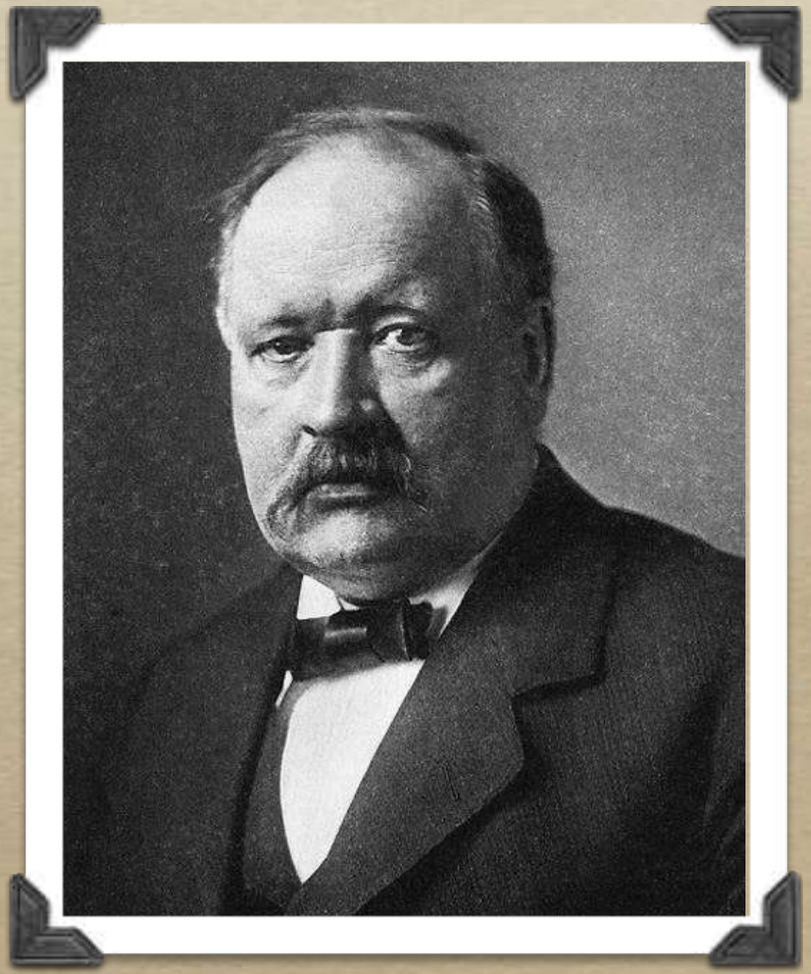
acids and bases

10/75

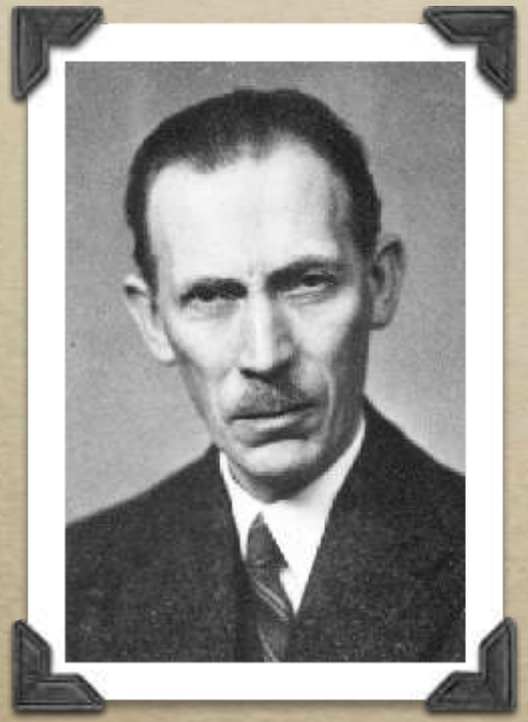
definitions

- ***Arrhenius*** *defined acids and bases*
- *an* ***acid*** *produces hydrogen ions (H^+) and a* ***base*** *produces hydroxide ions(OH^-)*
- *(working with acids made him sour)*

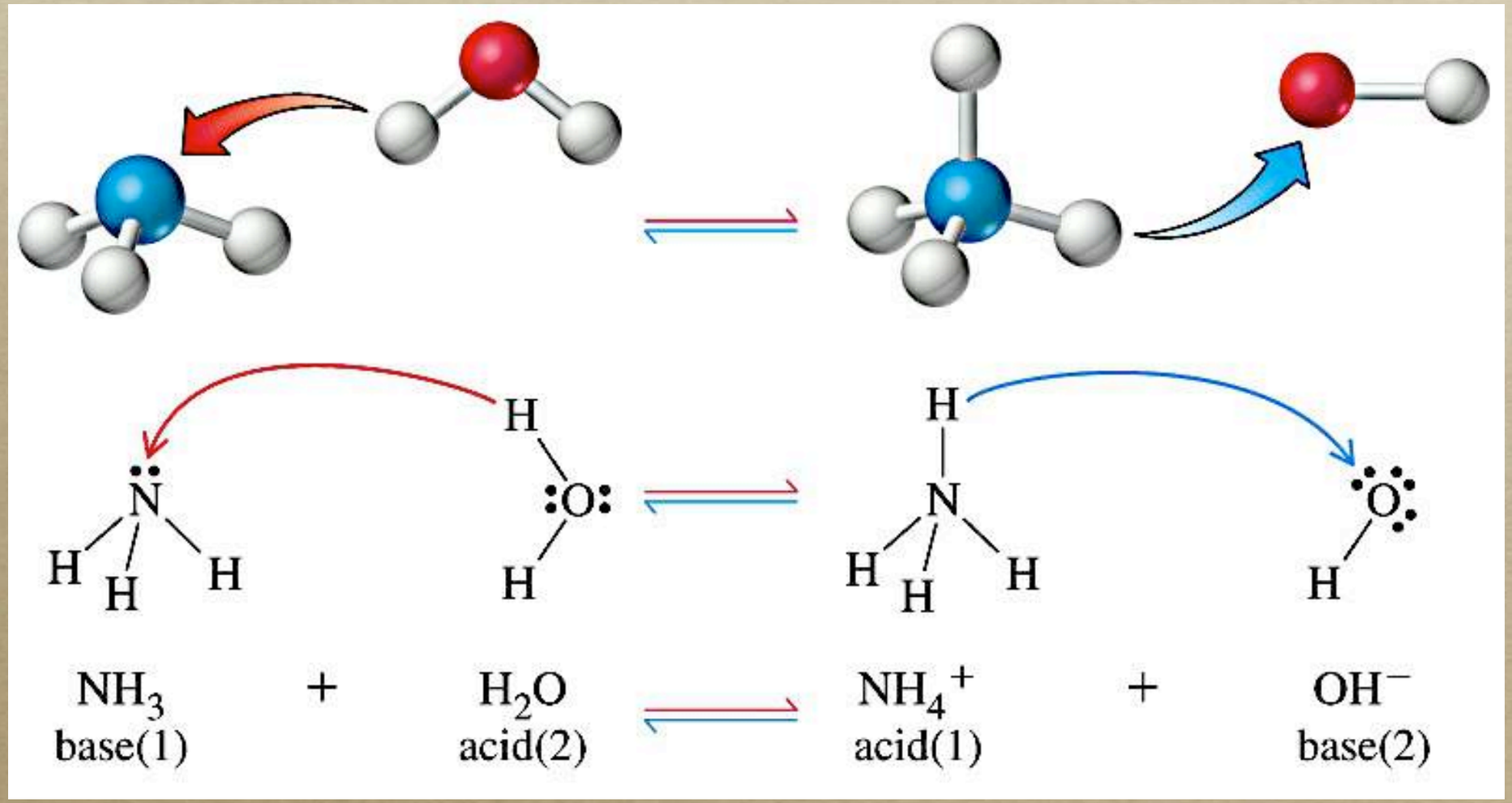


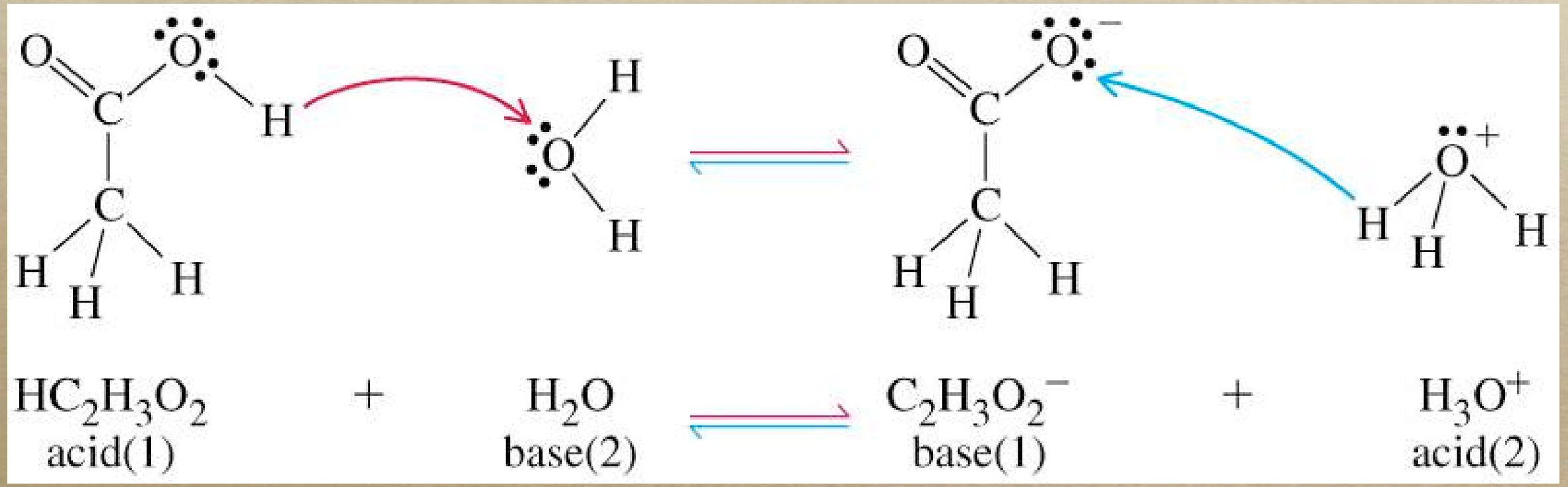
brØnsted-lowry

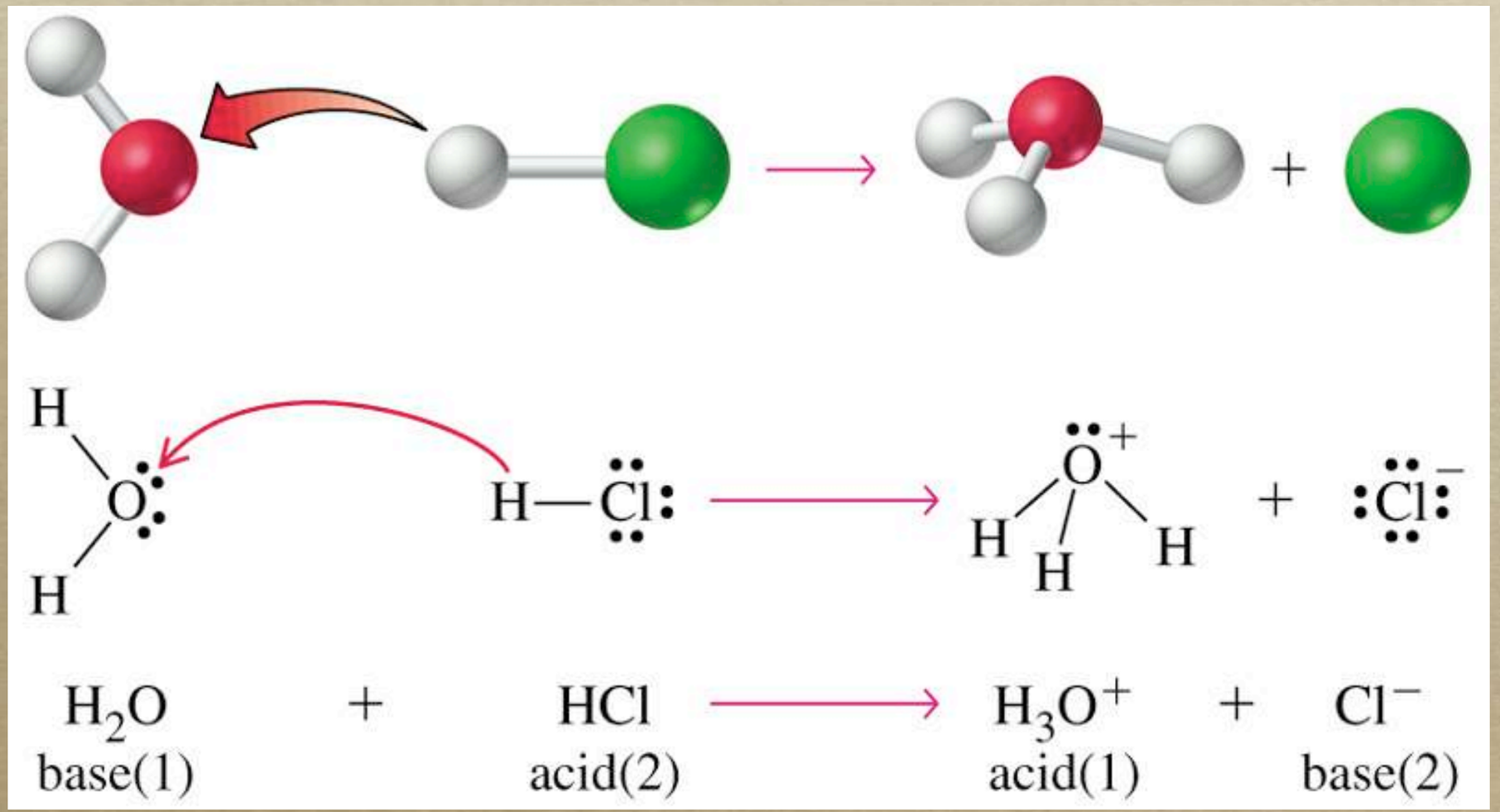
- *these guys made it easier:*
- *an **acid** is a proton (H^+) **donator***
- *a **base** is a proton **acceptor***
- *(working with acids made them sour)*

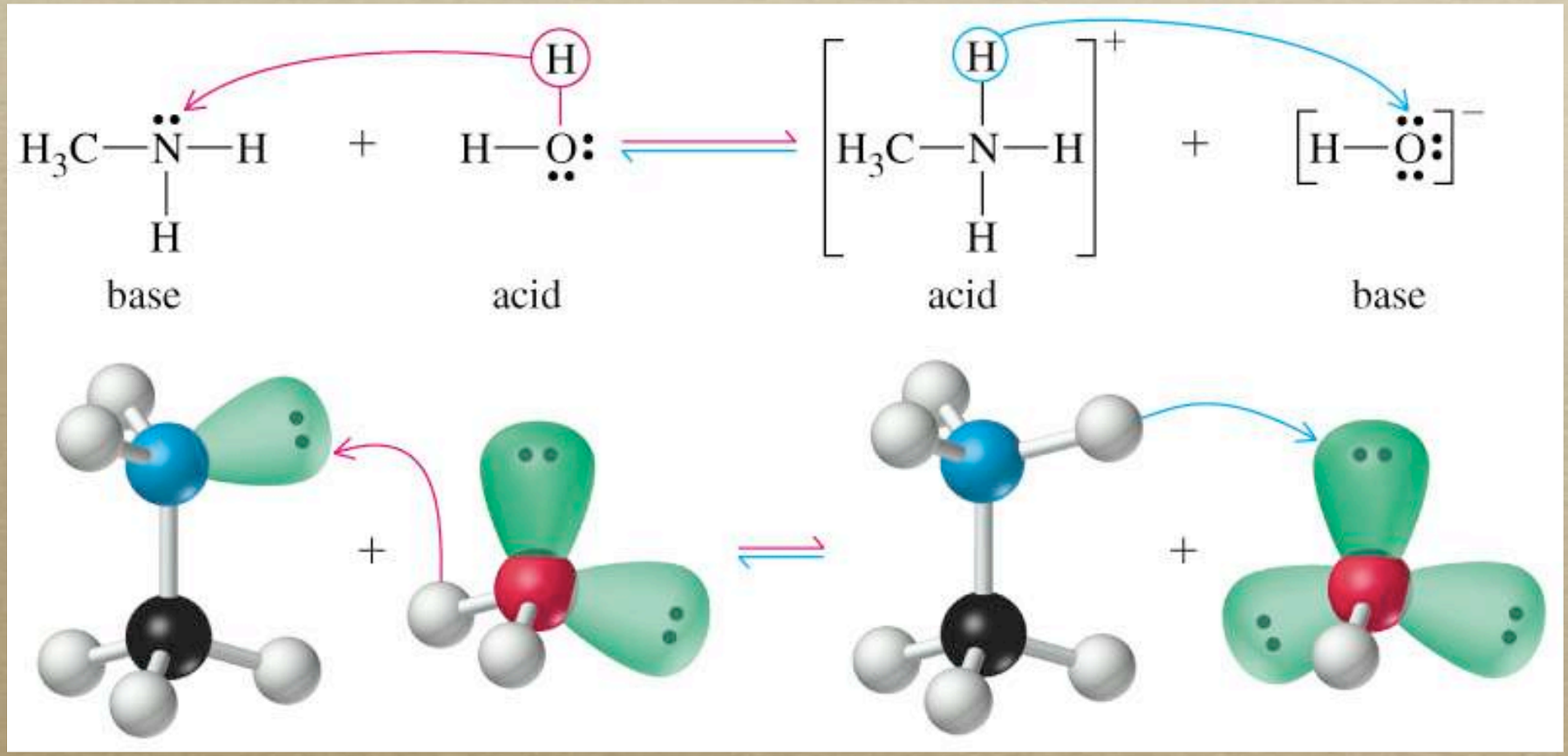


- $\mathbf{HC_2H_3O_2 + H_2O \rightleftharpoons C_2H_3O_2^- + H_3O^+}$
- *acetic acid and hydronium ion are* ***acids***
- *water and acetate ion are* ***bases***
- *the acetic acid/acetate ion pair are* ***conjugate pairs****; they differ by one proton*
- *so are water and hydronium ion*


NH3
base(1)
+
H2O
acid(2)
NH4+
acid(1)
+
OH−
base(2)


$HC_2H_3O_2$
acid(1)
+
H_2O
base(2)
$C_2H_3O_2^-$
base(1)
+
H_3O^+
acid(2)

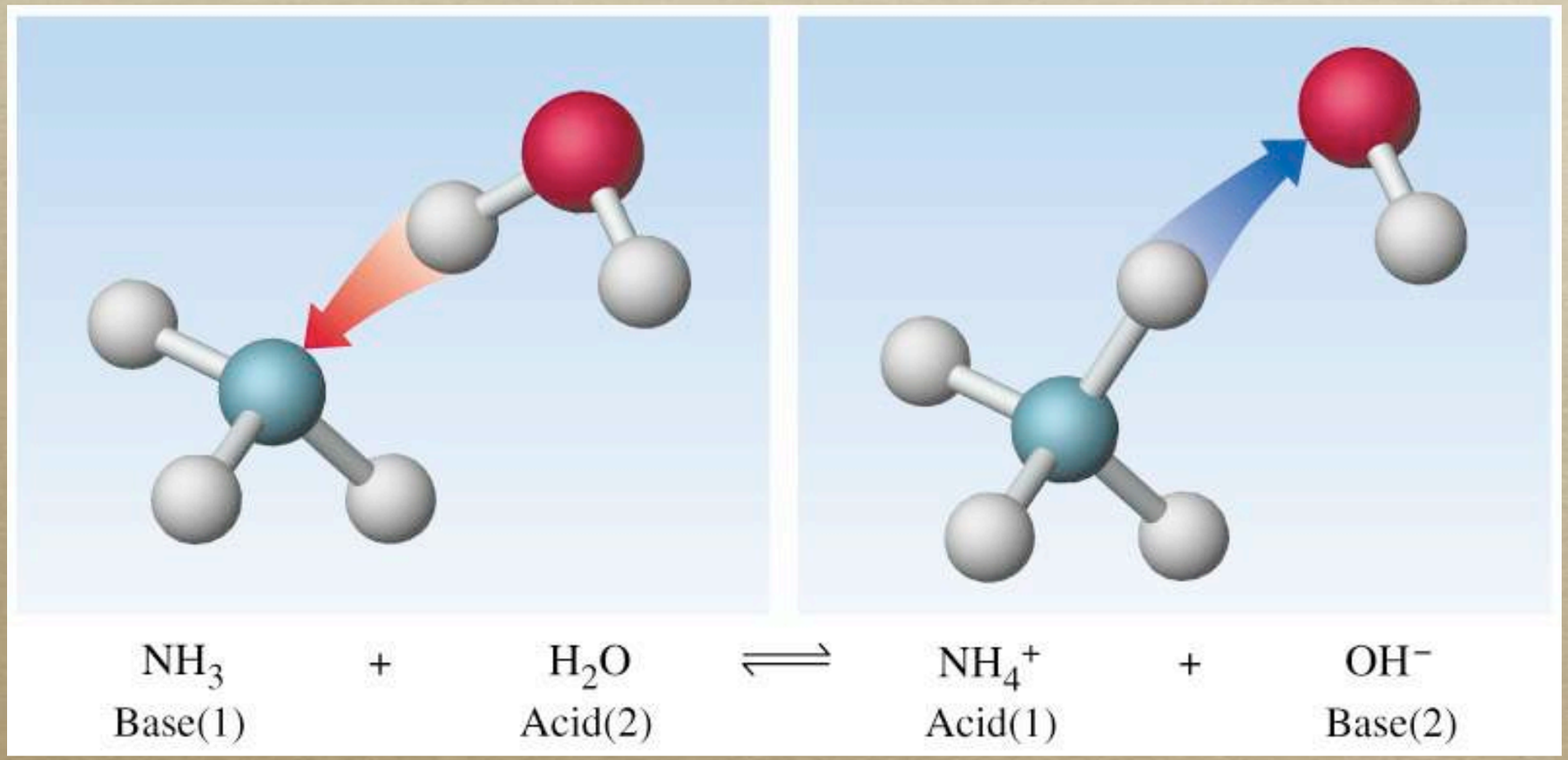

H
O
H
H—Cl
O+
H
H
H
+
Cl−
H2O
base(1)
+
HCl
acid(2)
H3O+
acid(1)
+
Cl−
base(2)


base
acid
acid
base

Ionic compound that contains the cation from the base and the anion from the acid

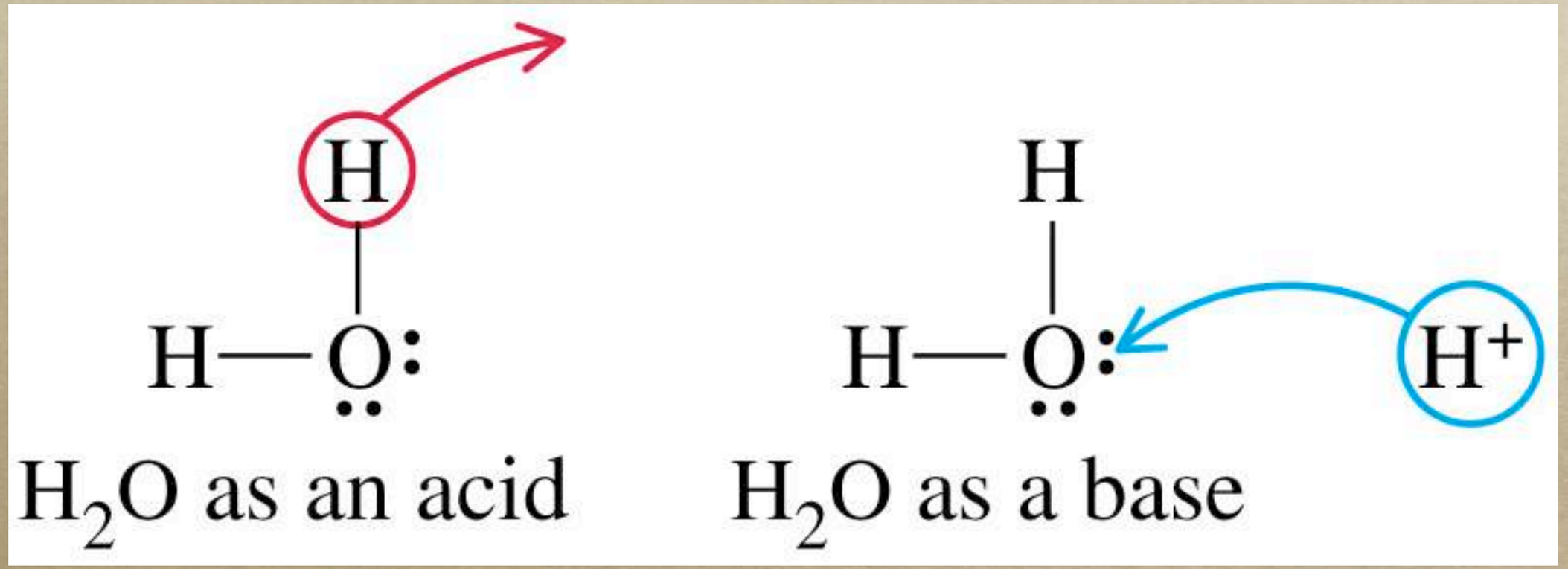
Acid + Base ⟶ Water + Salt

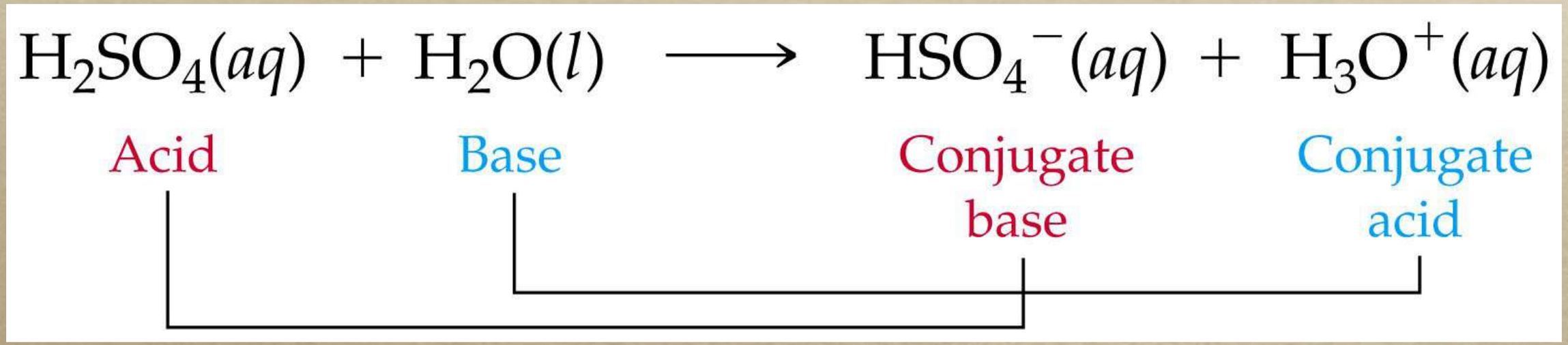
- *what happens **most** of the time (but not all!)*

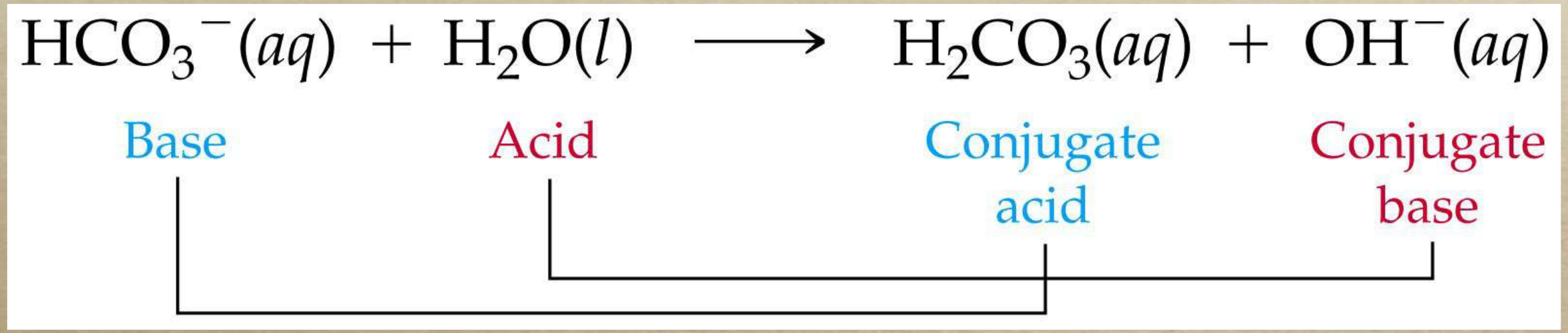


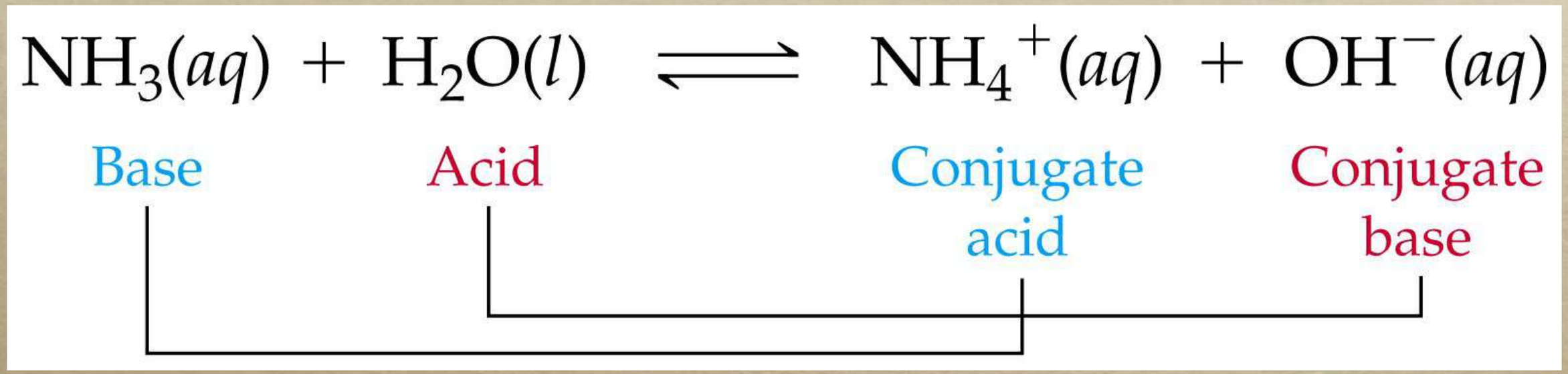
NH_3 + H_2O $\rightleftharpoons$ NH_4^+ + OH^-

Base(1) Acid(2) Acid(1) Base(2)


H
H—O:
H
H—O:
H+
H2O as an acid
H2O as a base

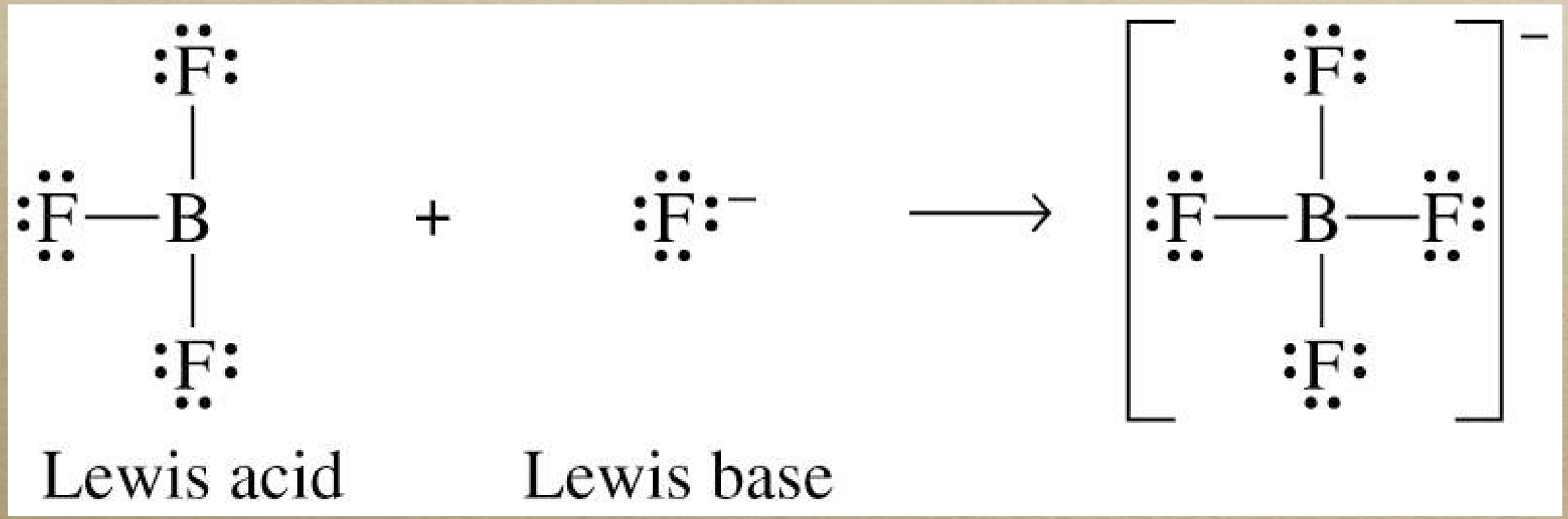

$H_2SO_4(aq) + H_2O(l) \longrightarrow HSO_4^-(aq) + H_3O^+(aq)$
Acid
Base
Conjugate base
Conjugate acid

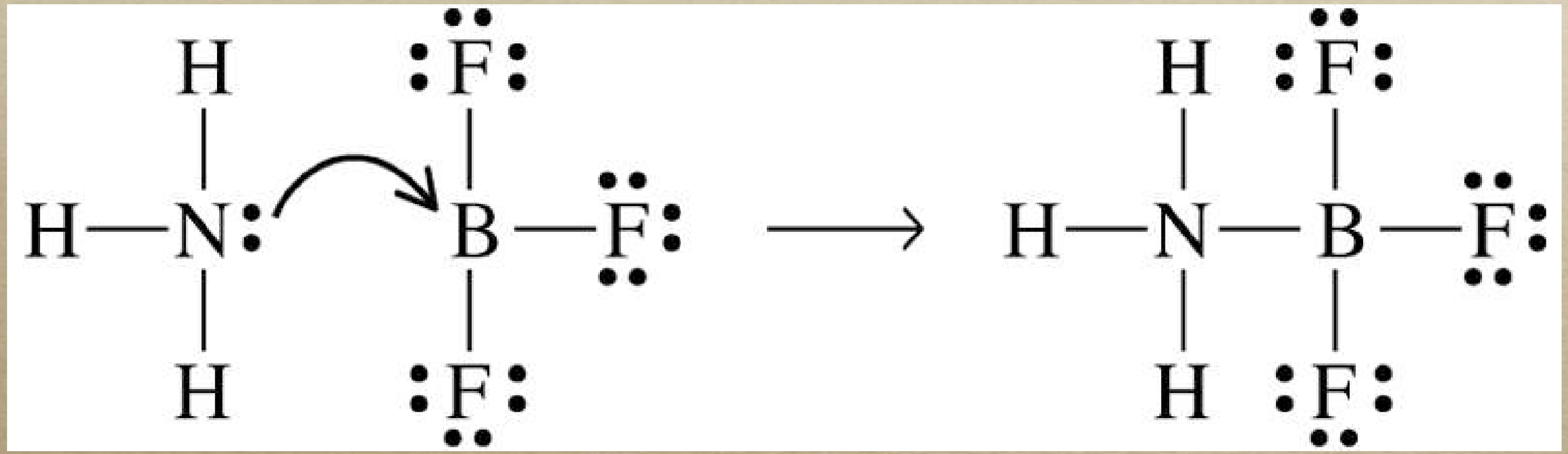

$HCO_3^-(aq) + H_2O(l) \longrightarrow H_2CO_3(aq) + OH^-(aq)$
Base
Acid
Conjugate acid
Conjugate base


NH3(aq) + H2O(l) ⇌ NH4+(aq) + OH−(aq)
Base
Acid
Conjugate acid
Conjugate base

lewis

- *G. N. Lewis looked at these reactions from the **electrons'** p.o.v.*
- *here an acid = **e^- pair acceptor**; a base = **e^- pair donor***
- *this would include all B/L acids and bases **but** included more that had no protons at all...*


Lewis acid
Lewis base



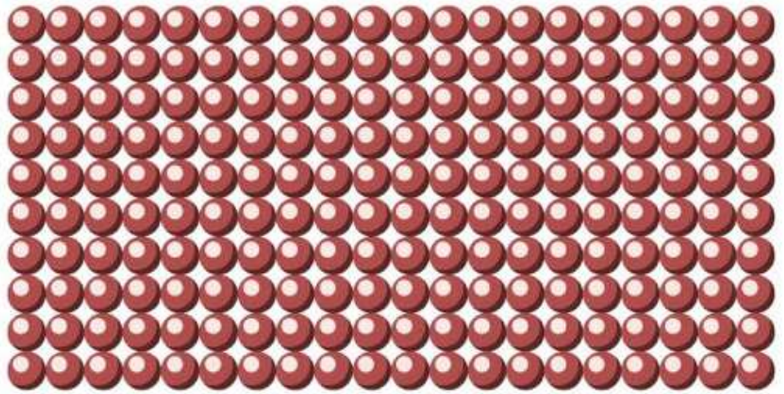
- *which is lewis acid???*

Homework

27,29,119,123

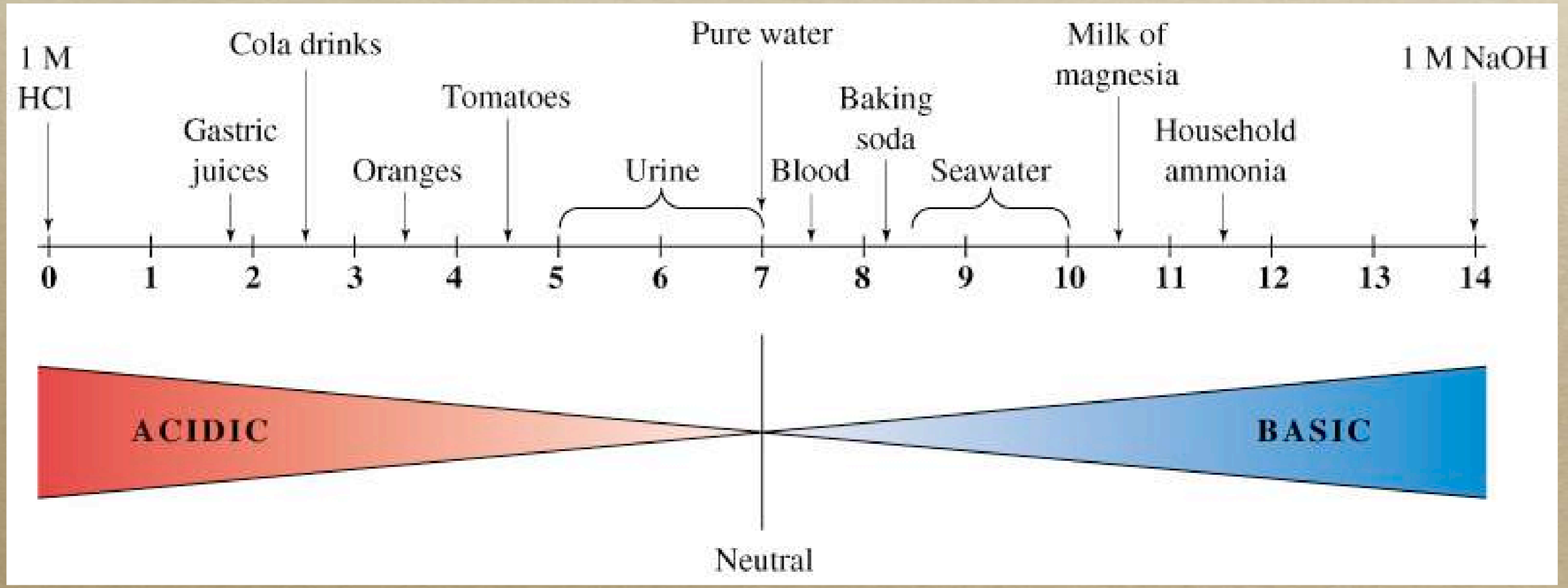
pH

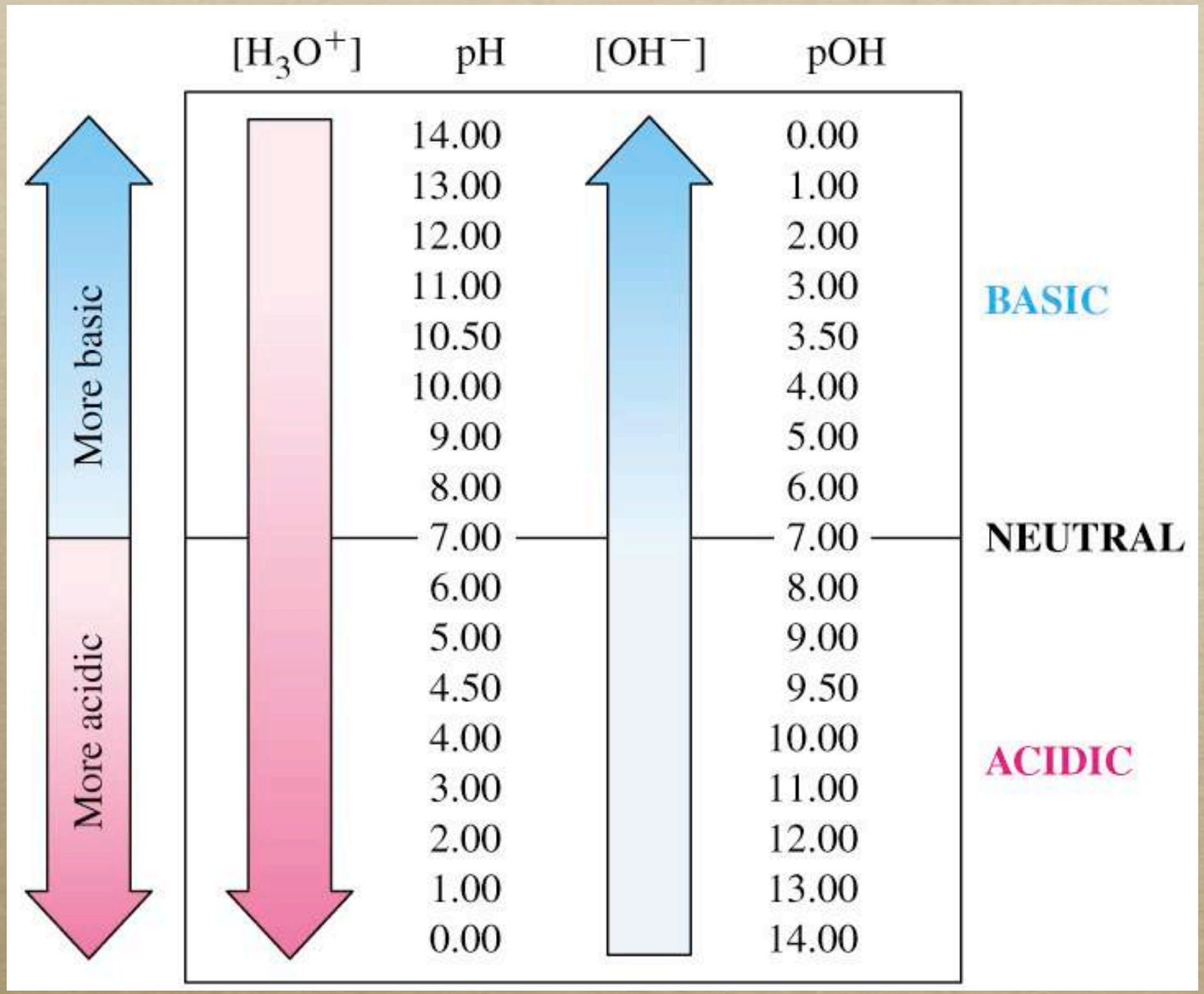
- *pH is used all the time to measure how concentrated an acid soln is*
- ***pH = –log[H^+]***
- *or... –log[H_3O^+]*
- ***pOH = –log[OH^-]***

pH	$[H_3O^+]$	$[H_3O^+]$ Representation
4	10^{-4}	
3	10^{-3}	
2	10^{-2}	

(each circle represents $\frac{5\times10^{-5}\ \text{mol}\ H^+}{\text{L}}$)

- *when…*
- *$[H^+] = [OH^-]$ we have a neutral soln!*
  pH = 7
- *$[H^+] > [OH^-]$ we have an acid soln!*
  pH < 7
- *$[H^+] < [OH^-]$ we have a basic soln!*
  pH > 7


1 M HCl
Gastric juices
Cola drinks
Oranges
Tomatoes
Urine
Pure water
Blood
Baking soda
Seawater
Milk of magnesia
Household ammonia
1 M NaOH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
ACIDIC
BASIC
Neutral


[H3O+]
pH
[OH−]
pOH
More basic
More acidic
14.00
13.00
12.00
11.00
10.50
10.00
9.00
8.00
7.00
6.00
5.00
4.50
4.00
3.00
2.00
1.00
0.00
0.00
1.00
2.00
3.00
3.50
4.00
5.00
6.00
7.00
8.00
9.00
9.50
10.00
11.00
12.00
13.00
14.00
BASIC
NEUTRAL
ACIDIC

- *sometimes you'll see* pK_a
  - $\boldsymbol{pK_a = -\log K_a}$
- *see in next slide how the* pK_a *is related to the strength of the acid, to how well it ionizes...*

Ionization Constants of Some Weak Acids and Weak Bases in Water at 25 °C

	Ionization Equilibrium	Ionization Constant K	pK
Acid		K_a =	pK_a =
Iodic acid	$HIO_3 + H_2O \rightleftharpoons H_3O^+ + IO_3^-$	1.6×10^{-1}	0.80
Chlorous acid	$HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$	1.1×10^{-2}	1.96
Chloroacetic acid	$HC_2H_2ClO_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_2ClO_2^-$	1.4×10^{-3}	2.85
Nitrous acid	$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	7.2×10^{-4}	3.14
Hydrofluoric acid	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	6.6×10^{-4}	3.18
Formic acid	$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$	1.8×10^{-4}	3.74
Benzoic acid	$HC_7H_5O_2 + H_2O \rightleftharpoons H_3O^+ + C_7H_5O_2^-$	6.3×10^{-5}	4.20
Hydrazoic acid	$HN_3 + H_2O \rightleftharpoons H_3O^+ + N_3^-$	1.9×10^{-5}	4.72
Acetic acid	$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$	1.8×10^{-5}	4.74
Hypochlorous acid	$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$	2.9×10^{-8}	7.54
Hydrocyanic acid	$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	6.2×10^{-10}	9.21
Phenol	$HOC_6H_5 + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^-$	1.0×10^{-10}	10.00
Hydrogen peroxide	$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^-$	1.8×10^{-12}	11.74
Base		K_b =	pK_b =
Diethylamine	$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$	6.9×10^{-4}	3.16
Ethylamine	$C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$	4.3×10^{-4}	3.37
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}	4.74
Hydroxylamine	$HONH_2 + H_2O \rightleftharpoons HONH_3^+ + OH^-$	9.1×10^{-9}	8.04
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.5×10^{-9}	8.82
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	7.4×10^{-10}	9.13

Acid strength

Base strength

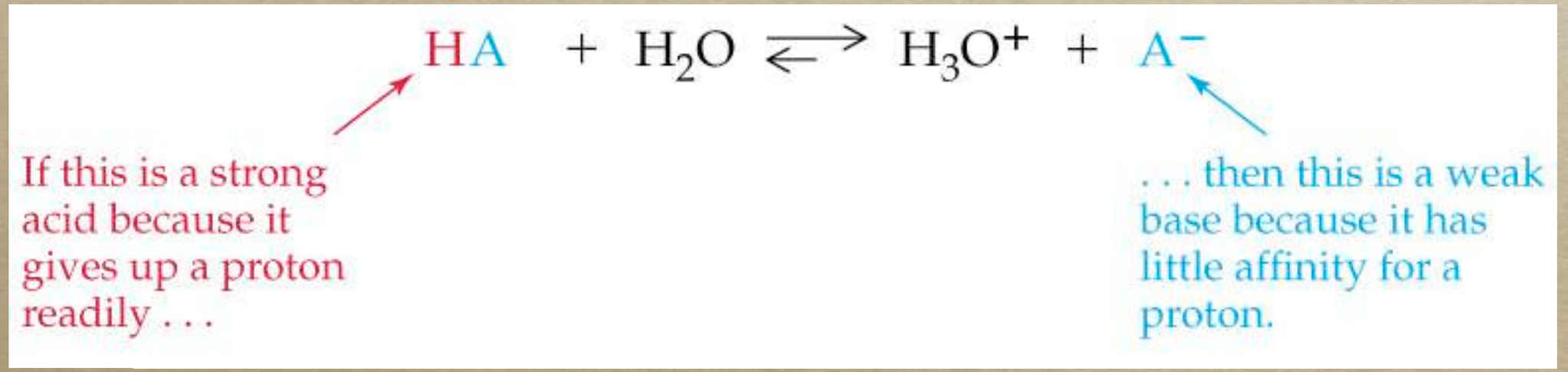
eocs

- *33,35*

Strong Acids

- ***Strong*** *acids completely dissociate; no equilibrium here*
- *Strong acids you should know: HCl, HBr, HI, and all the* ***oxyacids*** *in which the O's outnumber the H's by two or more (e.g.* HNO_3*)*
- *Important strong bases: Group IA hydroxides (e.g. NaOH) and Ba and Sr hydroxides*

- *This also means that since the strong acids are soooo* ***strong****, their* ***conjugate bases are wimpy***



strong acids and calculations

- *Finding pH for strong acids is a breeze because the whole thing dissociates*
- *So the $[H^+]$ is the same as the initial concentration! :)*

example

- *Find the pH for a 0.010 M soln of HCl*
- *0.010 M HCl means 0.010 M* H^+
- *So a simple pH calculation comes out to pH 2*
- *tada!*

Another Example

- *Calculate the pH of a 1.0 x 10^{-5} molar HNO_3 solution.*
- *What molarity of HBr would need to be used to get a pH of 3?*
- *#50*

Homework: 47,48,49,51

K_w

- *Even water has an equilibrium*
- $\boldsymbol{H_2O \rightleftharpoons H^+ + OH^-}$
- $K_w = [H^+][OH^-]$
- $K_w = 1 \times 10^{-14}$ @ 25˚C
- *Can you see then that* ***pH + pOH = 14***
- *aaaaaannnnnddd…*

- $K_w = 1 \times 10^{-14} = K_a K_b$
- $\boldsymbol{pK_a + pK_b = 14}$
- *all these are simple ways of finding one thing if given the other; they are all good ammo in case of test*

Examples

- ***Calculate [H+] and [OH-] for the following:***

pH = 2.0

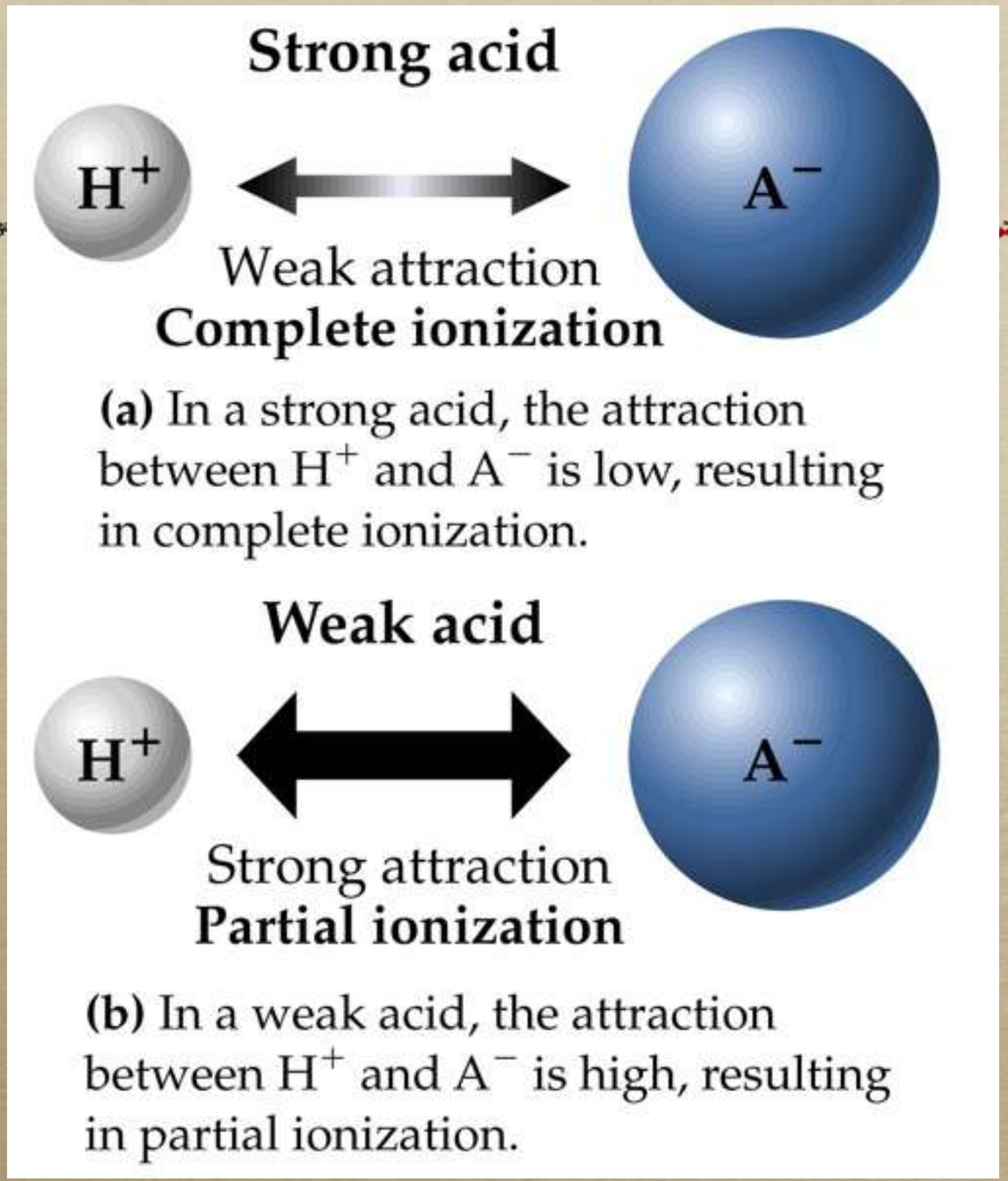
pOH = 5.0

Homework: 43,45

Weak Acids

- *That sort of acid which doesn't dissociate so well*
- *How **weak** a weak acid is can be found **quantitatively** (YAY!)*
- *We bring back our old friend K, specifically...*

- *if* $HA \leftrightharpoons H^+ + A^-$
  - $K_a = [H^+][A^-] / [HA]$
- ***the greater the K_a, the stronger the acid***



(a) In a strong acid, the attraction between H^+ and A^- is low, resulting in complete ionization.

(b) In a weak acid, the attraction between H^+ and A^- is high, resulting in partial ionization.

- *Same happens with bases, but we almost never mess with them…*
- *if* $B + H_2O \leftrightharpoons HB + OH^-$
- $\boldsymbol{K_b = [HB][OH^-]/[B]}$
- ***the greater the K_b the stronger the base***

weak acids and calculations

- *Time to pay attention*
- *If I give you K_a and [HA], you can find pH*
- *ready?...*

example

- *For acetic acid ($HC_2H_3O_2$) we got us a 0.20 M soln, and it's K_a is 1.8×10^{-5}.* ***What's the pH?***
- *hint: pH is hidden in [H+] ;)*
- *can't we just take the concentration and* ***–log*** *it???*
- *no! not all of it dissociated into H^+!*
- *what to do????*

- $K_a = [H^+][C_2H_3O_2^-]/[HC_2H_3O_2]$
- *do you see that the* $[H^+]$ *and* $[C_2H_3O_2^-]$ *are the* **same**???...
- *if so, then* $[H^+] = [C_2H_3O_2^-]$
- *and* $[H^+] = [C_2H_3O_2^-] = x$
- *and* $[HC_2H_3O_2^-] = 0.20\ M - x$
- *but x is soooooo small that it drops out, so*

- $[HC_2H_3O_2^-] = 0.20\ M$
- *and…*
- $1.8 \times 10^{-5} = x^2/0.20$
- *and* $x = [H^+] = 1.9 \times 10^{-3}$
- *and* ***pH = 2.7***
- *YAY and derp!!!*

summary

	HA	$\rightleftharpoons H^+$	$+A^-$
init	0.20	0	0
Δ	-x	+x	+x
equilibrium	0.20-x	x	x

*(Note: this is also called the **ICE** method)*

Another Example

- *For propanoic acid ($HC_3H_5O_2$, $K_a = 1.3 \times 10^{-5}$), determine the concentration of all species present and the pH of a 0.100 M solution. (#56)*

- *Check 5% Rule (Know what I mean? You reading?)*

Homework: 53,55,57,59

Acid and Base Salts

- ***Most people think that a salt dissolved in water has no effect; but it does...***

Strong Base/Strong Acid

- *If salt is composed of conjugates of **strong base** and **strong acid**:* ***Neutral Solution***
- ***e.g. NaCl:***
  - *Na^+ has **no** desire to steal OH^- from water (NaOH will completely dissociate),*
    *Cl^- has **no** desire to steal H^+ from water (HCl just breaks up)*
  - ***So water is safe from being torn apart!***

Weak Base/Strong Acid

- *If salt is composed of conjugates of* ***weak base*** *and* ***strong acid****:* ***Acidic Solution***
- ***e.g. NH_4Cl:***
  - *NH_4^+ is cong acid of weak base* ***so some of the H+ will be lost to water to become H_3O^+,***
    Cl^- has ***no*** *desire to steal H^+ from water*
  - ***So overall more acidic!***

Strong Base/Weak Acid

- *If salt is composed of conjugates of* ***strong base*** *and* ***weak acid****:* ***Basic Solution***
- ***e.g. $NaC_2H_3O_2$:***
  - *Na^+ has no desire to steal OH^- from water (NaOH will dissociate),*
    but $C_2H_3O_2^-$ is conj base of weak acetic acid, ***so it can take some H+ from water leaving behind extra OH^-***
  - ***So overall more OH^- added to water!***

Weak Base/Weak Acid

- *If salt is composed of conjugates of **weak base** and **weak acid**: **toss up***
- *They want to go back to their weak origins and will steal H^+ and OH^- from water to get there*
- *Whoever steals more will have the greater influence*
- *Math required for these (ble!)*

TABLE 14.6 Acid–Base Properties of Various Types of Salts

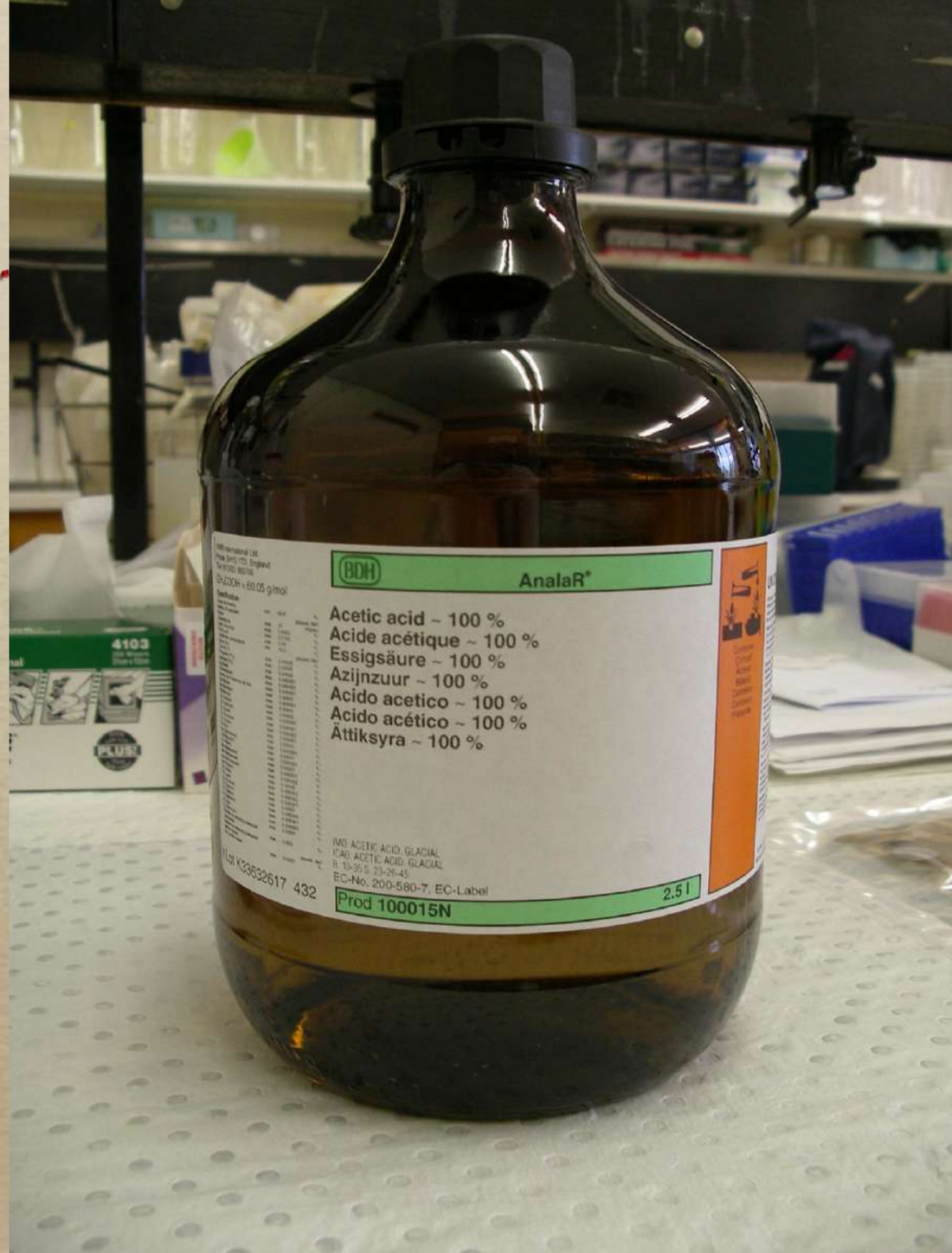
Type of Salt	Examples	Comment	pH of Solution
Cation is from strong base; anion is from strong acid	KCl, KNO_3, $NaCl$, $NaNO_3$	Neither acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	$NaC_2H_3O_2$, KCN, NaF	Anion acts as a base; cation has no effect on pH	Basic
Cation is conjugate acid of weak base; anion is from strong acid	NH_4Cl, NH_4NO_3	Cation acts as acid; anion has no effect on pH	Acidic
Cation is conjugate acid of weak base; anion is conjugate base of weak acid	$NH_4C_2H_3O_2$, NH_4CN	Cation acts as an acid; anion acts as a base	Acidic if $K_a > K_b$, basic if $K_b > K_a$, neutral if $K_a = K_b$
Cation is highly charged metal ion; anion is from strong acid	$Al(NO_3)_3$, $FeCl_3$	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

Acid-Base Salts and Calculations

- *Sometimes we actually have to find the pH of a salt solution!*
- *Not to worry!*
- *Remember these?*
  - $K_a K_b = 1 \times 10^{-14}$
    $pH + pOH = 14$

Example!

- ***You have a 0.10 M $NaC_2H_3O_2$ soln. K_a for $HC_2H_3O_2$ is 1.8×10^{-5} What's the pH?...***



Example

- *We know that the salt will give us a basic soln*
- *(remember, Na^+ will do nothing, but the $C_2H_3O_2^-$ will try and steal back an H^+ from water leaving OH^-)*
- *So we predict a basic pH...*

Example

- *Since it is acting as a **base** let's find K_b for this:*
- $\boldsymbol{C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-}$
- $K_b = [HC_2H_3O_2][OH^-]/[C_2H_3O_2^-]$
- *Since* $K_aK_b = 1 \times 10^{-14}$
- $K_b = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$
- *Now we have the facts; now we are ready.*

example

- *Do you see that since* $C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$ *is true, that...*
- $[HC_2H_3O_2] = [OH^-] = x$*, and...*
- *Since it is such a weak rxn that the amount of acetate ion LOST is so small that* $[C_2H_3O_2^-] = (0.10 - x) = 0.10\ M$
- *?????*

	$[C_2H_3O_2^-]$	$\rightleftharpoons HC_2H_3O_2]$	$+[OH^-]$
init	0.10	0	0
Δ	-x	+x	+x
equilibrium	0.10-x	x	x

example

- *Now back to K_b!*
- ***$K_b = [HC_2H_3O_2][OH^-]/[C_2H_3O_2^-]$***
- *$5.6 \times 10^{-10} = (x)(x)/0.10$*
- *$x = [OH^-] = 7.5 \times 10^{-6}$*
- *and one last step...*

example

- $\boldsymbol{pOH = -log[OH^-]} = -log(7.5 \times 10^{-6}) = 5.1$
- *and since* $\boldsymbol{pH + pOH = 14}$
- *then pH = 14 - 5.1 =* ***8.9***

Another Example & Homework

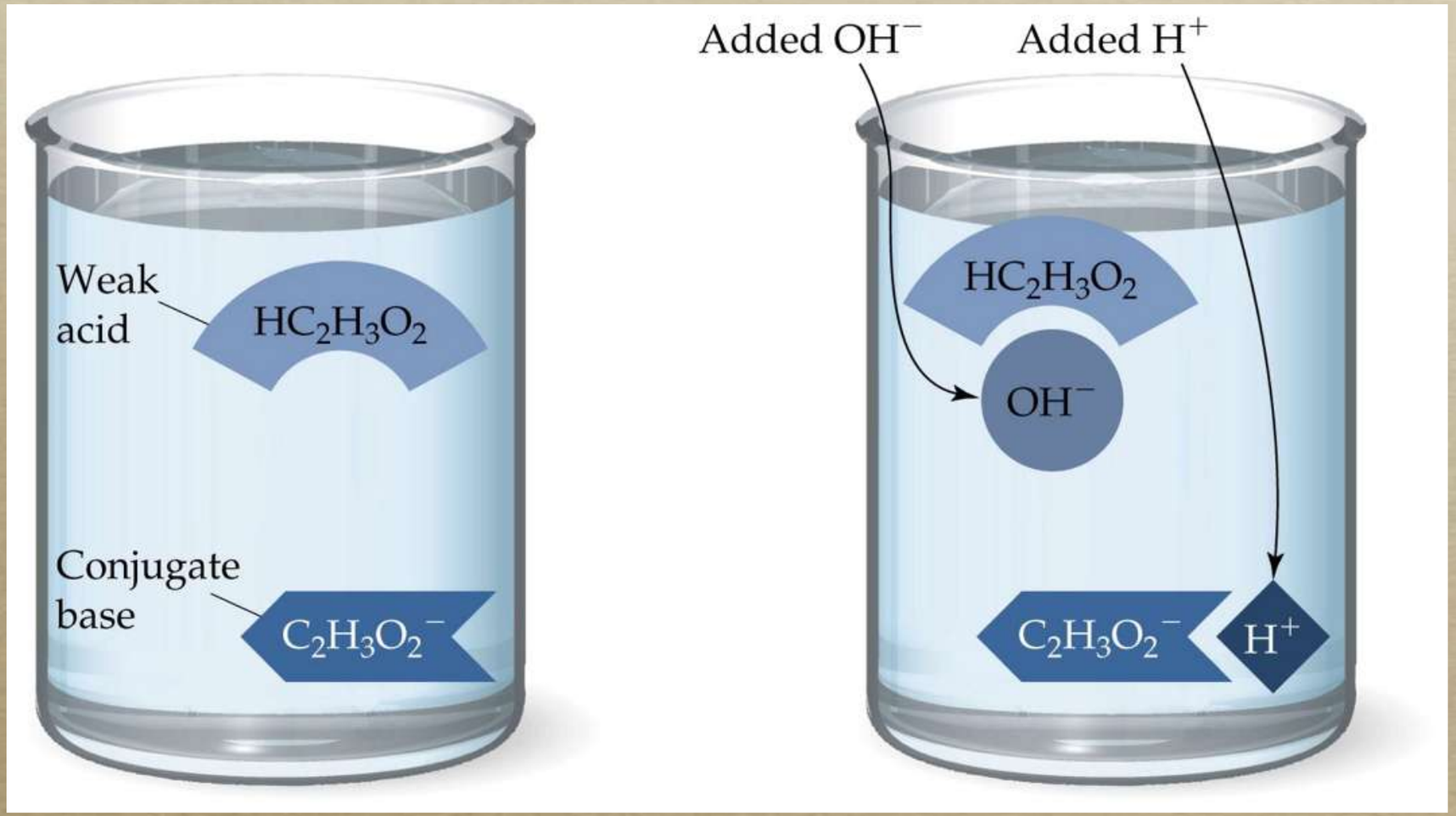
106c: Calculate the pH of a 0.40M NH_4ClO_4 solution

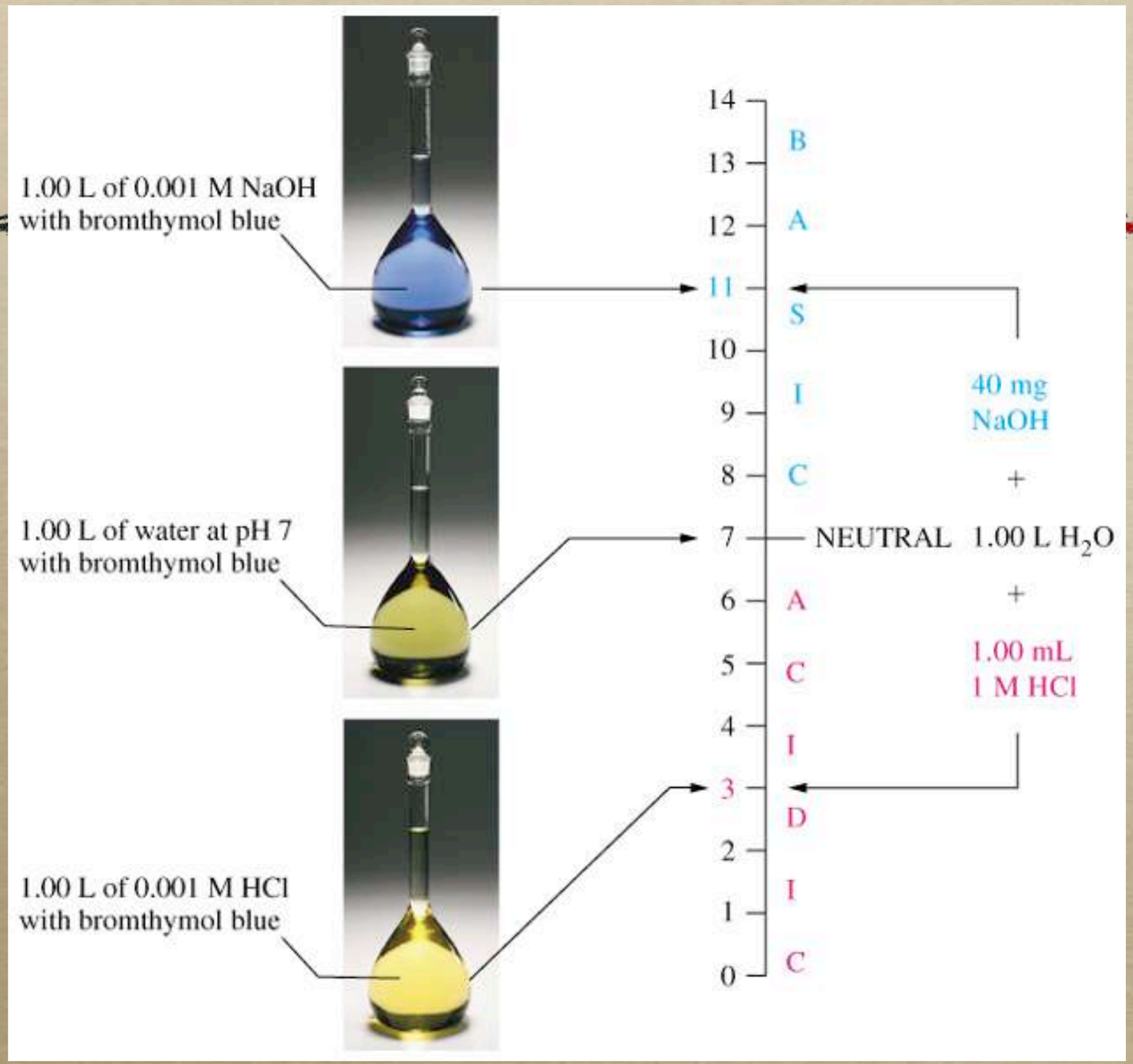
 # 101, 102, 111, 103, 105, 106

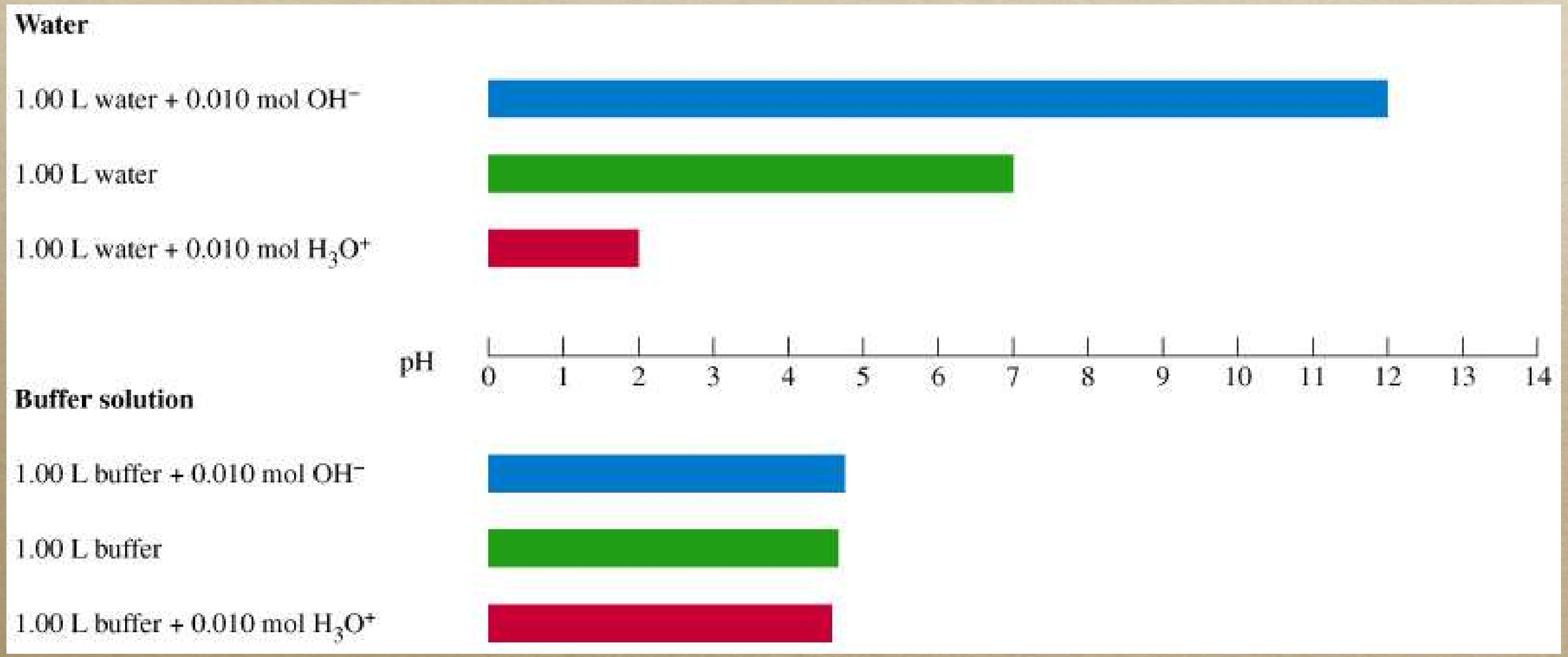
Buffers

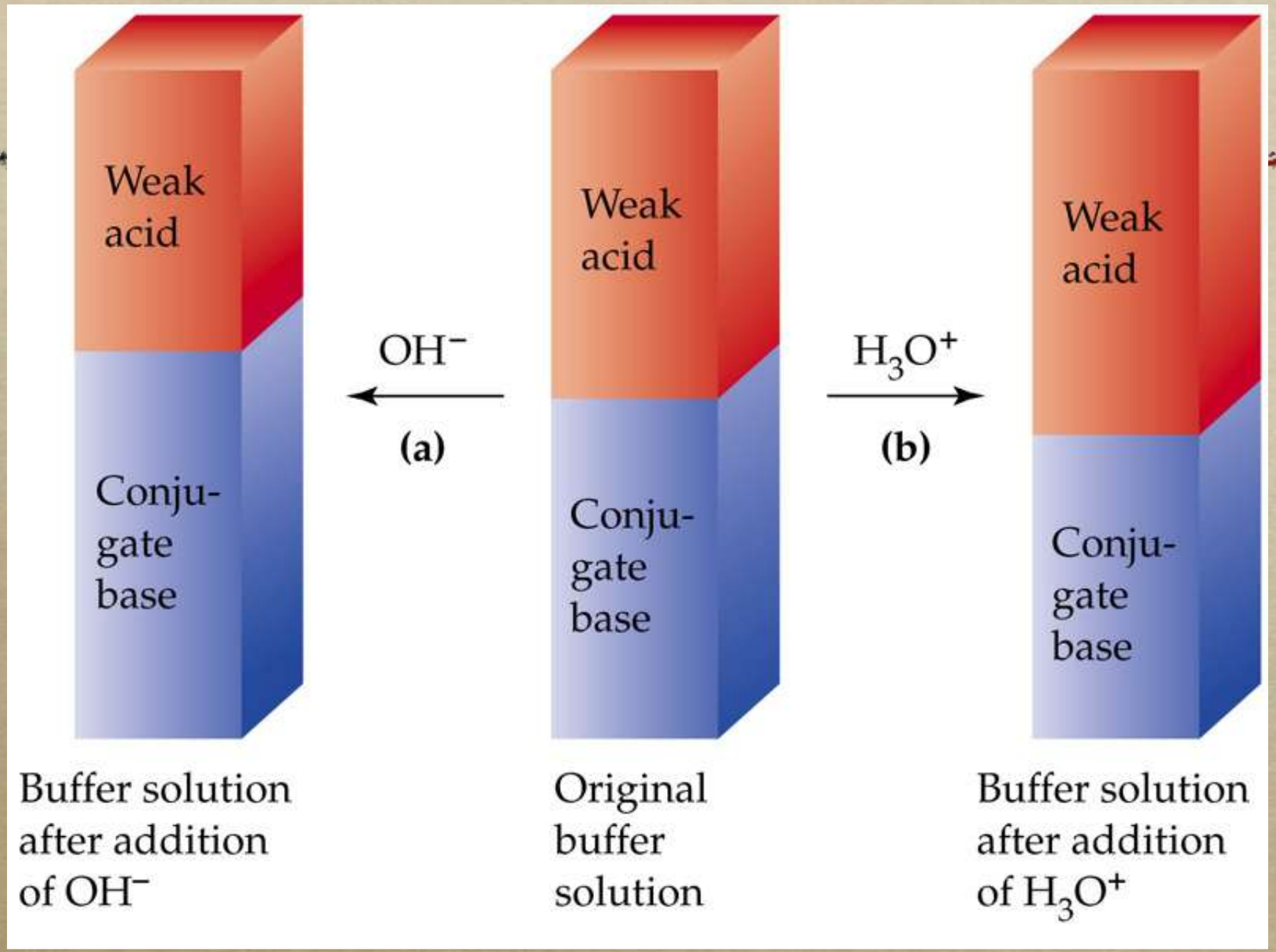
- ***= a soln with a very stable pH***
- *Add a little acid or base, add water or evaporate it, the pH stays essentially the same*
- ***= a good amount of weak acid (or base) and its conjugate***
- *How it works….*

- *e.g. when a weak acid/conjugate base are in a soln they act as **a team***
- *Any EXTRA H^+ put in there gets eaten up by the conjugate base, any EXTRA OH^- gets neutralized by the weak acid*
- ***Overall effect: little to no change in pH***


Weak acid
$HC_2H_3O_2$
Conjugate base
$C_2H_3O_2^-$
Added OH^-
Added H^+
$HC_2H_3O_2$
OH^-
$C_2H_3O_2^-$
H^+


1.00 L of 0.001 M NaOH
with bromthymol blue
1.00 L of water at pH 7
with bromthymol blue
1.00 L of 0.001 M HCl
with bromthymol blue
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
B
A
S
I
C
NEUTRAL
A
C
I
D
I
C
40 mg
NaOH
+
1.00 L H_2O
+
1.00 mL
1 M HCl


Water
1.00 L water + 0.010 mol OH⁻
1.00 L water
1.00 L water + 0.010 mol H3O+
pH
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
Buffer solution
1.00 L buffer + 0.010 mol OH⁻
1.00 L buffer
1.00 L buffer + 0.010 mol H3O+


Weak acid
Conju-gate base
OH⁻
(a)
Weak acid
Conju-gate base
H3O+
(b)
Weak acid
Conju-gate base
Buffer solution after addition of OH⁻
Original buffer solution
Buffer solution after addition of H3O+

- *Sadly, we have to deal with this quantitatively*
- *Which is where we need the* ***Henderson-Hasselbach equation!!!!***
- $\boldsymbol{pH = pK_a + \log [A^-]/[HA]}$
  - *[HA] = concentration of undissociated weak acid*
    $[A^-]$ = concentration of conjugate base

Example

- *What is the pH of a buffer soln with 0.20 M $HC_2H_3O_2$ and 0.50 M $C_2H_3O_2^-$? (K_a for acetic acid is 1.8×10^{-5})*
- ***pH = pK_a + log $[C_2H_3O_2^-]/[HC_2H_3O_2]$***
- *pH = $-\log(1.8 \times 10^{-5}) + \log (0.50/0.20)$*
- *pH = $-\log(1.8 \times 10^{-5}) + \log (2.5)$*
- *pH = 4.7 + 0.40 = 5.1*

Example

- *What is the pH of a buffer soln with 0.20 M $HC_2H_3O_2$ and 0.20 M $C_2H_3O_2^-$? (K_a for a/acid is 1.8×10^{-5})*
- ***pH = pK_a + log $[C_2H_3O_2^-]/[HC_2H_3O_2]$***
- *pH = $-\log(1.8 \times 10^{-5}) + \log (0.20/0.20)$*
- *pH = $-\log(1.8 \times 10^{-5}) + \log (1)$*
- *pH = 4.7 + 0 = 4.7*

*Do you see that when concentrations of wk acid and its conj base are **equal**, then **$pK_a = pH$**?*

*So, when you need a **good buffer** (lots of both wk acid and conj base) pick an acid with **pK_a near the pH** you're looking for!!!*

Select a weak acid with a pK_a close to the desired pH.

↓

Calculate the necessary ratio $\frac{[\text{conjugate base}]}{[\text{acid}]}$ to give the desired pH.

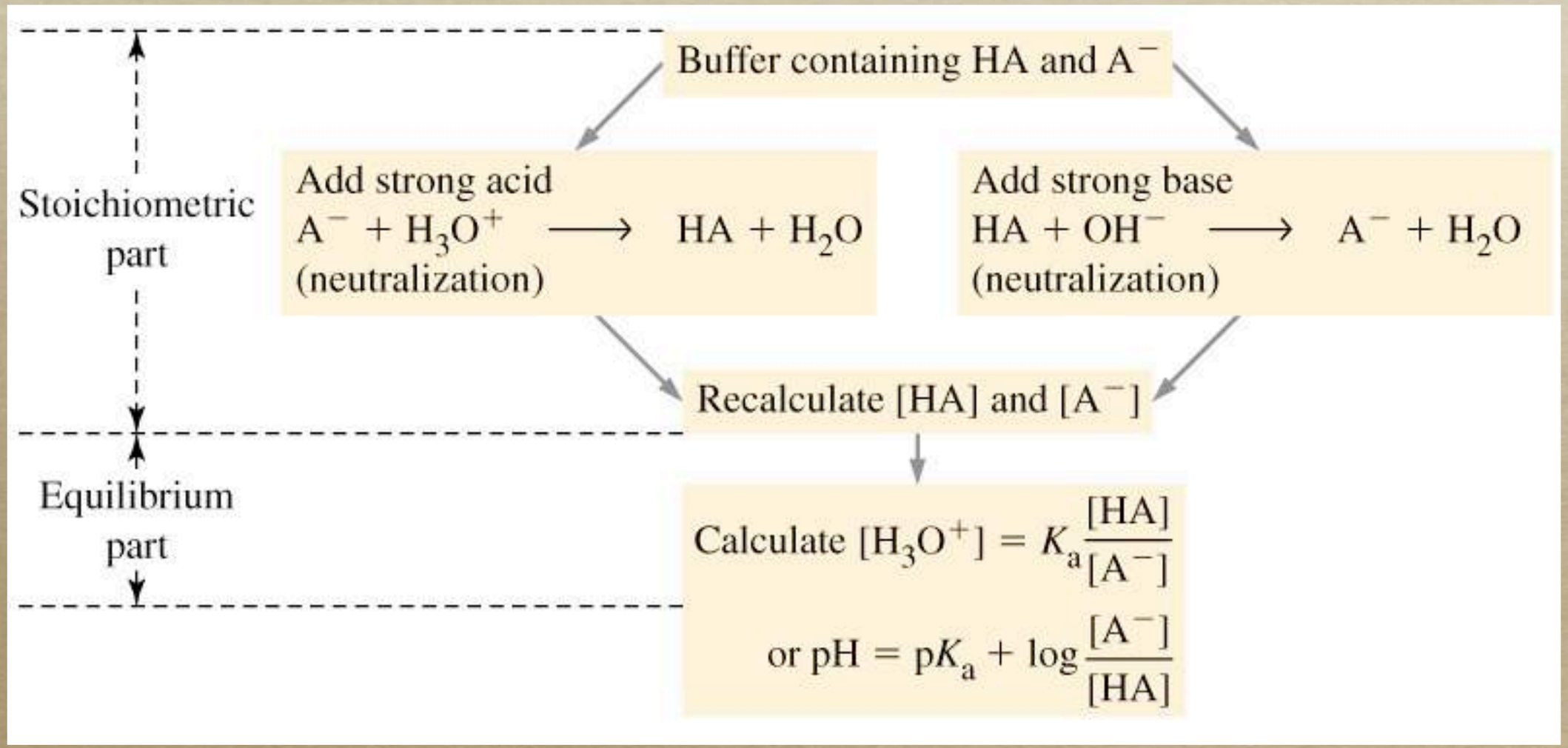
↓

Calculate the necessary concentrations of conjugate base and acid.

More Examples and Homework Too

- ***Chapter 15 #38***
  - ***A buffered solution is made by adding 50.0 g NH_4Cl to 1.00 L of a 0.75 M solution of NH_3. Calculate the pH of the final solution. (assume no volume change)***

- ***Chapter 15: 21, 23, 33, 34, 37***


Buffer containing HA and A⁻
Add strong acid
A⁻ + H₃O⁺ ⟶ HA + H₂O
(neutralization)
Add strong base
HA + OH⁻ ⟶ A⁻ + H₂O
(neutralization)
Stoichiometric part
Recalculate [HA] and [A⁻]
Equilibrium part
Calculate [H₃O⁺] = Ka [HA]/[A⁻]
or pH = pKa + log [A⁻]/[HA]

Buffers

Calculate the pH of a solution that is 0.60 M HF and 1.00 M KF. ($K_a = 7.2 \times 10^{-4}$) *pH=3.36*

Calculate the pH after 0.10mol NaOH is added to 1.00L of the above solution. *pH=3.48*

Calculate the pH after 0.20mol of HCl is added to 1.00L of the above solution. *pH=3.14*

HW: Ch15 #33 & 35

Polyprotic Acids & Amphoteric Substances

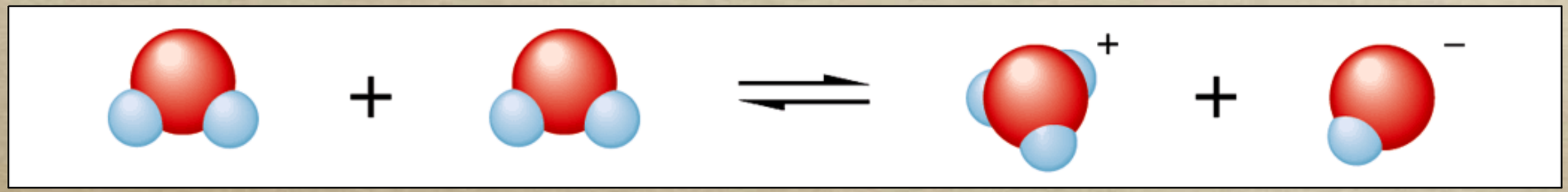
- *Poly**prot**ic means it gives up more than one proton!*
- *The first proton always comes off much more easily than the next ones*
- ***$H_3PO_4 > H_2PO_4^- > HPO_4^{2-}$***
- *Don't be alarmed: Another **easy-mode** is coming*

TABLE 14.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid*	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	

- *But now we got us a whole new category of things called...*

- ***Amphoteric*** *- having both acidic and basic characteristics*
- *As in $H_2PO_4^-$ can either* ***accept*** *a proton to become H_3PO_4 or* ***lose*** *one to become HPO_4^{2-}*



- *Of course water can, too, to become both H_3O^+ and OH^-*

Polyprotic Example

Kindaa Chapter 14 #95

Calculate the pH and the concentrations of all species in a 0.10 M solution of H_2CO_3

$$K_{a1} = 4.3 \times 10^{-7}$$

$$K_{a2} = 5.6 \times 10^{-11}$$