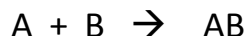


### Unit 3: Equilibrium and Acid-Base Chemistry

#### Dynamic Equilibrium in Chemical Systems (pg 424)

Although a chemical reaction may appear to have stopped completely, reactions at the molecular level (not visible to the eye) may still be occurring. For example in the reaction:



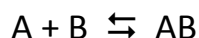
When A & B react to form AB, it can be expected that AB is also trying to react to form A & B again. So we essentially end up with two reactions:

- 1) **Forward reaction:** the left-right reaction ( $A + B \rightarrow AB$ )
- 2) **Reverse reaction:** the right-left reaction ( $AB \rightarrow A + B$ )

A situation where both the forward and reverse reactions are occurring is called dynamic equilibrium.

**Dynamic equilibrium:** a balance between forward and reverse processes occurring at the same rate

Equilibrium equations are written with double arrows showing that both reactions are occurring.



There are also different forms of dynamic equilibrium:

- 1) **Solubility equilibrium:** dynamic equilibrium between a solute and a solvent eg.  $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq})$
- 2) **Phase equilibrium:** dynamic equilibrium between different physical states of a pure substance eg.  $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$
- 3) **Chemical reaction equilibrium:** dynamic equilibrium between reactants and products of a chemical system

This leads to the concept of **reversible reactions:** a reaction that can achieve equilibrium in the forward or reverse reaction. All chemical reactions are now considered to be reversible, but they are distinguished in terms of to what extent they go one way or the other.

- 1) **Reactants strongly favoured:** observable reaction is <1%, so mixing reactants has no observable results.
- 2) **Products strongly favoured:** observable reaction is > 99%. Reactions are considered complete and are represented using only a single  $\rightarrow$  to show that reverse reaction is pretty much negligible.
- 3) **Reactants achieving equilibrium:** always significant amounts of both product and reactant present. If more reactants present, then reverse reaction is favoured more, and if more products present, then forward reaction favoured more.

### Calculating Concentrations at Equilibrium (pg 433)

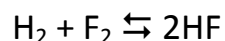
To calculate equilibrium concentrations, we will use an **ICE** table.

	A	B	$\rightleftharpoons$	AB
Initial Concentration				
Change in concentration				
Equilibrium concentration				

\*\* equation must be balanced to use ICE tables!!

### Example 1 (pg 433)

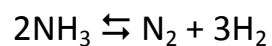
Consider the following equation for the formation of hydrogen fluoride from its elements at SATP:



If the reaction begins with 1.00 mol/L concentrations of  $\text{H}_2$  and  $\text{F}_2$  and no HF, calculate the concentrations of  $\text{H}_2$  and HF at equilibrium if the equilibrium concentration of  $\text{F}_2$  is measured to be 0.24 mol/L.

Example 2 (pg 435)

When ammonia is heated, it decomposes into nitrogen gas and hydrogen gas according to the following equation.



When 4.0 mol of  $\text{NH}_3$  is introduced into a 2.0 L rigid container and heated to a particular temperature, the amount of ammonia changes to 1.0 mol/L.

Determine the equilibrium concentrations of the other 2 entities.

*Practice pg 437 #6,7*

*Pg 437-8 #5, 8, 9a*

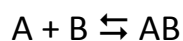
### Qualitative Changes in Equilibrium Systems (pg 450)

**Le Chatelier's Principle:** when a chemical system at equilibrium is disturbed by a change in a property, the system adjusts in a way that opposes the change. This results in an **equilibrium shift:** movement of a system equilibrium, resulting in a change in the concentrations of reactants and products

Variable	Type of Change	Response of System
Concentration	Increase	Shift to consume added reactant or product
	Decrease	Shift to replace added reactant or product
Temperature	Increase	Shift to consume added thermal energy
	Decrease	Shift to replace removed thermal energy
Volume	Increase (decrease pressure)	Shift to side with larger amount of gaseous entities
	Decrease (increase pressure)	Shift to side with smaller amount of gaseous entites

#### Example 1.

Consider the reaction:



Predict shift if you:

- Increase [A], decrease [AB]
- Increase temperature of products, decrease temperature of reactants
- Increase volume, decrease volume

### Changes That Do Not Affect the Position of Equilibrium Systems (pg 455)

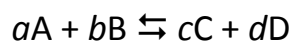
- 1) **Adding catalysts:** decreases time to reach equilibrium, but does not affect position of equilibrium
- 2) **Adding inert gas:** gas doesn't react but does increase pressure. However it adds pressure to reactants and products so there is no effect on shift for equilibrium.

Practice pg 457 # 1, 3, 4

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### Equilibrium Law in Chemical Reactions (pg 439)

#### **Equilibrium Law Expression:**



$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where,

A, B, C, and D are chemical entities in gas or aqueous phases

$a$ ,  $b$ ,  $c$ , and  $d$  are the coefficients in the balanced chemical equation

K is the **equilibrium constant**

**Equilibrium constant:** value obtained from the mathematical combination of equilibrium concentrations using the equilibrium law expression

Eg.  $H_2 + I_2 \rightleftharpoons 2HI$

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

\* products **always** on top and reactants **always** on the bottom

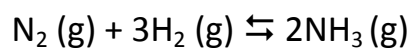
\*\* exponents are **always** the coefficients

\*\*\* concentrations are **always** the concentrations at **equilibrium!!**

Calculating K (pg 442)

Example 1. (pg 443)

Nitrogen and hydrogen combine to form ammonia, according to the following balanced equation:



Calculate the value of the equilibrium constant for this reaction if the following concentrations were measured at equilibrium, at 500°C,

$$[\text{N}_2] = 1.50 \times 10^{-5} \text{ M}$$

$$[\text{H}_2] = 3.45 \times 10^{-1} \text{ M}$$

$$[\text{NH}_3] = 2.00 \times 10^{-4} \text{ M}$$

Example 2 (pg 443)

Calculate the value of the equilibrium constant for the decomposition of ammonia at 500°C into its elements. Use the same equilibrium concentrations as example 1.

**\*Note:** if any part of the equation is a liquid or solid, it is **not** included in the equilibrium law expression (see example pg 446)

*Practice pg 442 #1*

*Practice pg 444 #2-6*

*Practice pg 447 # 7bc*

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### The Magnitude of K (pg 447)

The value of K can tell you about the level of equilibrium occurring in the reaction.

- 1)  $K \gg 1$ : [products] much greater than [reactants] at equilibrium
- 2)  $K \approx 1$ : [products] and [reactants] are approximately equal at equilibrium
- 3)  $K \ll 1$ : [reactants] much greater than [products] at equilibrium

### Quantitative Changes in Equilibrium Systems (pg 463)

We looked at equilibrium shift above using LeChatelier's principle, but what if you are only given numerical values? You can determine shifts if you know the concentration values and measure of K at equilibrium.

**Reaction Quotient, Q:** calculated value using measured concentrations in a system

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The formula is the same for K, but you will be calculating Q and comparing it to a known value of K. So values used to calculate Q may not be at equilibrium.

To use Q and K to determine equilibrium shift:

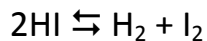
- 1)  $Q = K$ : system is at equilibrium
- 2)  $Q > K$ : more products than reactants, so reaction shifts left
- 3)  $Q < K$ : more reactants than products, so reaction shifts right

Example 1 (pg 464)

In a container at 450°C, nitrogen and hydrogen react to produce ammonia. The equilibrium constant,  $K$ , is 0.064. When the system is analyzed the concentrations are found to be as follows:  $[N_2]$  is 4.0 mol/L,  $[H_2]$  is  $2.0 \times 10^{-2}$  mol/L, and  $[NH_3]$  is  $2.2 \times 10^{-4}$  mol/L. Determine whether the system is at equilibrium and if it is not, predict the direction in which the reaction will proceed.

Example 2 (pg 464)

The following reaction occurs in a closed container at 445°C. The equilibrium constant,  $K$ , is 0.020.



Is the system at equilibrium in each of the following cases. If not, predict the direction in which the reaction will proceed to reach equilibrium.

- a)  $[HI] = 0.14$  M,  $[H_2] = 0.04$  M,  $[I_2] = 0.01$  M
- b)  $[HI] = 0.20$  M,  $[H_2] = 0.15$  M,  $[I_2] = 0.09$  M

*Practice pg 465 # 1, 2*

*Also if you know  $K$  and some [], you can find an unknown [] for the reaction. Pg 466 #3-4*

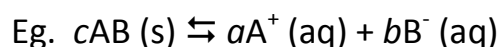


## The Solubility Product Constant (pg 483)

**Solubility:** numerical value stating maximum concentration of a solute dissolved in a saturated solution

Since soluble substances will dissolve, we will be looking at calculations for substances that are insoluble or sparingly soluble.

**Solubility product constant,  $K_{sp}$ :** value obtained from equilibrium law applied to saturated solutions



$$K_{sp} = \frac{[A^+]^a[B^-]^b}{[AB]^c}$$

\*But if you recall, you don't include solids in the equation to calculate K so you know get:

$$K_{sp} = [A^+]^a[B^-]^b$$

where,

$A^+$  and  $B^-$  are ions formed in aqueous phases

$a$ , and  $b$  are the coefficients in the balanced ionic equation

$K_{sp}$  is the solubility product constant

Values may be found on pg 484, appendix C or the back of your periodic table.

Example 1. (pg 485)

Magnesium fluoride is a hard, slightly soluble salt that is used to make spectral lenses for technical instruments. Calculate  $K_{sp}$  for magnesium fluoride at 25°C, given a solubility of 0.00172g/100mL.

Example 2. (pg 485)

Calculate the molar solubility of zinc hydroxide where  $K_{sp}$  is  $7.7 \times 10^{-17}$ .

*Practice pg 486 # 1-4*

### Predicting Precipitation (pg 487)

\*See table 487 to determine solubility of products

Recall calculating the reaction quotient,  $Q$ . You can calculate  $Q$  again (this time it is called **trial ion product**) and determine a substance's solubility.

- 1)  $Q = K_{sp}$ : system cannot dissolve more, saturated (no precipitate)
- 2)  $Q > K_{sp}$ : more ions dissolved than necessary, supersaturated (precipitate)
- 3)  $Q < K_{sp}$ : all ions dissolved, unsaturated (no precipitate)

### Example 1. (pg 488)

If 100 mL of 0.100 M  $\text{CaCl}_2$  and 100 mL of 0.0400 M  $\text{Na}_2\text{SO}_4$  are mixed at  $20^\circ\text{C}$ , determine whether or not a precipitate will form. For  $\text{CaSO}_4$  at  $20^\circ\text{C}$ ,  $K_{sp}$  is  $3.6 \times 10^{-5}$ .

Example 2. (pg 488)

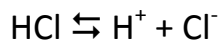
Would a precipitate of lead (II) sulphate ( $K_{sp} = 1.8 \times 10^{-8}$ ) form if 255 mL of 0.00016 M lead (II) nitrate is poured into 456 mL of 0.00023 M sodium sulphate?

*Practice pg 489 #5*

The Common Ion Effect (pg 490)

**Common ion effect:** reduction in solubility of a salt caused by the presence of another salt have a common ion

Consider the 2 reactions:



NaCl dissolves in water. But if you add HCl to the NaCl solution, you can precipitate out the NaCl. This is because HCl adds  $\text{Cl}^-$  ions to the product and because of Le Chatelier's principle, the reaction will shift to the left, and hence precipitate out the NaCl.

Example 1 (pg 491)

What is the molar solubility of  $\text{PbCl}_2$  in a 0.2 M NaCl solution at SATP?

*Practice pg 492 #7, 9-11*

## Acid-Base Equilibrium (pg 529)

If you recall, we have stated that acids start with  $H^+$  and bases end with  $OH^-$ .

However, there are certain times when something is acidic or basic, but doesn't contain H or OH.

## Bronsted-Lowry Theory

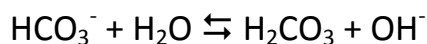
Note:  $H^+$  is equivalent to a proton.

According to the Bronsted-Lowry concept,

A Bronsted-Lowry acid is a proton donor

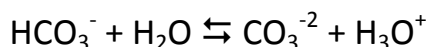
A Bronsted-Lowry base is a proton acceptor

Eg.



$HCO_3^-$  is the base because it **gained** a proton to form  $H_2CO_3$ .

$H_2O$  is the acid because it **donated** the proton and was left as  $OH^-$ .



**Now,**

$HCO_3^-$  is the acid because it **donated** a proton to be left as  $CO_3^{2-}$ .

$H_2O$  is the base because it **gained** the proton to form  $H_3O^+$ .

In the above reactions,  $H_2O$  is **amphoteric**: a substance capable of acting as an acid or base in different chemical reactions.

**Conjugate pairs:** two substances in an equation whose formulas differ only by one  $H^+$  unit

So in the first example above,  $HCO_3^-$  is the base and  $H_2CO_3$  is its conjugate acid.

This is because if you reversed the reaction, the  $H_2CO_3$  would be the acid and

$HCO_3^-$  would be the base (making it the conjugate base). And,  $H_2O$  is the acid and

its conjugate base is  $OH^-$ .

**Strong Acids:** placing strong acids in water involves a reaction that is almost completely in the forward direction

**Weak Acids:** placing weak acids in water involves a reaction that favours the reverse direction

\* Note: strong and concentrated do not mean the same thing! Do not use the terms incorrectly!

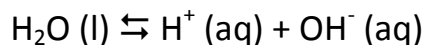
The above statements lead to the following generalization:

The stronger the acid, the weaker its conjugate base, and conversely, the weaker an acid, the stronger its conjugate base.

*Practice pg 532 # 1, 2*

### The Autoionization of Water (pg 532)

In a sample of pure water, collisions of water molecules leads to water **autoionization:** water separating into its ions.



From this, we get another constant known as **ion product constant for water,  $K_w$** .

$$K_w = [\text{H}^+][\text{OH}^-]$$

\*at equilibrium  $K_w = 1.0 \times 10^{-14}$ ;  $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$  mol/L

\*\*  $K_w$  value is valid at SATP, but not at values much higher or lower. Some values are given in table 1, pg 534.

You can also state the following about solutions:

Neutral solutions  $[\text{H}^+] = [\text{OH}^-]$

Acidic solutions  $[\text{H}^+] > [\text{OH}^-]$

Basic solutions  $[\text{H}^+] < [\text{OH}^-]$

### Strong Acids (pg 534)

Since acids fully favour the formation of its ions, you can use the values now of  $K_w$  to calculate concentrations of  $H^+$  and  $OH^-$  in strong acid solutions.

### Example 1 (pg 535)

A 0.15 mol/L solution of hydrochloric acid at SATP is found to have a hydrogen ion concentration of 0.15 mol/L. Calculate the concentration of the hydroxide ions.

### Example 2 (pg 536)

Calculate the hydroxide ion concentration in 0.25 mol/L HBr solution.

*Practice pg 537 # 4-6*



### Strong Bases (pg 537)

The same principles apply to strong bases.

Note: if there are 2 hydroxides ( eg.  $\text{Ca}(\text{OH})_2$ ), you must multiply the base concentration by 2.

ie. If concentration of  $\text{Ca}(\text{OH})_2 = 0.10 \text{ mol/L}$

Concentration of  $\text{OH}^- = 2 \times 0.10 = 0.20 \text{ mol/L}$

### Example 1. (pg 538)

Calculate the hydrogen ion concentration in a  $0.025 \text{ mol/L}$  solution of barium hydroxide, a strong base.

### Example 2. (pg 539)

Determine the hydrogen ion and hydroxide ion concentrations in 500 mL of an aqueous solution containing 2.6 g of dissolved sodium hydroxide.

*Practice pg 540 # 8-10*

## Hydrogen Ion Concentration and pH (pg 540)

**pH:** relates to  $H^+$  concentration

**pOH:** relates to  $OH^-$  concentration

### pH and Acidity

Acid solutions      pH 0-7

Neutral solutions      pH = 7

Basic solutions      pH = 7-14

Some formulae to know:

$$pH = -\log[H^+] \qquad pOH = -\log[OH^-]$$

$$[H^+] = 10^{-pH} \qquad [OH^-] = 10^{-pOH}$$

$$pH + pOH = 14.00$$

Furthermore:

$$pK_w = -\log K_w \qquad pH + pOH = pK_w$$

### Example 1 (pg 541)

Calculate the pH of a solution with a hydrogen ion concentration of  $4.7 \times 10^{-11}$  M.

### Example 2 (pg 542)

Calculate the pOH of a solution with a hydroxide ion concentration of  $3.0 \times 10^{-6}$  M.

### Example 3 (pg 543)

What is the pOH of a solution whose pH is measured to be 6.4?

pH of Strong Acids (pg 544)

We can now use all of the above formulae to determine pH of a strong acid.

Example 1 (pg 545)

Calculate the pH, pOH, and  $[\text{OH}^-]$  of a 0.042 M  $\text{HNO}_3$  solution.

Example 2. (pg 545)

Calculate the pH, pOH, and  $[\text{OH}^-]$  of a 0.0020 M HBr solution.

*Practice pg 546 #12-14*

pH of Strong Bases (pg 547)

Again use the same principles to apply to strong bases!

Example 1. (pg 547)

Calculate the pH of a 0.02 M NaOH solution.

Example 2. (pg 547)

Calculate the pH and pOH of a solution prepared by dissolving 4.3 g of  $\text{Ba}(\text{OH})_2$  in water to form a 1.5 L solution.

*Practice pg 549 # 17-19*

### Weak Acids and Bases (pg 551)

**Weak acid:** acid that partially ionizes in solution but exist primarily in the form of its molecules

**Weak base:** base that has a weak attraction for protons

### Percent Ionization of Weak Acids

$$[\text{H}^+] = p/100 \times [\text{HA}]$$

where,

p is percent ionization

[HA] is concentration of acid

Percent ionization refers to how much a weak acid separates into its ions.

### Example 1. (pg 553)

The pH of a 0.10 mol/L methanoic acid solution is 2.38. Calculate the percent ionization of methanoic acid.

Example 2. (pg 553)

Calculate the percent ionization of propanoic acid,  $\text{HC}_3\text{H}_5\text{O}_2$ , if a 0.050 M solution has a pH of 2.78.

*Practice pg 554 #1, 2*

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Ionization Constants for Weak Acids (pg554)

Weak acids and bases often ionize less than 50%. Because weak acids and bases do not completely ionize, we cannot use the ionization constant for water ( $K_w$ ). Instead of using  $K_w$ , we will use  **$K_a$  – acid ionization constant**. These are calculated constants and are found in tables (see front of your periodic table).

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

Example 1. (pg 554)

Calculate the acid ionization constant,  $K_a$ , of acetic acid if a 0.1000 M solution at equilibrium at SATP has a percent ionization of 1.3%.

Example 2. (pg 555)

Calculate the  $K_a$  of hydrofluoric acid, HF, if a 0.100 M solution at equilibrium at SATP has a percent ionization of 7.8%.

*Practice pg 556 # 3-5*

**#4 – HF percent = 7.8%, HCN % = 0.0078%**



### Ionization Constants for Weak Bases

The same steps apply for weak bases:

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

Furthermore, you can now relate  $K_a$  and  $K_b$  together with  $K_w$  to get:

$$K_a K_b = K_w \quad \text{or} \quad K_b = K_w / K_a \quad \text{or} \quad K_a = K_w / K_b$$

#### Example 1. (pg 561)

What is the value of the base ionization constant,  $K_b$ , for the acetate ion,  $C_2H_3O_2^-$ , at SATP?

#### Example 2. (pg 561)

The  $K_b$  for hydrazine,  $N_2H_4$ , a rocket fuel, is  $1.7 \times 10^{-6}$ . What is the  $K_a$  of its conjugate acid,  $N_2H_5^+$ ?

*Practice pg 563 #6*

The pH of Weak Acid Solutions and Weak Base Solutions (pg 563 & 570)

You will now use ICE tables and either  $K_a$  or  $K_b$ , as well as the pH and pOH equations to solve weak acid and weak base problems.

Example 1. (pg 563)

Calculate the hydrogen ion concentration and the pH of a 0.10 M acetic acid solution.

Example 2. (pg 569)

You measure the pH of a 0.100 M hypochlorous acid, HOCl solution, and find it to be 4.23. What is the  $K_a$  for hypochlorous acid?

Example 3. (pg 573)

Morphine,  $C_{17}H_{19}NO_3$ , is a weak base and a powerful painkiller. A solution of morphine has a concentration of 0.01 M. Determine the pH of this solution. The  $K_b$  of morphine is  $7.5 \times 10^{-7}$ .

*Practice pg 568 #7, 8; pg 570 #9, 10; pg 574 #12-13*

## Hydrolysis of Metal and Non-metal Oxides (pg 590)

### **Rules:**

Metal oxides react with water to form **basic** solutions.

Nonmetal oxides react with water to form **acidic** solutions.

### Example 1. (pg 591)

Predict whether solutions produced will be acidic, neutral, or basic.

- a) Magnesium oxide
- b) Sulphur dioxide
- c) Copper (I) oxide

*Practice pg 594 #5*

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## Acid-Base Titration (pg 595)

Acid-base titrations are used to determine how much acid or base is required to neutralize another base or acid, respectively.

**Titration:** precise addition of a solution in a buret into a measure volume of a sample solution

**Titrant:** solution in a buret during a titration

**Sample:** solution being analyzed in a titration

Samples containing unknown concentrations can be measured against similar samples of known concentrations to determine the amount of product present in a sample.

**Primary standard:** a chemical available in pure and stable form, for which an accurate concentration can be prepared

**Equivalence point:** measured quantity of titrant recorded at the point at which chemically equivalent amounts have reacted

**Endpoint:** point in a titration at which a sharp change in a measurable and characteristic property occurs; eg. A colour change in an acid-base indicator

### Basic Titration Calculations

You can use the following formula to determine concentration and volume in acid-base titrations:

$$c_A v_A n_A = c_b v_b n_b$$

$c_A$  = [acid]

$v_A$  = volume of acid

$n_A$  = moles of acid (subscript beside H in formula)

$c_b$  = [base]

$v_b$  = volume of base

$n_b$  = moles of base (subscript beside OH in formula)

#### Example 1

You titrate 40 ml of NaOH with 25 ml of 2.0 M HCl. What is the concentration of the NaOH?

#### Example 2

How much 2.5 M NaOH will you need to titrate 50 ml of a 1.8 M solution of  $H_2SO_4$ ?

*See Practice*

Titrating a Strong Acid with a Strong Base (pg 596)

Example 1 (pg 596)

In a titration, 20.00 mL of 0.300 M HCl is titrated with standardized 0.300 mol/L NaOH. What is amount of unreacted HCl and the pH of the solution after the following volumes of NaOH have been added?

- a) 0 mL
- b) 10.0 mL
- c) 20.0 mL

*Practice pg 599 #1, 2*

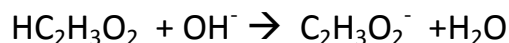
### Buffers (pg 615)

**Buffer:** a mixture of a conjugate acid-base pair that maintains a nearly constant pH when diluted or when a strong acid or base is added

Buffers occur in a region on the titration curve that is nearly horizontal where an addition of acid/base doesn't really affect the pH significantly. Usually buffers are prepared by mixing a weak acid with a soluble salt containing its conjugate base (eg. Acetic acid and sodium acetate) or a weak base with its salt of a conjugate acid (ammonia with ammonium chloride). The two components of a buffer are mixed to produce approximately equal molar concentrations of the conjugate acid-base pair.

### Explaining Buffers (pg 615)

Consider the reaction of NaOH with acetic acid-acetate buffer:



Adding a small amount of the hydroxide would convert a small amount of acetic acid into acetate ions. The overall effect is a small decrease in the ratio of acetic acid to acetate ions in the buffer and a slight increase in pH. The change is so small that the pH changes only very little.

Buffers are synthesized or exist naturally (eg. Blood) for a purpose of counteracting small amounts of acid or base that may be inadvertently added to the mixture.

### Capacity of a Buffer (pg 616)

There is however a limit to the amount of strong acid or base a buffer can neutralize before its pH begins to rise rapidly. A buffer's capacity depends on the concentrations of its conjugate acid-base pair.

Example 1. (pg 616)

A 1.0 L buffer is prepared that contains 0.20 M acetic acid and 0.20 M sodium acetate at equilibrium.

- a) Calculate the pH of the buffer.
- b) If 0.10 M of  $H^+$  is added to the buffer without changing its volume, calculate the pH.
- c) Compare the change in pH to the change expected if the same amount of  $H^+$  is added to water to make a 1.0 L solution.

*Practice pg 620 # 3 (practice)*