aqueous acid/base reactions

a. a little bit more about water Water is a polar substance. This means water is able to "solvate" ions rather well. Another important characteristic of water is its ability to undergo self-ionization into hydrogen and hydroxide ions - to a very slight degree, as shown by the equation HOH = $H^{+1}_{(aq)}$ + $OH^{-1}_{(aq)}$. At a given temperature the amount of water ionized (i.e., present as hydrogen ions and hydroxide ions) is very small but remains constant. This causes the product of hydrogen ion concentration and hydroxide ion concentration to be constant. Due to this self-ionization, water can be considered as very a weak electrolyte.

The acidic, basic, or neutral condition of an aqueous solution depends on the relative concentrations of hydrogen and hydroxide ions present. Aqueous solutions are *neutral* when $[H^{+1}] = [OH^{-1}]$, *acidic* when $[H^{+1}] > [OH^{-1}]$, and *basic* when $[H^{+1}] < [OH^{-1}]$. However, no matter what the concentrations of these two ions, their product is a constant.

The acidic/basic/neutral condition of aqueous solutions is often detected using small amounts of organic acids that display colors ("indicators"). The color displayed under acidic conditions is different from the color under basic conditions.

b. acid/base chemistry - definitions and degree of ionization

DEFINED: acids **donate protons** to the solution and *increase* $[H^{1+}{}_{(aq)}]$ of the solution. bases **accept protons** from solution, and *decrease* $[H^{1+}{}_{(aq)}]$ of the solution (and simultaneously *increase* $[OH^{1-}{}_{(aq)}]$).

i. STRONG ACIDS in aqueous solutions, are COMPLETELY dissociated into ions. For example hydrochloric acid, having the formula HCl, exists in solution ONLY as the separated and independent ions - as shown by $HCl_{(aq)}$! $H^{1+}{}_{(aq)}$ + $Cl^{1-}{}_{(aq)}$ (note the ONE WAY arrow) no HCl molecules are present in solution. Other common strong acids are nitric, HNO_3 ; sulfuric, H_2SO_4 ; perchloric, $HClO_4$; hydrobromic, HBr ; and hydroiodic, HI

ii. WEAK ACIDS in aqueous solutions, are very slightly dissociated into ions. For example, acetic acid, having the formula, $HC_2H_3O_2$, exists primarily in molecular form, with few hydrogen and acetate ions as shown by $HC_2H_3O_{2\,(aq)}$ **Ø** $H^{1+}{}_{(aq)}$ + $C_2H_3O_2{}^{1-}{}_{(aq)}$ (note the TWO WAY arrow) Based on its *very limited ionization*, $HC_2H_3O_2$ is called a WEAK acid. Other common weak acids are hydrofluoric, HF, formic, HCOOH ; citric; butyric, i.e., all organic acids.

iii. STRONG BASES In a parallel manner, strong bases are COMPLETELY ionized in aqueous solution. Examples are hydroxides of group I alkali metals - MOH ; and group II alkaline earth - $M(OH)_2$.

iv. WEAK BASES Weak bases exist largely in molecular form in aqueous solution, with very few ions present. Examples are ammonia, NH_3 ; and amines, such as CH_3-NH_2 . Weak bases operate in a manner slightly different from weak acids; they do not furnish hydroxide ions directly, rather they **accept protons** (from solvent water molecules) and leave hydroxide ions in their wake - as shown by

$NH_{3\,(aq)}$ + HOH = $NH_4{}^{1+}{}_{(aq)}$ + $OH_{(aq)}{}^{1-}$ (note both charges and mass balance)

DEMO Test strong/weak acids/bases to show presence/absence of ions in aqueous solutions. Strong acids/bases are completely ionized (bright light) Weak acids/bases are very slightly ionized (dim light).

Illustration of understanding about strong/weak acid/base character, requires writing the correct ionization equation for each of the above cases as shown. For this purpose remember the examples of the following four substances: HCl, NaOH, NH_3, and $HC_2H_3O_2$ as models for strong acid and base, and weak base and acid respectively.

c. acid / base chemistry - stoichiometry When concentration of one component (the acid or base) is known, then it can be used to determine the concentration of the other component by measuring volumes required for complete reaction, and then using (moles A) = (moles B) x [Conversion Factor]. Burets and pipets measure reacting volumes, and indicators signal the complete end-of-reaction. Such reaction processes are called titrations.

Write a balanced net ionic equation for each of the following acid-base reactions in water:

- i. butyric acid ($HC_4H_7O_2$, a weak acid) with potassium hydroxide (KOH, a strong base)
- ii. ammonia (NH_3, a weak base) with hydrobromic acid (HBr, a strong acid)
- iii. nitric acid (HNO_3, a strong acid) with lithium hydroxide (LiOH, a strong base)

Work each of the following acid / base stoichiometry problems:

iv. A titration required 32.78 mL of a 0.164 M potassium hydroxide solution, to neutralize 25.00 mL of a nitric acid solution. What is the molarity of the nitric acid solution?

v. Analysis of a barium hydroxide solution was conducted by titrating against hydrochloric acid. It was found that 27.48 mL of a 0.215 M hydrochloric acid solution was required to neutralize 20.00 mL of a barium hydroxide solution of unknown concentration. What is the molarity of the barium hydroxide solution?

vi. What volume of a 0.137 M solution of phosphoric acid, H_3PO_4 , would be required to neutralize 50.00 mL of a 0.314 M solution of calcium hydroxide? H_3PO_4 is a polyprotic acid and calcium hydroxide is a poly base. In this reaction assume that phosphoric acid furnishes three moles hydrogen ion per mole acid, and that calcium hydroxide furnishes two moles hydroxide anion per mole base.

vii. When 20.00 mL of a 0.154 M solution of hydrobromic acid, HBr , is slowly added to 45.00 mL of a 0.0941 M solution of lithium hydroxide, LiOH, what is the final concentration of hydroxide ion in solution?

viii. Suppose 21.10 mL of a 0.228 M solution of sulfuric acid, H_2SO_4 , is reacted with 26.21 mL of a 0.363 M solution of sodium hydroxide, NaOH . What is the final concentration of the ion from water present in excess? In this reaction assume that sulfuric acid furnishes two moles hydrogen ion per mole acid.

Stoichiometry - Ground Rules

1. Matter is conserved in chemical reactions. (Law of Conservation of Mass)

2. $$Standard\ Mass\ Substance = \sum(atomic\ mass_r)(\#\ atoms_r)$$

3. Molarity(M) is a unit of solution concentration;

$$M = \frac{moles\ solute}{Vol.of\ solution\ in\ Liter\ units} = \frac{moles}{Liters}$$

4. where $moles\ solute\ (actually\ any\ solid) = \left(\frac{mass\ substance}{standard\ mass\ substance}\right)$

5. and, $moles\ solute\ (in\ a\ solution) = (Molarity)(Vol.in\ Liters)$

6. For all chemical reactions: $moles\ A = moles\ B\ [Conversion\ Factor(s)...]$

i. Starting Information:

Concentrations expressed in Terms of...	Acid/Base? Strong? Weak?	But what's really present in the solution is...
reactant solution A: butyric acid $HC_4H_7O_2$ (an organic acid)	WEAK ACID	$HC_4H_7O_{2\,(aq)} \Leftrightarrow H^{1+}_{(aq)} + C_4H_7O_2{}^{1-}_{(aq)}$ **only** this is present; hardly any ions
and		
reactant solution B: potassium hydroxide KOH	STRONG BASE	$KOH_{(aq)} \Rightarrow K^{1+}_{(aq)} + OH^{1-}_{(aq)}$ none present; **only** ions are present

Will any combination of the above produce a net reaction?

Net Ionic equation:

$$HC_4H_7O_{2\,(aq)} + K^{1+}_{(aq)} + OH^{1-}_{(aq)} \Longrightarrow C_4H_7O_2{}^{1-}_{(aq)} + HOH + K^{1+}_{(aq)}$$

Hydroxide anion, as the base, is a proton acceptor. Butyric acid contains an ionizable hydrogen ion (i.e., proton - shown in green color). So it donates this proton to hydroxide anion to form water, and leaves butyrate anion behind. Potassium cation is a spectator ion in this reaction and should be eliminated from the above equation so it becomes...

$$HC_4H_7O_{2\,(aq)} + OH^{1-}_{(aq)} \Longrightarrow C_4H_7O_2{}^{1-}_{(aq)} + HOH$$

Note the same net number of charges on both sides of the equation (i.e., balance of charges).

ii. Starting Information:

Concentrations expressed in Terms of...		Acid/Base? Strong? Weak?	But what's really present in the solution is...
reactant solution A	ammonia NH_3	WEAK BASE	$NH_{3\,(aq)} + HOH \Leftrightarrow NH_4^{1+}{}_{(aq)} + OH^{1-}{}_{(aq)}$ **only** this is present ($NH_{3\,(aq)}$ + HOH); hardly any ions
and			
reactant solution B	hydrobromic acid HBr	STRONG ACID	$HBr_{(aq)} \Rightarrow H^{1+}{}_{(aq)} + Br^{1-}{}_{(aq)}$ none present ($HBr_{(aq)}$); **only** ions are present

Will any combination of the above produce a net reaction?

Net Ionic equation:

$$NH_{3\,(aq)} + H^{1+}{}_{(aq)} + Br^{1-}{}_{(aq)} \Rightarrow NH_4^{1+}{}_{(aq)} + Br^{1-}{}_{(aq)}$$

Ammonia molecule, as the base, is a proton acceptor. Hydrobromic acid is completely ionized and furnishes all of its protons to the solution. These protons are accepted by ammonia to form ammonium cation. Bromide anion is a spectator ion in this reaction and should be eliminated from the above equation so it becomes...

$$NH_{3\,(aq)} + H^{1+}{}_{(aq)} \Rightarrow NH_4^{1+}{}_{(aq)}$$

Note the same net number of charges on both sides of the equation (i.e., balance of charges).

iii. Starting Information:

Concentrations expressed in Terms of...		Acid/Base? Strong? Weak?	But what's really present in the solution is...
reactant solution A	nitric acid HNO_3	STRONG ACID	$HNO_{3\,(aq)} \Longrightarrow H^{1+}_{(aq)} + NO_3{}^{1-}{}_{(aq)}$ $HNO_{3\,(aq)}$: **none** present; $H^{1+}_{(aq)} + NO_3{}^{1-}{}_{(aq)}$: only ions present
and			
reactant solution B	lithium hydroxide LiOH	STRONG BASE	$LiOH_{(aq)} \Longrightarrow Li^{1+}_{(aq)} + OH^{1-}_{(aq)}$ $LiOH_{(aq)}$: none present; $Li^{1+}_{(aq)} + OH^{1-}_{(aq)}$: **only** ions present

Will any combination of the above produce a net reaction?

Net Ionic equation:

$$H^{1+}_{(aq)} + NO_3{}^{1-}{}_{(aq)} + Li^{1+}_{(aq)} + OH^{1-}_{(aq)} \Longrightarrow HOH + NO_3{}^{1-}{}_{(aq)} + Li^{1+}_{(aq)}$$

The strong acid and base are completely ionized. Component ions of water combine to form water, and remaining ions do not form precipitates in this case or otherwise react. These latter ions are spectator ions. They should be eliminated from the above equation so it becomes...

$$H^{1+}_{(aq)} + OH^{1-}_{(aq)} \Longrightarrow HOH$$

Note the same net number of charges on both sides of the equation (i.e., balance of charges).

iv. Starting Information:

Concentrations expressed in Terms of...	Acid/Base? Strong? Weak?	But what's really present in the solution is...
reactant solution A: potassium hydroxide, KOH, 32.78 mL 0.164M	STRONG BASE	$KOH_{(aq)} \Rightarrow K^{1+}_{(aq)} + OH^{1-}_{(aq)}$ — KOH: **none** present; K^{1+} + OH^{1-}: only ions present
and		
reactant solution B: nitric acid, HNO_3, 25.00 mL ?M	STRONG ACID	$HNO_{3(aq)} \Rightarrow H^{1+}_{(aq)} + NO_3^{1-}{}_{(aq)}$ — HNO_3: none present; H^{1+} + NO_3^{1-}: **only** ions present

Will any combination of the above produce a net reaction?

Net Ionic equation:

$$H^{1+}_{(aq)} + OH^{1-}_{(aq)} \Rightarrow HOH$$

moles A = moles B [C.F.]   moles HNO_3 = moles KOH [C.F]

$$(?\ M)(25.00\ mL) = (0.164\ M)(32.78\ mL)\left[\frac{1\ moles\ OH^-}{1\ moles\ KOH}\right]\left[\frac{1\ moles H^+}{1\ moles\ OH^-}\right]\left[\frac{1\ mole\ HNO_3}{1\ moles\ H^+}\right]$$

? M of HNO_3 = 0.215 Molar

v. Starting Information:

Concentrations expressed in Terms of...	Acid/Base? Strong? Weak?	But what's really present in the solution is...
reactant solution A: barium hydroxide $Ba(OH)_2$ 20.00 mL ? M	STRONG BASE	$Ba(OH)_{2(aq)} \Longrightarrow Ba^{2+}_{(aq)} + 2\ OH^{1-}_{(aq)}$ — **none** present / only ions present
and		
reactant solution B: hydrochloric acid HCl 27.48 mL 0.215M	STRONG ACID	$HCl_{(aq)} \Longrightarrow H^{1+}_{(aq)} + Cl^{1-}_{(aq)}$ — none present / **only** ions present

Will any combination of the above produce a net reaction?

Net Ionic equation:

$$H^{1+}_{(aq)} + OH^{1-}_{(aq)} \Longrightarrow HOH$$

moles A = moles B [C.F.]   moles $Ba(OH)_2$ = moles HCl [C.F]

$$(?\ M)(20.00\ mL) = (0.215\ M)(27.48\ mL)\left[\frac{1\ moles\ H^{+}}{1\ moles\ HCl}\right]\left[\frac{1\ moles\ OH^{-}}{1\ moles\ H^{+}}\right]\left[\frac{1\ mole\ Ba(OH)_2}{2\ moles\ OH^{-}}\right]$$

? M of $Ba(OH)_2$ = 0.148 Molar

vi. Starting Information:

Concentrations expressed in Terms of...	Acid/Base? Strong? Weak?	But what's really present in the solution is...
reactant solution A — phosphoric acid H_3PO_4 ? mL 0.137 M	WEAK ACID	$H_3PO_{4(aq)} \longrightarrow 3\,H^{1+}_{(aq)} + PO_4^{3-}{}_{(aq)}$ **only** present (under $H_3PO_{4(aq)}$); hardly any ions (under $3\,H^{1+}_{(aq)} + PO_4^{3-}{}_{(aq)}$)
and		
reactant solution B — calcium hydroxide $Ca(OH)_2$ 50.00 mL 0.314M	STRONG BASE	$Ca(OH)_{2\,(aq)} \longrightarrow Ca^{2+}{}_{(aq)} + 2\,OH^{1-}{}_{(aq)}$ none present (under $Ca(OH)_{2\,(aq)}$); **only** ions present (under $Ca^{2+}{}_{(aq)} + 2\,OH^{1-}{}_{(aq)}$)

Will any combination of the above produce a net reaction?

Net Ionic equation: Hydroxide anion is a proton acceptor. Phosphoric acid has 3 protons to donate.

$$H_3PO_{4\,(aq)} + 3\,OH^{1-}{}_{(aq)} \longrightarrow 3\,HOH + PO_4^{3-}{}_{(aq)}$$

moles A = moles B [C.F.]   moles H_3PO_4 = $Ca(OH)_2$ [C.F]

$$(0.137\ M)(\ ?\ mL) = (0.314\ M)(50.00\ mL)\left[\frac{2\ moles\ OH^{1-}}{1\ moles\ Ca(OH)_2}\right]\left[\frac{1\ moles\ H_3PO_4}{3\ moles\ OH^{-}}\right]$$

? Vol. of H_3PO_4 solution = 76.40 mL

vii. Starting Information:

Concentrations expressed in Terms of...	Acid/Base? Strong? Weak?	But what's really present in the solution is...
reactant solution A: hydrobromic acid HBr 20.00 mL 0.154M	STRONG ACID	$HBr_{(aq)} \Rightarrow H^{1+}_{(aq)} + Br^{1-}_{(aq)}$ — HBr: **none** present; H^{1+} + Br^{1-}: only ions present
and		
reactant solution B: lithium hydroxide LiOH 45.00 mL 0.0941 M	STRONG BASE	$LiOH_{(aq)} \Rightarrow Li^{1+}_{(aq)} + OH^{1-}_{(aq)}$ — LiOH: none present; Li^{1+} + OH^{1-}: **only** ions present

Will any combination of the above produce a net reaction?

Net Ionic equation:

$$H^{1+}_{(aq)} + OH^{1-}_{(aq)} \Rightarrow HOH$$

Recognize this as a limiting reagent type of a problem because moles of both reactants are given (moles = M x L). It will be solved using a slightly different approach, everything will be based on moles (or millimoles) reactants and the net ionic equation.

First determine millimoles of hydrogen cation furnished by hydrobromic acid, and then similarly determine millimoles of hydroxide anion furnished by lithium hydroxide.

mmoles $\mathbf{H^{1+}}_{(aq)}$ = mmoles **HBr** [C.F.]= (0.0941 M)(45.00 mL) $\left[\dfrac{1\ moles\ H^{1+}}{1\ moles\ HBr}\right]$ = **3.08 mmoles H^{1+}**

mmoles $\mathbf{OH^{1-}}_{(aq)}$ = mmoles **LiOH** [C.F.]=(0.154 M)(20.00 mL) $\left[\dfrac{1\ moles\ OH^{1-}}{1\ moles\ LiOH}\right]$ = **4.24 mmoles OH^{1-}**

Construct a 4X4 matrix as shown. Place the net ionic equation into the first row, and enter starting amounts of all substances in the **B4** row (B4 = before reaction occurs). Clearly, hydrogen cation is the limiting reagent so it will all be used up (i.e., lost, therefore minus sign). Consequently, enter a negative 3.08 in the react row, as shown in red.

	$1\ H^{1+}$	$1\ OH^{1-}$ ⟶	$1\ HOH$
B4	**3.08**	**4.24**	**lots**
REACT (-1:-1:+1)	**-3.08**	**-3.08**	**+3.08**
AFTR	**none**	**1.16**	**lots + 3.08 = lots**

Since ONE H^{1+} reacts with **ONE OH^{1-}** (i.e., the coefficients for these two reactants is 1 : 1) the same amount of hydroxide must also react. So this value is entered and is shown in green. The proper amount of water formed (i.e., gained, therefore plus sign) is also in green. For reactants, *subtract* **REACT** moles from **B4** moles to find what remains after reaction is complete (**AFTR**). For products, *add* **REACT** moles to **B4** moles. These values are shown in black. The concentration of the hydroxide anion present in an excess amount is then found to be...

$$[\ OH^{1-}\ ] = \left(\frac{mmoles\ solute}{mL\ solution}\right) = \left(\frac{1.16}{(45+20)}\right)$$ = **0.0178 M in hydroxide anion**

viii. Starting Information:

Concentrations expressed in Terms of...	Acid/Base? Strong? Weak?	But what's really present in the solution is...
reactant solution A: sulfuric acid H_2SO_4 21.10 mL 0.228M	STRONG ACID	$H_2SO_{4\,(aq)} \Longrightarrow 2\,H^{1+}_{(aq)} + SO_4{}^{2-}_{(aq)}$ **none** present ... only ions present*
and		
reactant solution B: sodium hydroxide NaOH 26.21 mL 0.363 M	STRONG BASE	$NaOH_{(aq)} \Longrightarrow Na^{1+}_{(aq)} + OH^{1-}_{(aq)}$ none present ... **only** ions present

*(not completely true)

Will any combination of the above produce a net reaction?

Net Ionic equation:

$$H^{1+}_{(aq)} + OH^{1-}_{(aq)} \Longrightarrow HOH$$

Recognize this as a <u>limiting reagent</u> type of a problem because moles of both reactants are given (moles = M x L). It will be solved using the same approach as for problem vii, everything will be based on moles (or millimoles) reactants and the net ionic equation.

First determine millimoles of hydrogen cation furnished by sulfuric acid, and then similarly determine millimoles of hydroxide anion furnished by sodium hydroxide.

mmoles $H^{1+}_{(aq)}$ = mmoles H_2SO_4 [C.F.]= (0.228 M)(21.10 mL)$\left[\dfrac{2\ moles\ H^{1+}}{1\ moles\ H_2SO_4}\right]$

= **9.62 mmoles H^{1+}**

mmoles $OH^{1-}_{(aq)}$ = mmoles **NaOH** [C.F.]=(0.363 M)(26.21 mL) $\left[\dfrac{1\ moles\ OH^{1-}}{1\ moles\ NaOH}\right]$

= **9.51 mmoles OH^{1-}**

Construct a 4X4 matrix as shown. Place the net ionic equation into the first row, and enter starting amounts of all substances in the **B4** row (B4 = before reaction occurs). Clearly, hydrogen cation is the limiting reagent so it will all be used up (i.e., lost, therefore minus sign). Consequently, enter a negative 7.27 in the react row, as shown in red.

	$1\ H^{1+}$	$1\ OH^{1-} \longrightarrow$	1 HOH
B4	**9.62**	**9.51**	**lots**
REACT (-1:-1:+1)	**-9.51**	**-9.51**	**+9.51**
AFTR	**0.11**	**none**	**lots +9.51 = lots**

Since ONE H^{1+} reacts with **ONE OH^{1-}** (i.e., the coefficients for these two reactants is 1 : 1) the same amount of hydroxide must also react. So this value is entered and is shown in green. The proper amount of water formed (i.e., gained, therefore plus sign) is also in green. For **AFTR** moles, *subtract* **REACT** moles from **B4** moles to find what remains after reaction is complete. For products, *add* **REACT** moles to **B4** moles. These values are shown in black. The concentration of the hydrogen cation present in an excess amount is then found to be...

$$[H^{1+}] = \left(\frac{mmoles\ solute}{mL\ solution}\right) = \left(\frac{0.11}{(21.10 + 26.21)}\right)$$ = **2.33E-3 M in hydrogen cation, (pH = 2.63)**