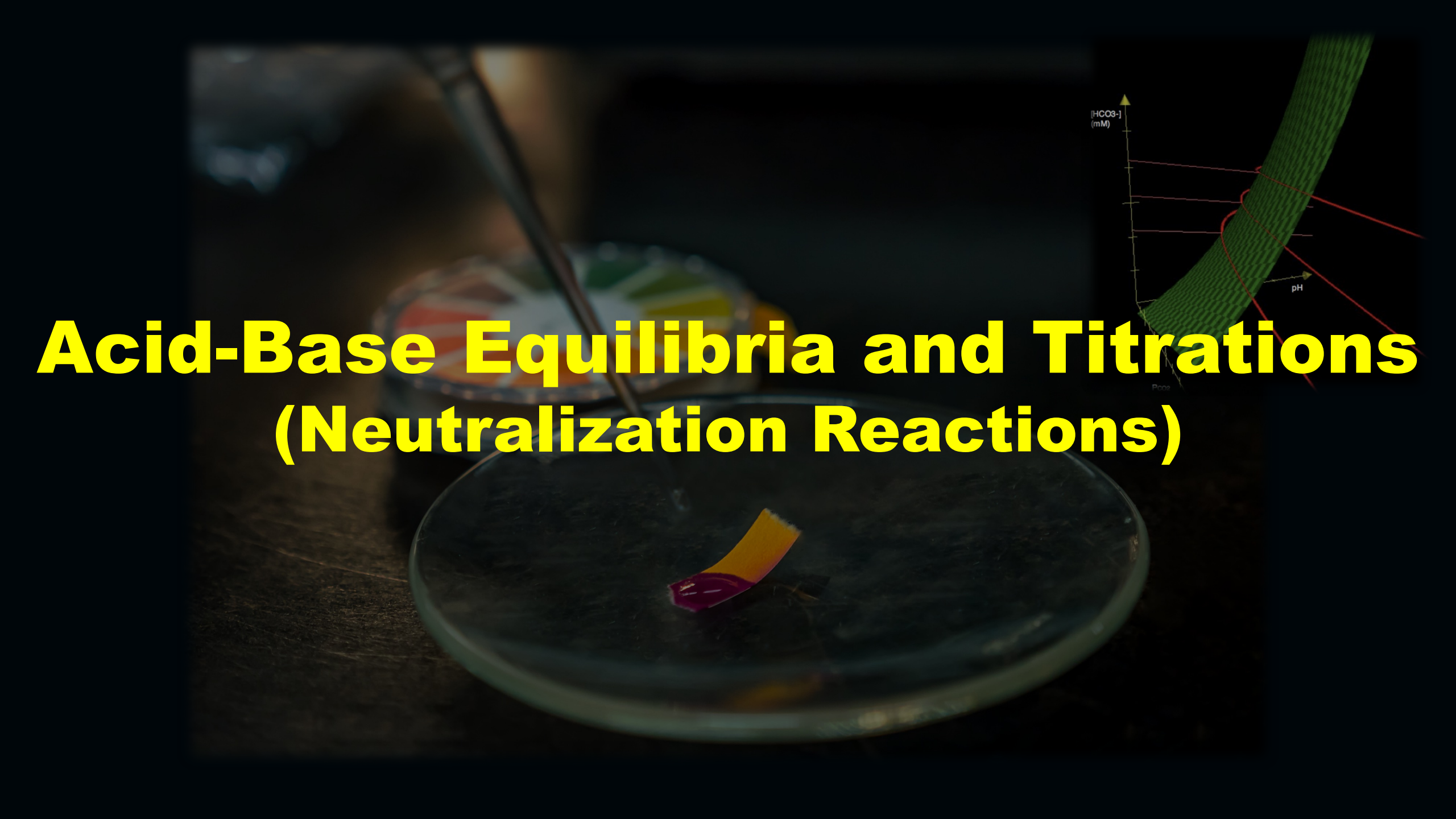
What is the approximate ***pH*** of a **0.005 M** solution of **HF** (K_A **= 5.0 ×10^{-4}**)?

Questions

What is the approximate ***pH*** of a **0.02 M** solution of **NaF** (the K_A of HF is **5.0×10^{-4}**)?

Questions

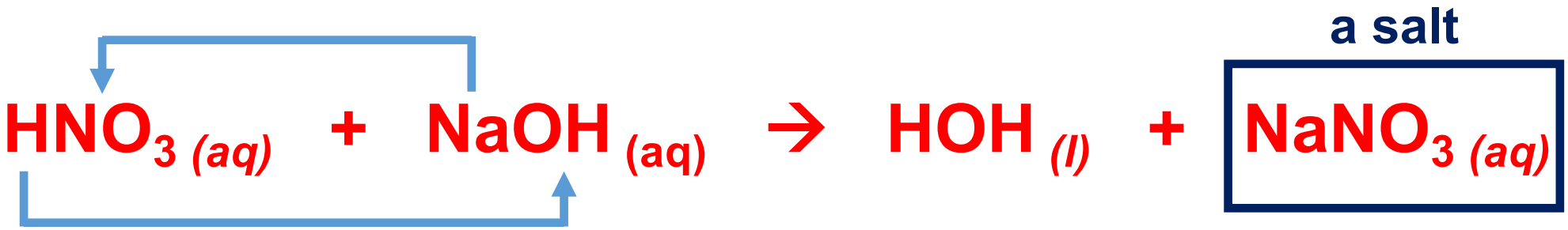
What is the approximate ***pH*** of a solution that is **0.02 M HF** (K_A = **5.0 ×10^{-4}**) and **0.02 M NaF**?



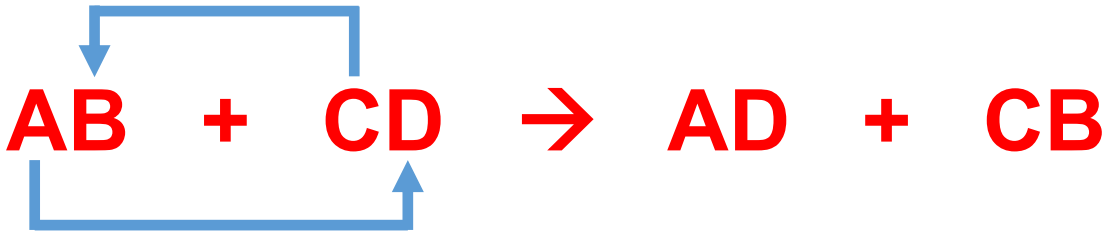
Acid-Base Equilibria and Titrations
(Neutralization Reactions)

Neutralization Reactions

Reactions between acids and bases are called ***neutralization reactions***. They always make **H_2O** and a **salt**:



You might recognize this as a specific kind of ***metathesis*** (***double-displacement***) reaction:



Neutralization Reactions

Neutralization reactions between a ***strong acid*** and a ***strong base*** always result in a neutral ***pH*** of **7.0**.

- Strong Acid + Strong Base: ***pH* = 7.0**
- Weak Acid + Strong Base: ***pH* > 7.0**
- Weak Base + Strong Acid: ***pH* < 7.0**

I'll talk about these latter two more later on.

Neutralization Reactions

Calculations with ***neutralization reactions*** often involve the following equation:

$$n_A M_A V_A = n_B M_B V_B$$

Where:

- M_A = the ***molarity*** of your acid
- M_B = the ***molarity*** of your base
- V_A = the ***volume*** of your acid
- V_B = the ***volume*** of your base
- n_A = the number of H^+ groups the acid can donate
- n_B = the number of OH^- groups the base can donate

What is Normality?

In prior videos, I taught you that:

$$\text{molarity (M)} = \frac{\text{moles solute}}{\text{L of solution}}$$

By comparison, ***normality*** (**N**) is:

$$\text{normality (N)} = \frac{\text{moles solute}}{\text{L of solution}}$$

What is Normality?

Normality is technically a little more correct than ***molarity***. For example, if I tell you that I have a 0.1 M solution of **HCl**, you might mistakenly think that I have 0.1 moles of **HCl** per liter of solution.

However, you would be wrong. Because **HCl** dissolves close to 100%, what I *actually* have is 0.1 M of $\mathbf{H^+}$ and 0.1 M of $\mathbf{Cl^-}$.

As far as ***neutralization reactions*** are concerned, ***normality*** does NOT depend on strong/weak status. Thus, for calculations that involve ***normality***, you consider all possible $\mathbf{H^+}$/$\mathbf{OH^-}$ donors. So $\mathbf{H_3PO_4}$, for example, donate three $\mathbf{H^+}$'s, so its $\mathbf{n_A}$ = 3.

Questions

How many liters of **1.0 M HCl** do you need to neutralize 2.0 L of **3.0 M NaOH**?

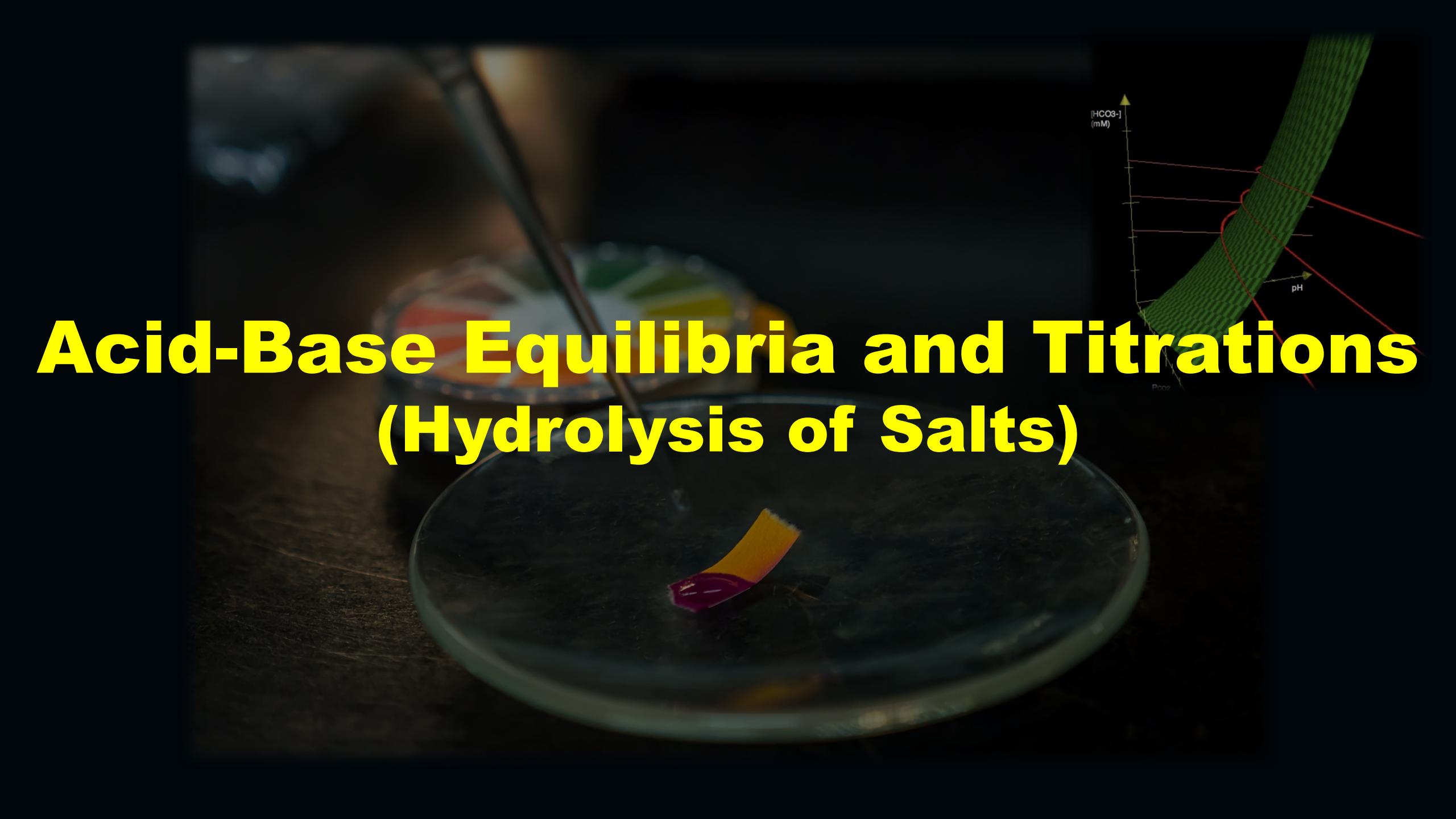
Questions

How many liters of **1.0 M HCl** do you need to neutralize 1.5 L of **3.0 M $Ca(OH)_2$**?

Questions

How many liters of **1.0 N H_2SO_4** do you need to neutralize 1.5 liters of **3.0 N $Sr(OH)_2$**?

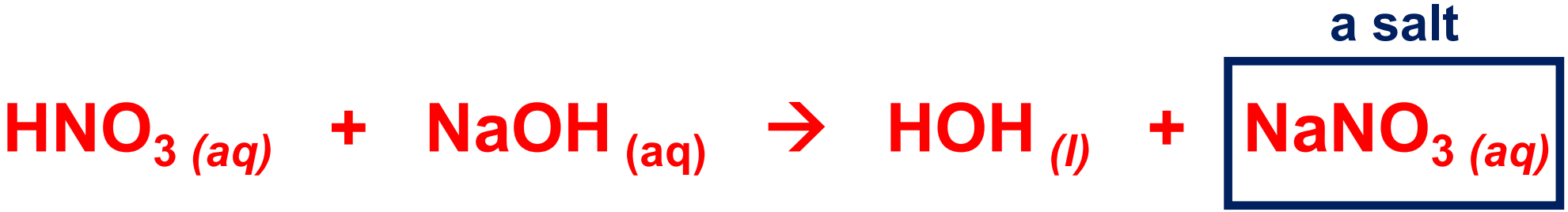
How many liters of **1.0 M H_2SO_4** do you need to neutralize 1.5 liters of **3.0 M $Sr(OH)_2$**?



Acid-Base Equilibria and Titrations
(Hydrolysis of Salts)

To Review

As I explained in an earlier video, ***neutralization reactions*** always produce **H_2O** and a **salt**:



Thus, one way to define the term ***salt*** is "the ionic product of a ***neutralization reaction***." The point is, in this video, I'll teach you about ***hydrolysis of salts***.

Neutralizing Salts

When I say ***hydrolysis of salts***, I'm talking about dissolving salts in water.

As it turns out, some salts actually *change* the water's ***pH*** when they dissolve. Other salts do not. How do you know which salts change the water's ***pH*** and which ones don't? By memorizing this table!

Neutral cations	Neutral anions
Group 1 metals Group 2 metals Metals with a +1 charge	Cl^- Br^- I^- NO_3^- ClO_4^- ClO_3^-

Neutralizing Salts

Also, you need to remember that with the exceptions shown in our table, ***cations*** typically act as acids (often, as ***Lewis acids***), while anions (other than the exceptions from our table) typically act as bases (often, as ***Lewis bases***). (Exception: **HSO_4^-** is an acid: **$HSO_4^- \rightarrow H^+ + SO_4^{2-}$**.

Neutral cations	Neutral anions
Group 1 metals Group 2 metals Metals with a +1 charge	Cl^- Br^- I^- NO_3^- ClO_4^- ClO_3^-

Neutralizing Salts

Are the following salts ***acidic***, ***basic***, ***neutral?***

$NH_4I \rightarrow NH_4^+ + \cancel{I^-}$ (acidic)

$NaNO_3 \rightarrow \cancel{Na^+} + \cancel{NO_3^-}$ (neutral)

$KF \rightarrow \cancel{K^+} + F^-$ (basic)

$ZnCl_2 \rightleftharpoons Zn^{2+} + 2\,\cancel{Cl^-}$ (acidic)

$Al(NO_3)_3 \rightarrow Al^{+3} + 3\,\cancel{NO_3^-}$ (acidic)

Neutral cations

Group 1 metals
Group 2 metals
Metals with a +1 charge

Neutral anions

Cl^-	Br^-
I^-	NO_3^-
ClO_4^-	ClO_3^-

cations ≈ acids

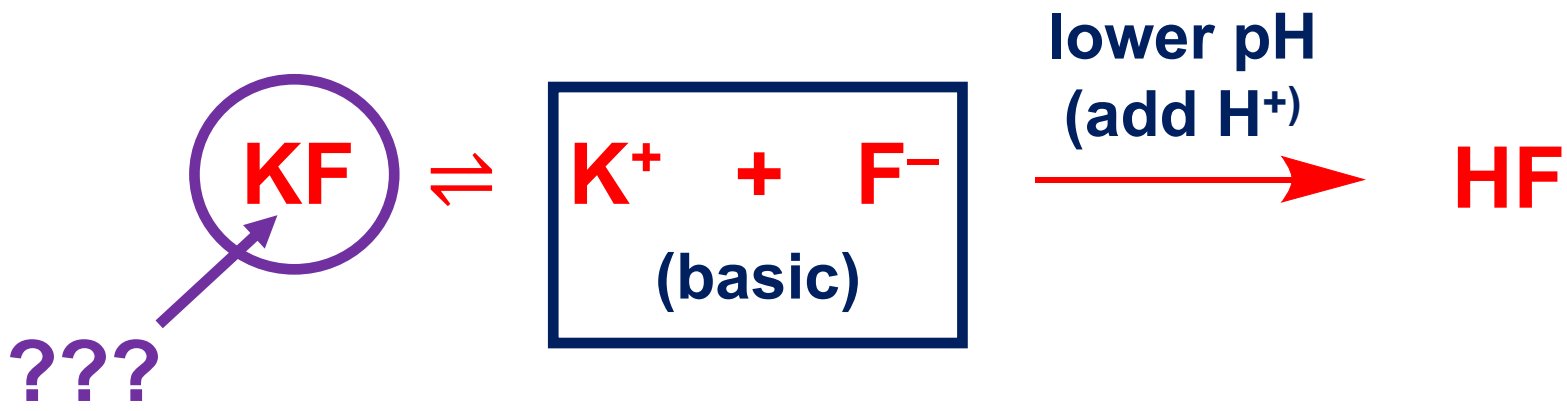
anions ≈ bases

(exception: HSO_4^-)

pH and Solubility

When a *non-neutral salt* is formed, changing the ***pH*** can increase or decrease the salt's solubility:

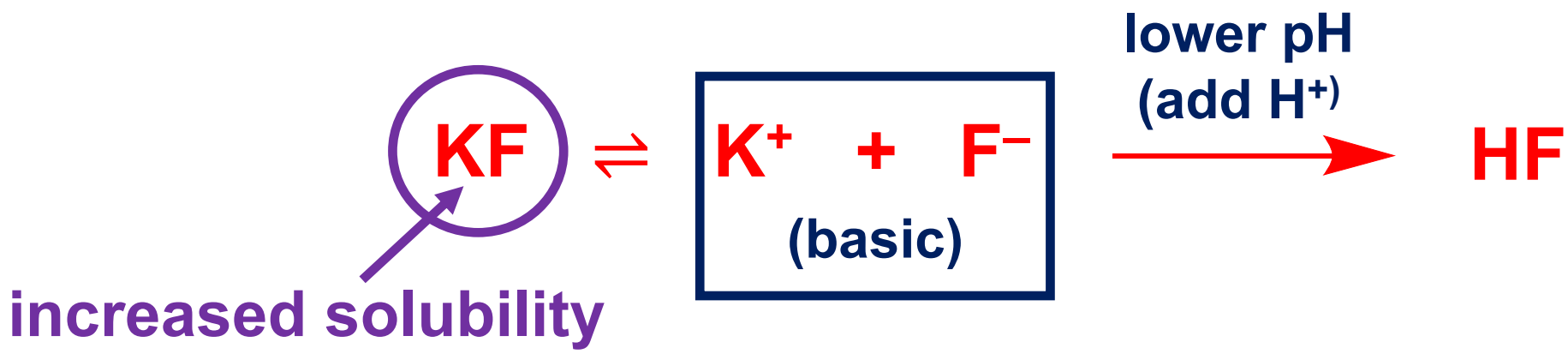
- If the salt forms a *basic* anion, then adding acid (lowering ***pH***) will increase solubility, because adding acid will syphon off the basic anion:



pH and Solubility

When a *non-neutral salt* is formed, changing the ***pH*** can increase or decrease the salt's solubility:

- If the salt forms a *basic* anion, then adding acid (lowering ***pH***) will increase solubility, because adding acid will syphon off the basic anion:



pH and Solubility

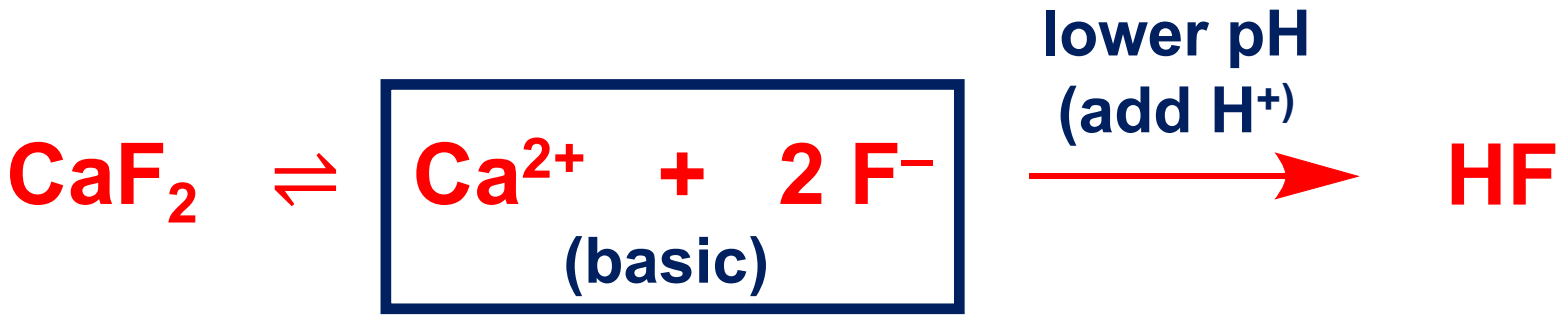
When a *non-neutral salt* is formed, changing the ***pH*** can increase or decrease the salt's solubility:

- If the salt forms a *basic* anion, then adding acid (lowering ***pH***) will increase solubility, because adding acid will syphon off the basic anion.

- For salts that form *acidic* cations, removing acid (increasing ***pH***) increases solubility, because removing acid syphons off the acidic cation.

Questions

In considering the following reaction:



. . . What could you add to increase the solubility of CaF_2? Why?

Questions

Which of the following could you add to increase the solubility of CaF_2?

~~A~~. $Ca(OH)_2$ **basic**

~~B~~. $NaNO_3$ **neutral**

~~C~~. KF **basic**

D. HCl **acidic**

~~E~~. KNO_3 **neutral**

$$CaF_2 \rightleftharpoons \underbrace{Ca^{2+} + 2\,F^-}_{\text{(basic)}} \xrightarrow[\text{(add } H^+\text{)}]{\text{lower pH}} HF$$

Questions

Which of the following could you add to increase the solubility of CaF_2?

A. $Ca(OH)_2$

B. $NaNO_3$

C. KF

D. HCl

E. KNO_3

Questions

Which of the following could you add to increase the solubility of NH_4Cl?

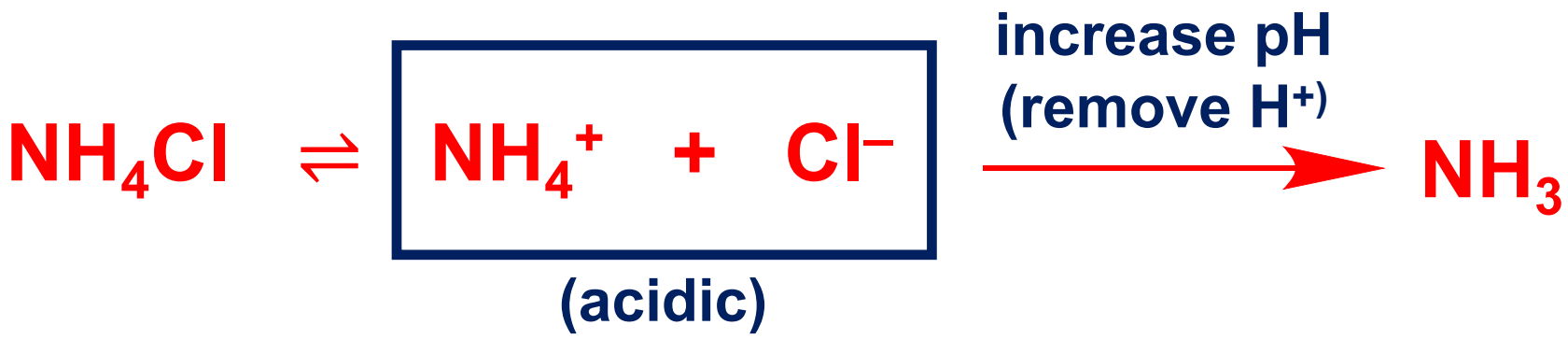
A. $Ca(OH)_2$ **basic**

~~B~~. $NaNO_3$ **neutral**

C. KF **basic**

~~D~~. HCl **acidic**

~~E~~. KNO_3 **neutral**



Questions

Which of the following could you add to increase the solubility of **NH_4Cl**?

A. $Ca(OH)_2$

B. $NaNO_3$

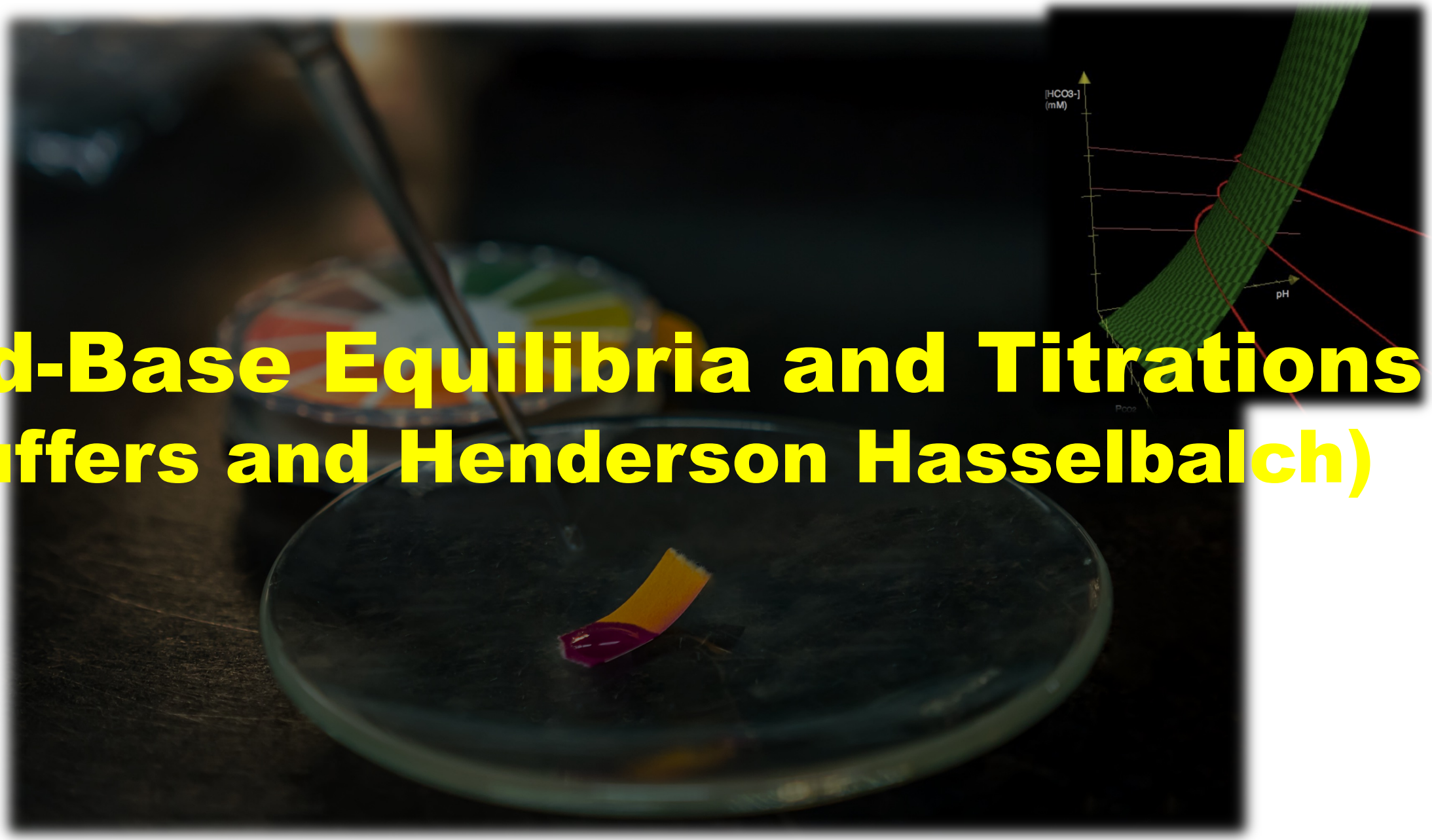
C. KF

D. HCl

E. KNO_3

Take-Homes

- Basic salts' solubilities *increase* by adding acid.
- Acidic salts' solubilities *increase* by adding base.



Acid-Base Equilibria and Titrations (Buffers and Henderson Hasselbalch)

What is a Buffer?

A ***buffer*** is a solution that resists ***pH*** change. ***Buffers*** are made by combining a ***weak acid*** with its ***conjugate base***.

For example, **CH_3COOH** (acetic acid) is a weak acid. **CH_3COO^-** (acetate) is its conjugate base. Thus, if you combine **CH_3COOH** and **CH_3COO^-**, you will form a ***buffer***.

Note: in real life, **CH_3COO^-** does not exist by itself. Instead, it must be paired with a metal ion, like **Na^+**. So an exam question will give you **$NaCH_3COO$**, and you will have to know it just means **CH_3COO^-**. **Na^+** is a spectator ion.

Preparing a Buffer (Method 1)

There are two methods of preparing a buffer. In **Method 1**, you mix a 1:1 ratio of a ***weak acid*** and its ***conjugate base*** or a 1:1 ratio of a ***weak base*** with its ***conjugate acid***.

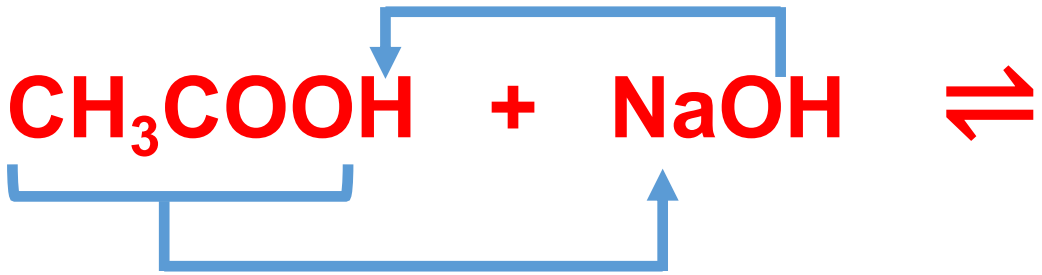
We never use a strong acid or a strong base in a buffer, except in the specific way described in Method 2.

Weak acid + its conjugate base = acidic pH

Weak base + its conjugate acid = basic pH

Preparing a Buffer (Method 2)

In **Method 2**, you prepare a buffer by mixing a ***weak acid*** and a *strong* base in a 2:1 ratio:



Preparing a Buffer (Method 2)

In **Method 2**, you prepare a buffer by mixing a ***weak acid*** and a *strong* base in a 2:1 ratio:

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + HOH$$

weak acid — ***conjugate base***

Preparing a Buffer (Method 2)

In **Method 2**, you prepare a buffer by mixing a ***weak acid*** and a *strong* base in a 2:1 ratio:

$$2\,CH_3COOH + 1\,NaOH \rightleftharpoons CH_3COO^- + HOH$$

weak acid ***conjugate base***

The reason is because with this ratio, the **NaOH** gets consumed and leaves behind a 1:1 ratio of **CH_3COOH** and **CH_3COO^-**. In other words, the **NaOH** ends up converting *half* of our weak acid into its ***conjugate base***, while leaving the *other* half as a weak acid. This is a 1:1 ratio of weak acid and its conjugate base, the same results of **Method 1**.

The Henderson Hasselbalch Equation

The most straightforward way of calculating the ***pH*** of a buffered (weak acid/conjugate base) system is to use the ***Henderson Hasselbalch equation***:

$$pH = pK_A \frac{[\text{conj. base}]}{[\text{weak acid}]}$$

The Henderson Hasselbalch Equation

The most straightforward way of calculating the ***pH*** of a buffered (weak acid/conjugate base) system is to use the ***Henderson Hasselbalch equation***:

$$pH = pK_A + \log \frac{[A^-]}{[HA]}$$

$$HA \rightleftharpoons A^- + HA$$

For a traditional ***buffer*** system, where A^- : **HA** is **1:1**, the **log $[A^-]/[HA]$ = log 1/1 = log 1 = 0**. In this situation, ***pH*** = pK_A.

The Henderson Hasselbalch Equation

Knowing that ***pH*** = ***pK_A*** for traditional ***buffers*** with a **1:1** conjugate-base:weak-acid ratio can help us identify which acid would be a useful buffer for a specific, target ***pH***. For example:

Acid

The Henderson Hasselbalch Equation

Knowing that ***pH*** = ***pK_A*** for traditional ***buffers*** with a **1:1** conjugate-base:weak-acid ratio can help us identify which acid would be a useful buffer for a specific, target ***pH***. For example:

Acid
CH_3CH_2COOH

Buffers work within a ±1 range around the target ***pH***. Thus, an acetic acid/acetate ***buffer*** would have a ***pH*** range of **3.9** to **5.9**.

Question

Please identify the missing ***pK_A*** values. Then determine which of the listed acids could be used to prepare a buffer with a ***pH*** of 9.0.

Acid	K_A	pK_A
CH_3CH_2COOH	1.3×10^{-5}	4.9

The Henderson Hasselbalch Equation

Knowing that ***pH*** = ***pK_A*** for traditional ***buffers*** with a **1:1** conjugate-base:weak-acid ratio can help us identify which acid would be a useful buffer for a specific, target ***pH***. For example:

Acid		
CH_3CH_2COOH	1.3×10^{-5}	4.9
HCOOH	1.8×10^{-4}	3.7
HNO_2	4.0×10^{-4}	3.4
HCN	6.0×10^{-10}	9.2

Buffers work within a ±1 range around the target ***pH***. Thus, an acetic acid/acetate ***buffer*** would have a ***pH*** range of **3.9** to **5.9**.

Question

Please identify the missing ***pK_A*** values. Then determine which of the listed acids could be used to prepare a buffer with a ***pH*** of 9.0.

Acid	K_A	pK_A
CH_3CH_2COOH	1.3×10^{-5}	4.9
$HCOOH$	1.8×10^{-4}	
HNO_2	4.0×10^{-4}	
HCN	6.0×10^{-10}	

Questions

Which of the following substances could be combined to form a buffer solution?

A. KI, HI

B. KBr, HBr

C. CuCl, HCl

D. NaI, HI

E. $NaCH_3COO$, CH_3COOH

Questions

Which of the following substances could be combined to form a buffer solution?

X A. I^-, HI

X B. Br^-, HBr

X C. Cl^-, HCl

X D. I^-, HI

E. CH_3COO^-, CH_3COOH

Remember: A standard buffer has a 1:1 mixture of a ***weak acid*** and its ***conjugate base***. *Strong* acids cannot be used to prepare ***buffers***.

Questions

HF has a pK_A of **3.2**. What is the *pH* of a solution comprised of 0.1 M HF and 0.1 M NaF?

This is a buffered solution of a weak acid, **HF**, and its conjugate base, F^-.

$$pH = pK_A + \log \frac{[\text{conj. base}]}{[\text{weak acid}]}$$

Questions

HF has a pK_A of **3.2**. What is the *pH* of a solution comprised of 0.1 M HF and 0.1 M NaF?

This is a buffered solution of a weak acid, **HF**, and its conjugate base, F^-.

$$pH = pK_A + 0$$

Questions

HF has a pK_A of **3.2**. What is the ***pH*** of a solution comprised of 0.1 M HF and 0.1 M NaF?

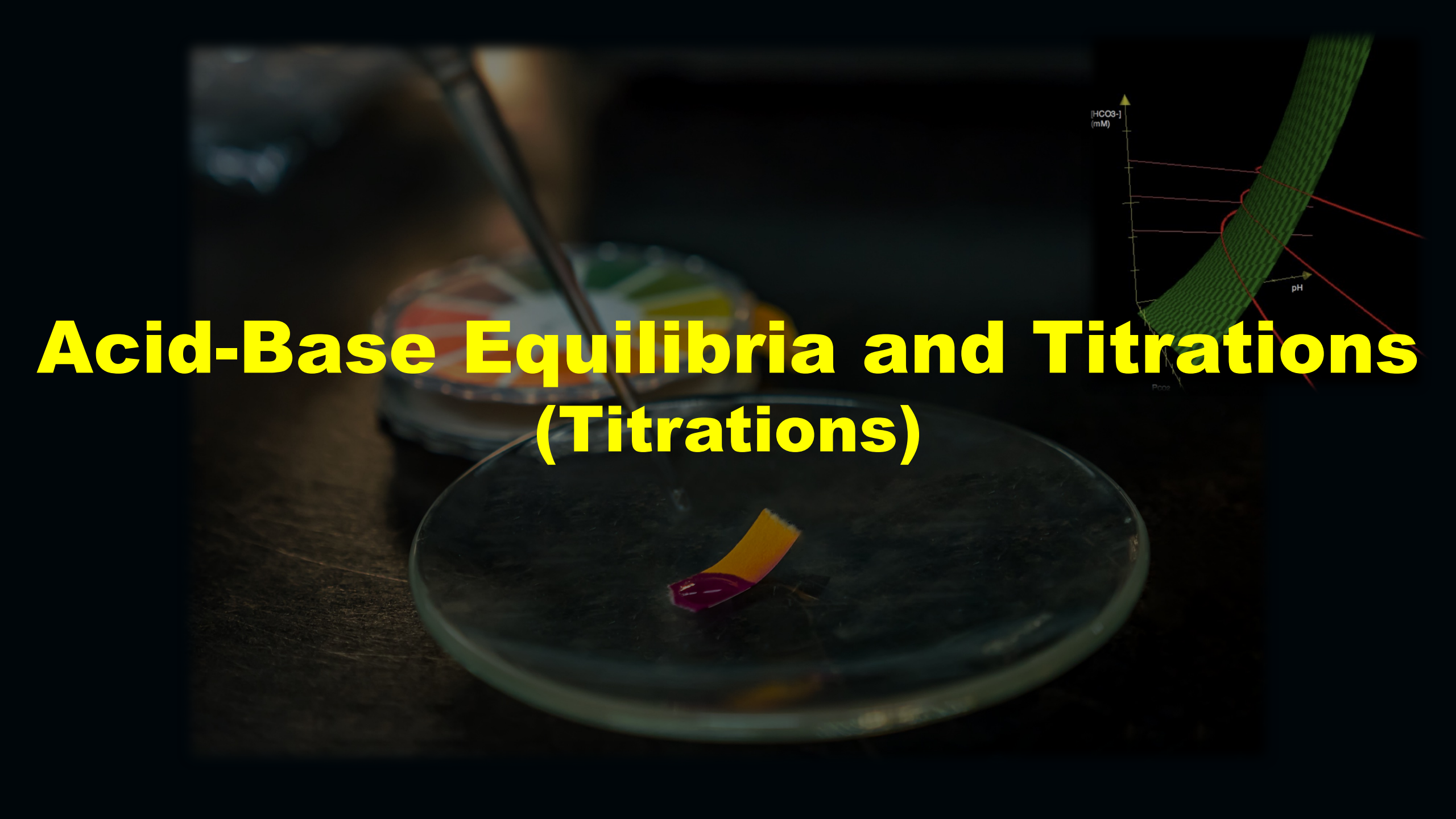
This is a buffered solution of a weak acid, **HF**, and its conjugate base, F^-.

pH **=** **3.2**

Questions

What is the pH of a solution comprised of 1.0 M HF (pK_A = **3.2**) and 0.1 M NaF?

What is the pH of a solution comprised of 0.1 M HF (pK_A = **3.2**) and 10 M NaF?



Acid-Base Equilibria and Titrations (Titrations)

What is a Titration?

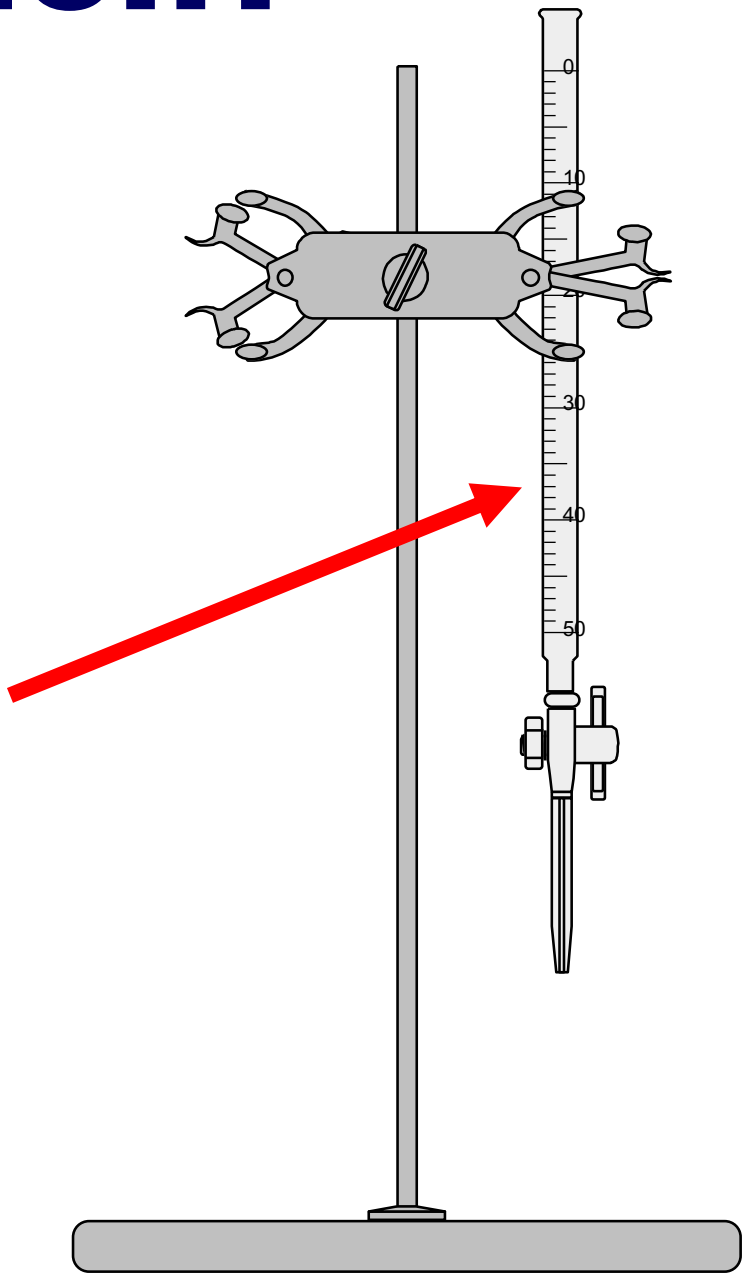
I want you to imagine that you are given the responsibility of determining the concentration of a specific strong acid in local groundwater. How could you do that?

One way might be to prepare a solution of base with a known concentration. You could then gradually combine this basic solution with a sample of groundwater until the ***pH*** is neutral. At that point (called the ***equivalence point***), moles of strong base = moles of strong acid. Because you know the concentration of your basic solution, you can calculate the concentration of strong acid in your groundwater sample.

This technique is called a ***titration***.

What is a Titration?

In a ***titration***, a solution of known concentration is placed inside a piece of glassware called a burette. This known solution is called the ***titrant***.

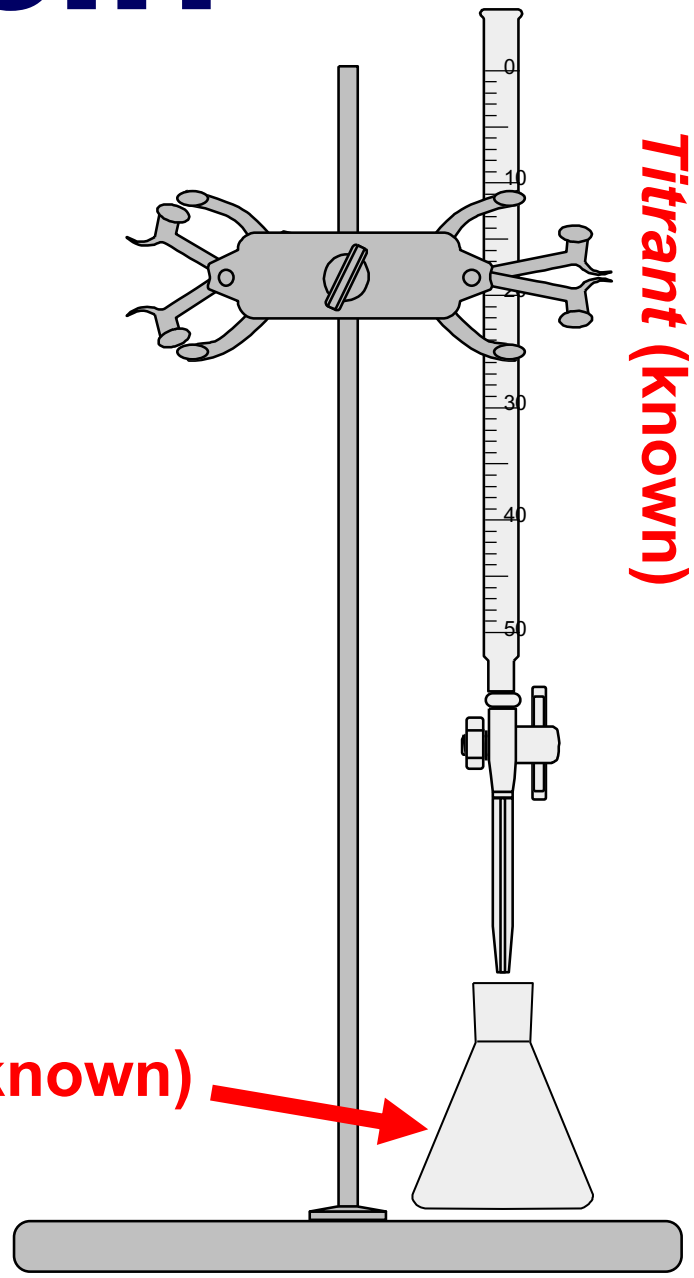


What is a Titration?

The unknown solution, called the ***titrand***, is then placed in an Erlenmeyer flask beneath the burette.

The known ***titrant*** is now added slowly to the ***titrand*** until a visible change (usually a color change) occurs.

By knowing the concentration of the known ***titrant*** and the volume that we added, we can calculate the concentration of the unknown ***titrand***.



Titration Curves

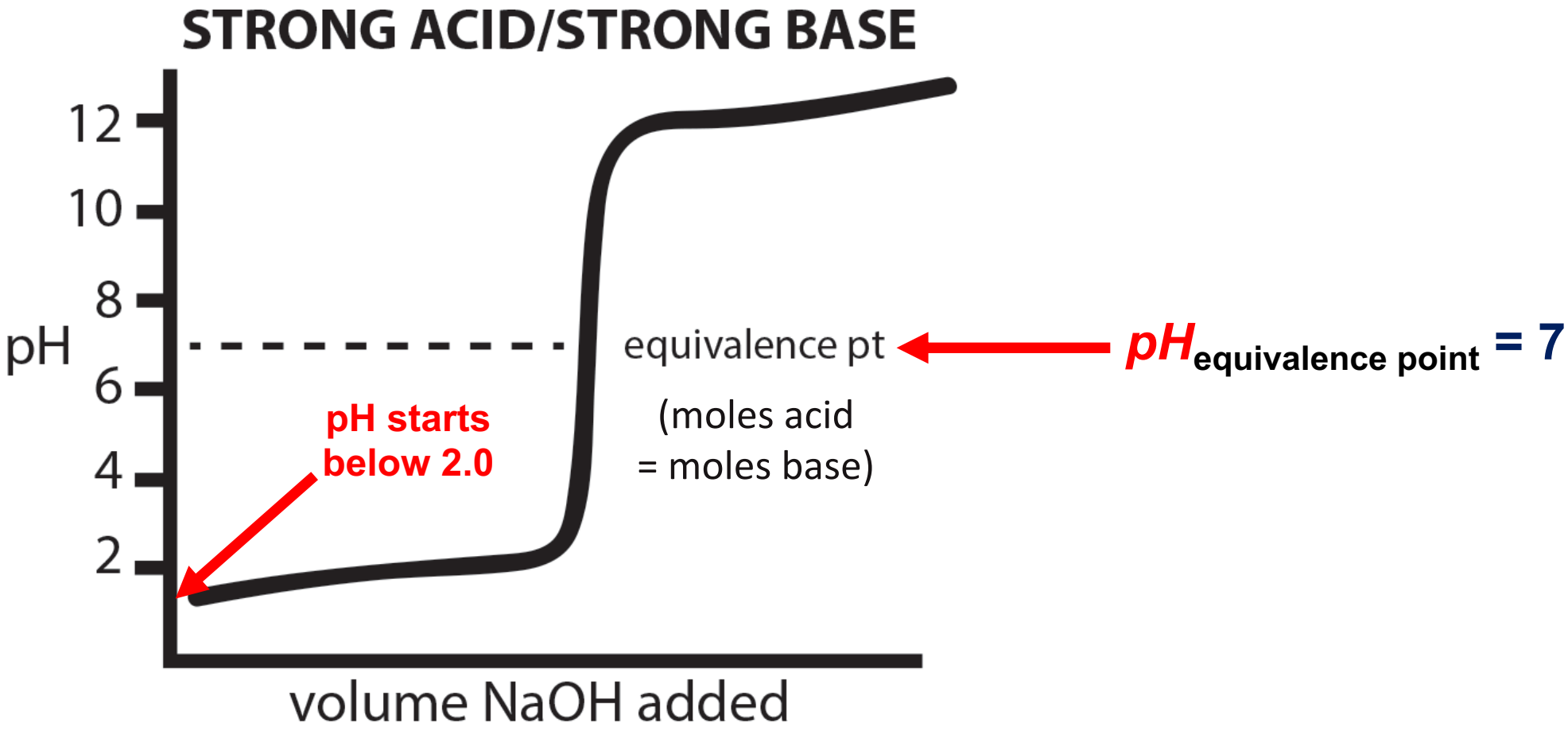
We can make a graph of how the ***titrand***'s ***pH*** changes when ***titrant*** is added. This graph is called a ***titration curve***. For the EXAM, you should *definitely* remember the following:

- Strong Acid/ Strong Base: $pH_{\text{equivalence point}} = 7$
- Weak Acid/ Strong Base: $pH_{\text{equivalence point}} > 7$
- Weak Base / Strong Acid: $pH_{\text{equivalence point}} < 7$

You should also definitely be able to identify what kind of titration you have (strong acid/strong base, weak acid/strong base, or weak base/strong acid) by noting the appearance of its ***titration curve***.

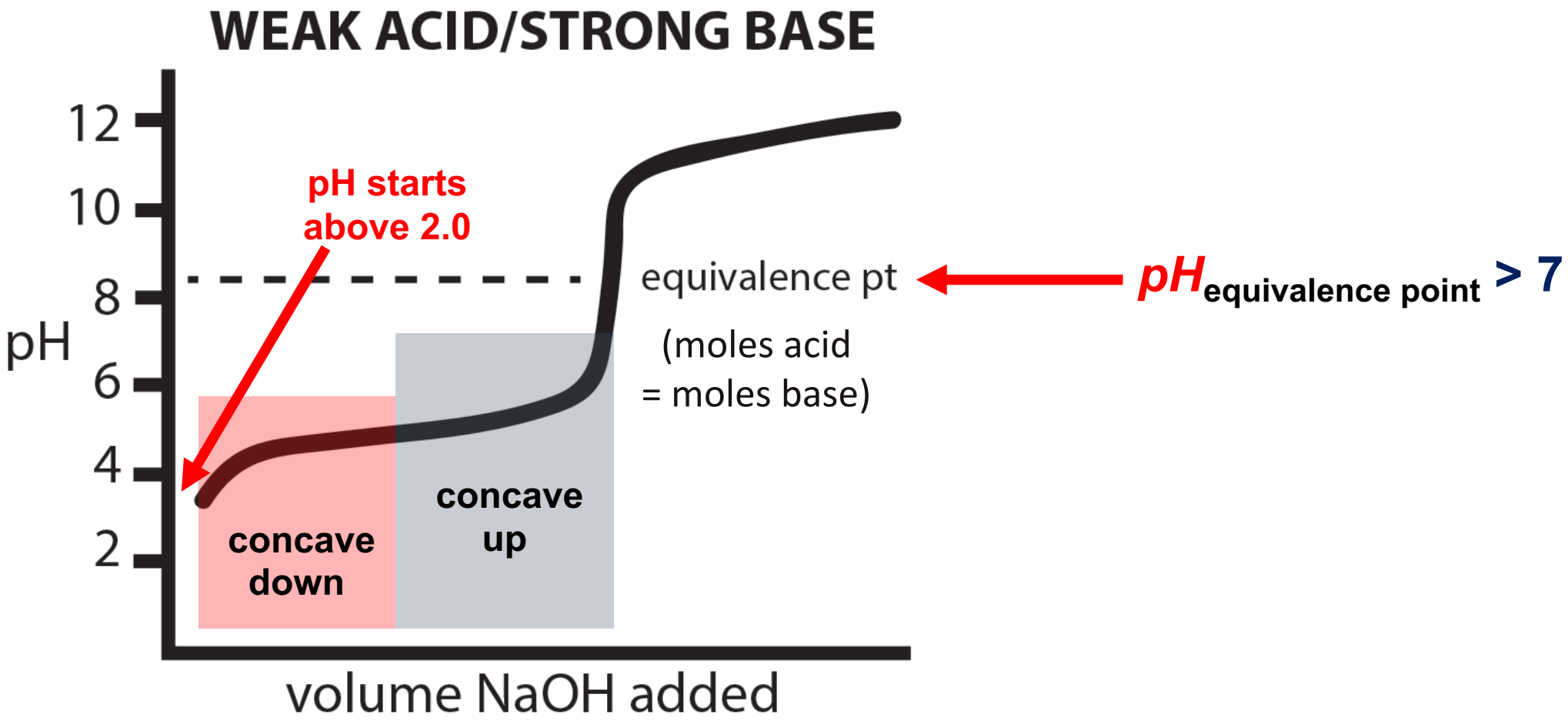
Strong Acid/Strong Base

This is what a ***titration curve*** of a strong acid titrated with a strong base:



Weak Acid/Strong Base

This is what a ***titration curve*** of a weak acid titrated with a strong base:



$pH_{\text{equivalence point}} > 7$

Why?

Before I go on, you might be wondering, “Why does a weak-acid titration’s equivalence point happen *above* pH 7.0?” The reason is that weak acids dissociate to form ***conjugate bases,*** which are . . . Basic. For example:

$$CH_3COOH + NaOH \rightleftharpoons HOH + CH_3COO^-$$

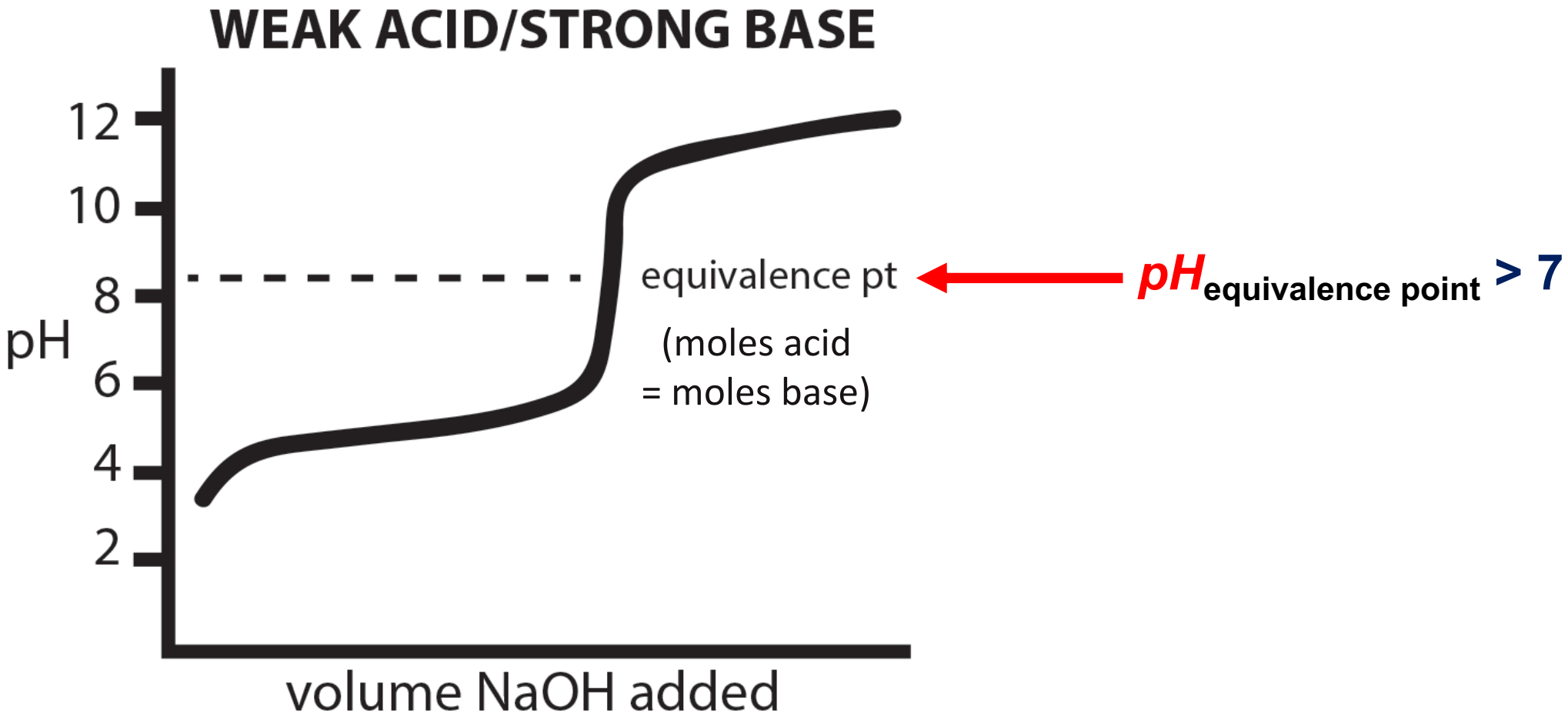
weak acid

conjugate base
(raises pH)

Thus, when a weak acid is titrated (reacted) with a strong base, the strong base neutralizes the *acidic* portion of the molecule, while freeing its ***conjugate base.*** That ***conjugate base*** increases the ***pH*** of the resulting solution.

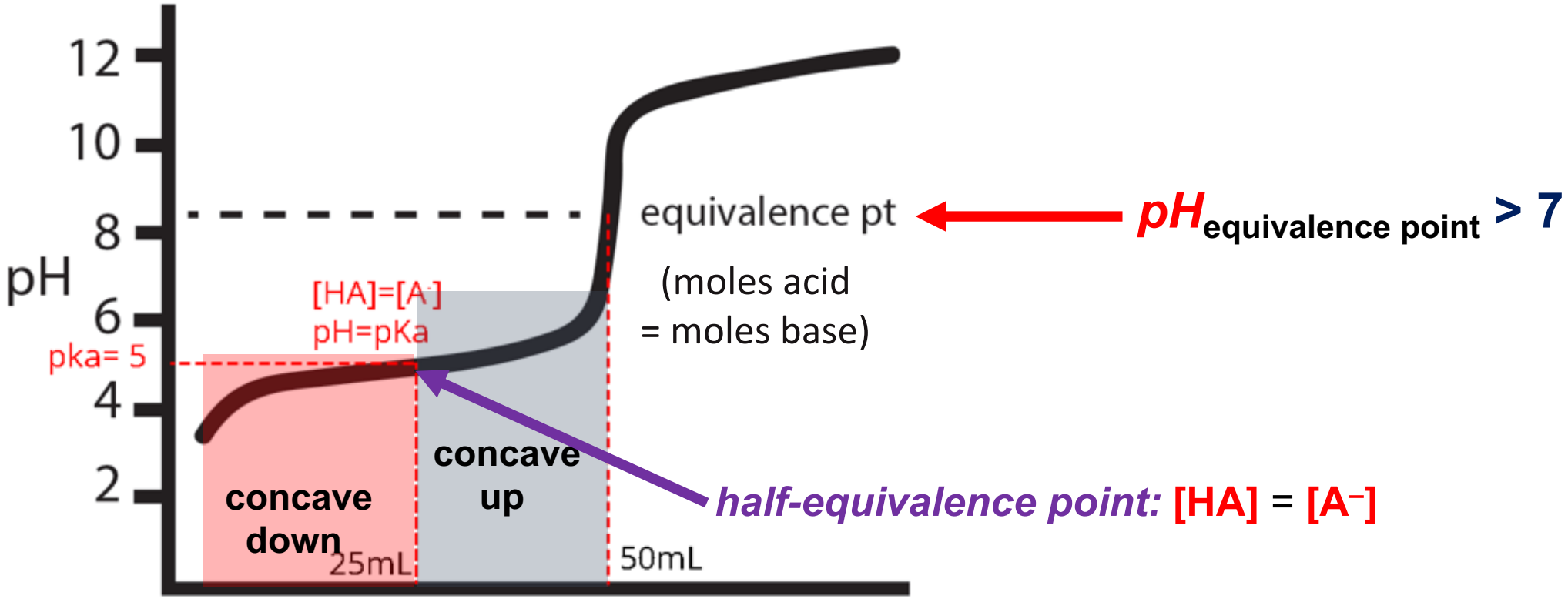
Weak Acid/Strong Base

This is why a weak acid/strong base ***titration curve*** has an equivalence point ***pH*** above **7.0**.



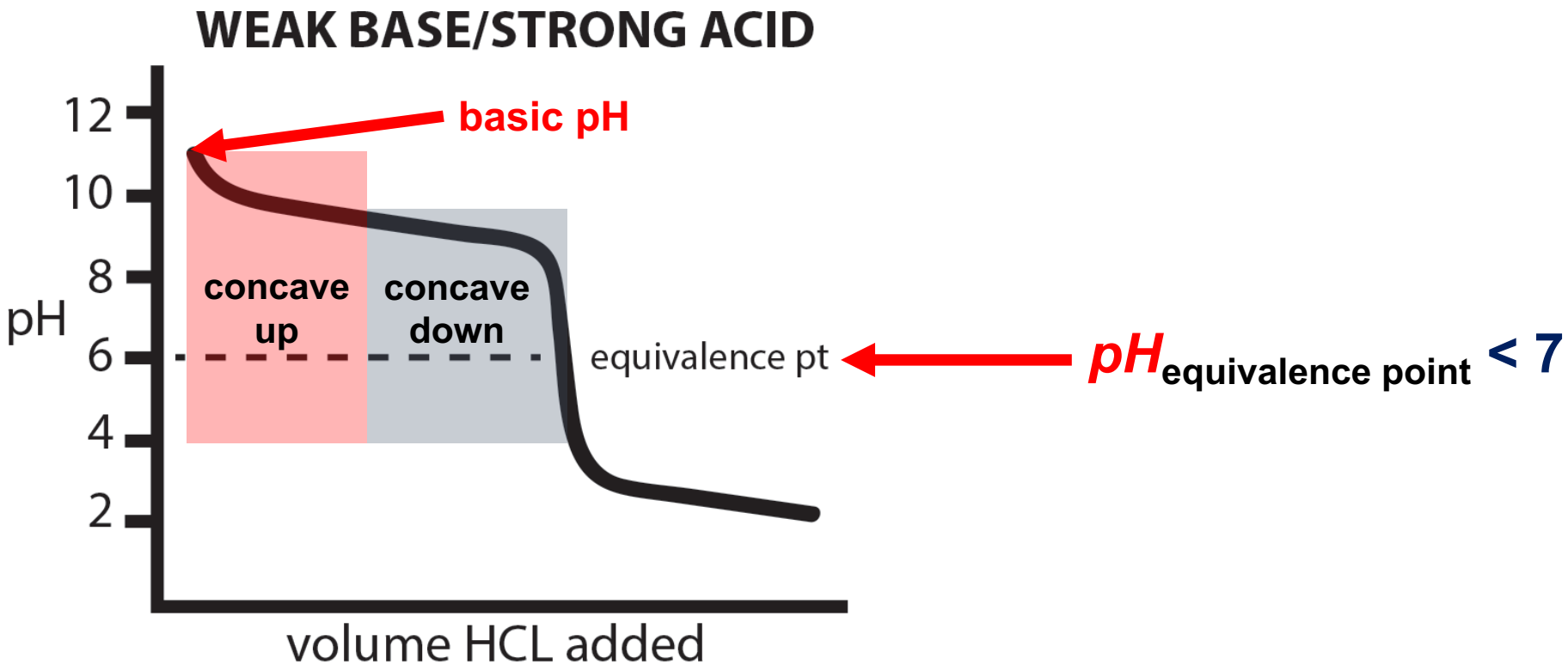
Weak Acid/Strong Base

Just so you know, the inflection point that separates the concave-down and concave-up sections of the curve indicates this weak acid's pK_A. This occurs when **[HA] = [A⁻]**. This place is called the ***half-equivalence point***.



Weak Base/Strong Acid

Similar logic explains the ***titration curve*** of a weak base titrated with a strong acid. The weak base's conjugate acid is acidic, which makes the equivalence point pH below 7.0.



Titration Curves

Please remember:

- Strong Acid/ Strong Base: $pH_{\text{equivalence point}} = 7$
- Weak Acid/ Strong Base: $pH_{\text{equivalence point}} > 7$
- Weak Base / Strong Acid: $pH_{\text{equivalence point}} < 7$

. . . And please make sure you can identify what kind of titration you have (strong acid/strong base, weak acid/strong base, or weak base/strong acid) by noting the appearance of its ***titration curve***.

Polyprotic Titrations

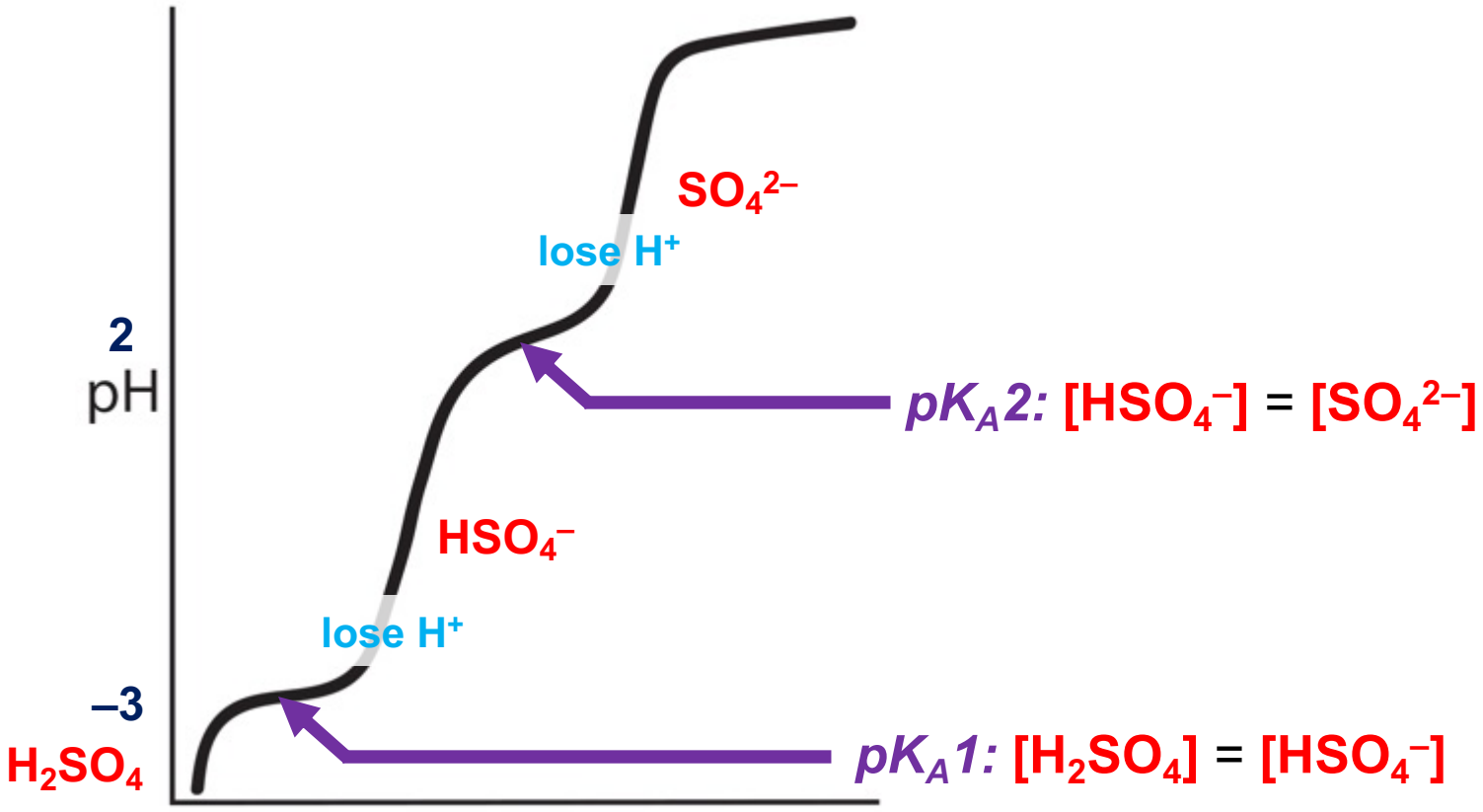
As we've discussed before, acids with multiple acidic H^+ (***proton***) groups are called ***polyprotic acids***. For example, H_2SO_4 is diprotic because it has *two* acidic hydrogen atoms:

$$H_2SO_4 \rightarrow H^+ + HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

Polyprotic acids, then, give multiple H^+'s. As a result, they actually have two pK_A values: pK_A1 and pK_A2.

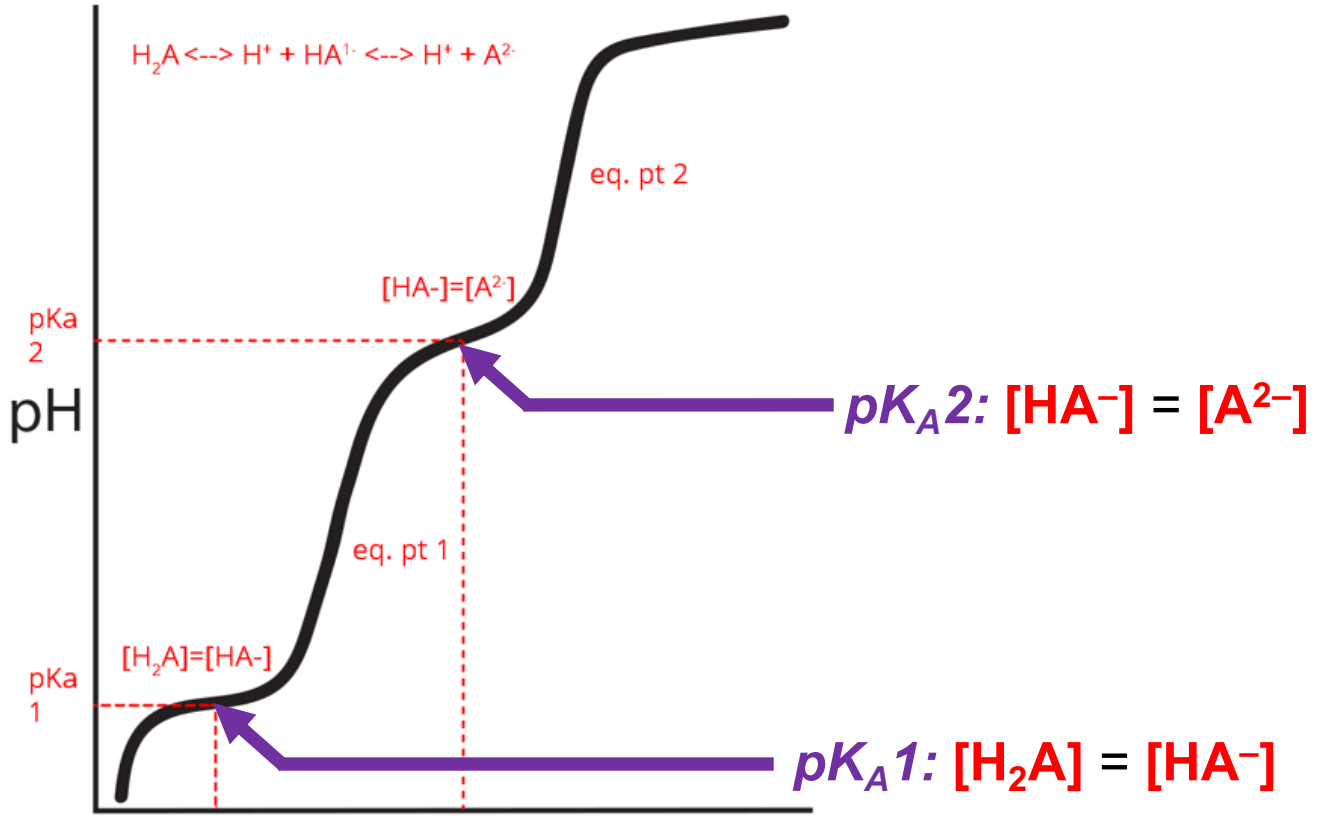
Polyprotic Titrations

$$H_2SO_4 \rightarrow H^+ + HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$



Polyprotic Titrations

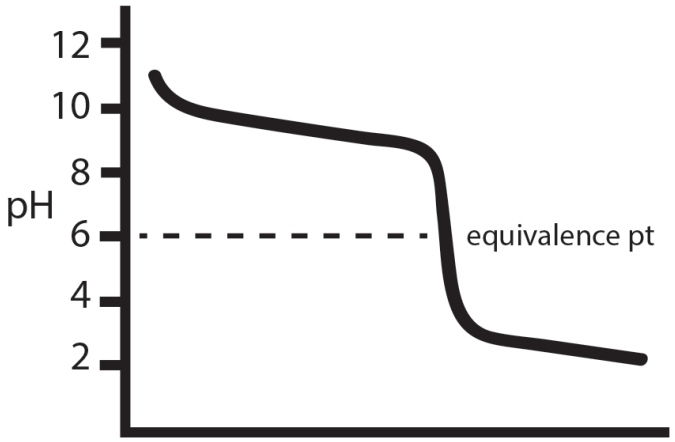
$$H_2A \rightarrow H^+ + HA^- \rightleftharpoons H^+ + A^{2-}$$

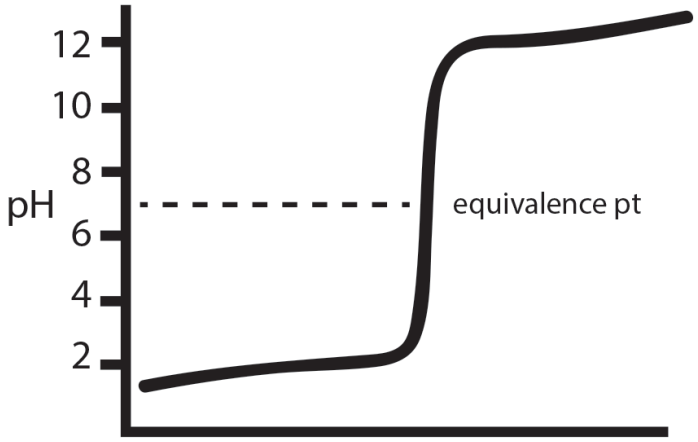


Questions

Please identify each of the ***titration curves*** below as: ***weak acid/strong base***, ***strong acid/strong base***, or ***weak base/strong acid***.

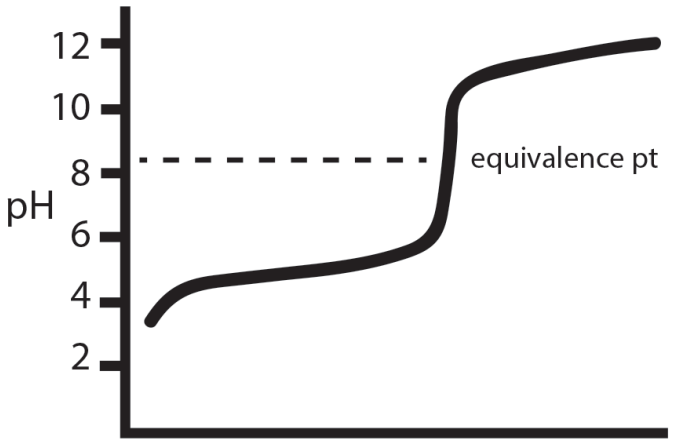
weak base/strong acid





strong acid/strong base

weak acid/strong base



Questions

What will the ***pH*** at equivalence point be for each of the following titrations?

A. $HCl + NaOH$

B. $HF + NaOH$

C. $NH_3 + HCl$

Questions

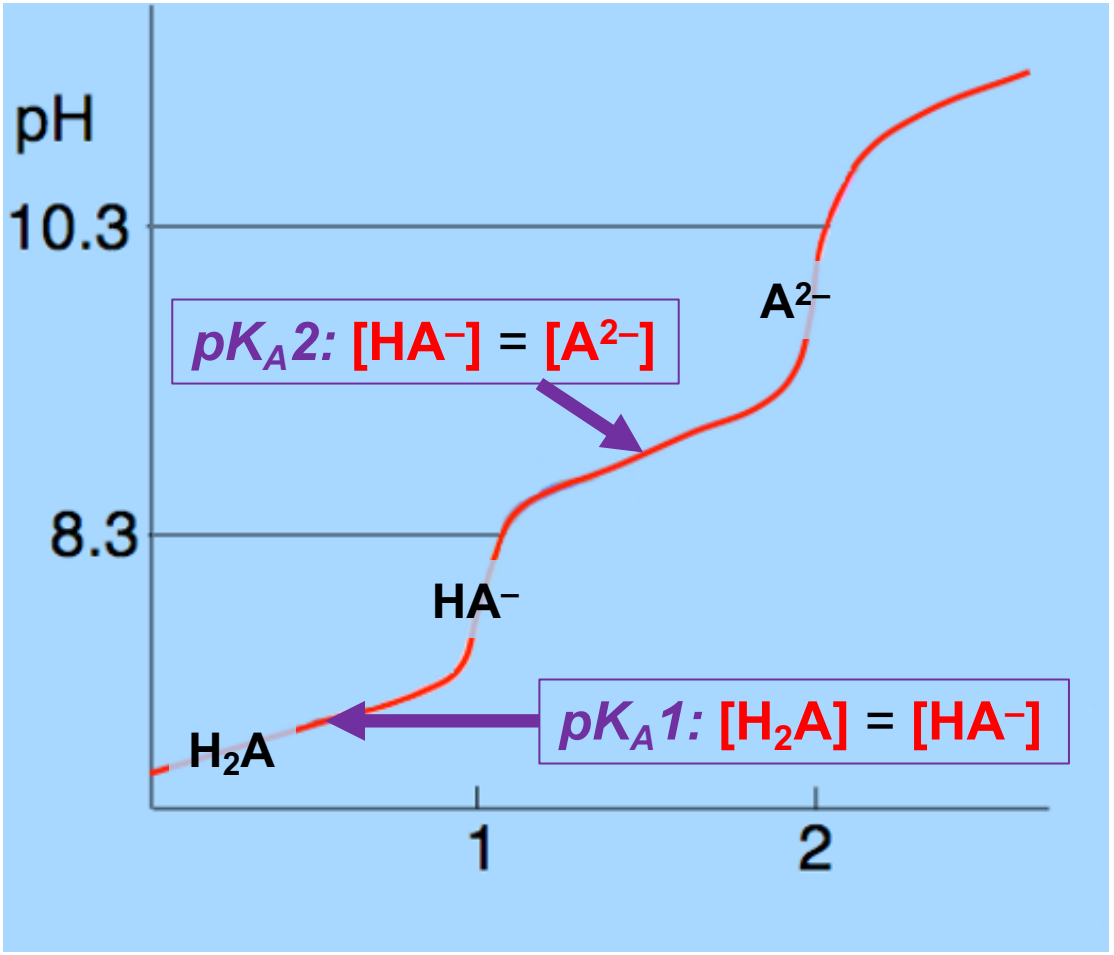
For a generic ***diprotic acid*** H_2A, whose titration curve is shown here:

- What are the values of pK_A1 and pK_A2?

  Happen at plateaus, not inclines.

  $pK_A1 \approx 7.0$ $pK_A2 \approx 9.0$

- Which molecule predominates:
  - When $pH < pK_A1$? H_2A
  - When $pK_A1 < pH < pK_A2$? HA^-
  - When $pH > pK_A2$? A^{2-}



$H_2A \rightarrow H^+ + HA^- \rightleftharpoons H^+ + A^{2-}$