pH AND ITS MEASUREMENTS

INTRODUCTION

One important property of an aqueous solution is its concentration of hydrogen ion. The $[H^+]$ (or $[H_3O^+]$) ion has great effect on the solubility of many compounds and on the rates of chemical reactions. It is important to know how to measure the concentration of hydrogen ion.

For convenience the concentration of H^+ ion is frequently expressed as the pH of the solution rather than as its molarity. The pH of the solution is defined by the following equation:

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

Where the logarithm is taken to the base 10. If the $[H^+]$ is 1×10^{-4} M, the pH of the solution is 4.0. If the $[H^+]$ is 5×10^{-2} M, the pH is 1.3.
In water solution the following equilibrium takes place:

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$

In distilled water, $[H^+]$ equals $[OH^-]$. Each is equal to 1×10^{-7} M. Therefore,

$$[H^+][OH^-]=K_w= 1\times10^{-14}$$

Where, K_w is the ion product constant for water.
The pH of distilled water is 7.0. Solutions in which $[H^+]>[OH^-]$ are said to be acidic and will have a pH less than 7.0; if $[H^+] < [OH^-]$, the solution is basic and its pH is more than 7.0. A solution with a pH of 10.0 will have a $[H^+]$ of 1×10^{-10} M and a $[OH^-]$ of 1×10^{-4} M

$[H^+]$, M	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
pH	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$[OH^-]$, M	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}

← more acidic   neutral   more basic →

MEASURING pH OF A SOLUTION

The experimental determination of the pH of a solution is commonly performed by either of two methods. The first of these methods involves the use of chemical dyes called indicators. These substances are generally weak acids/bases and can exist in either of two colored forms, depending on whether or not the molecule is protonated, HIn, or has been deprotonated, In^-. In aqueous solution, an equilibrium exists:

$$\underset{\text{First color}}{HIn} \rightleftharpoons \underset{\text{second color}}{H^+ + In^-}$$

Depending on what other acidic/basic substances are present in the solution, the equilibrium of the indicator will shift, and one or the other colored form of the indicator will predominate and impart its color to the entire solution.

Indicators commonly change colors over a relatively short pH range (about 2 pH units), and when properly chosen can be used to determine the range of the pH of the solution. A given indicator is useful for determining pH only in the region in which it changes color. Indicators are available for measurement of pH in all ranges of acidity and basicity.

Name of indicator	pH interval	Color range
Thymol blue	1.2-2.8	Red to yellow
Orange IV	1.3-3.0	Red to yellow
Methyl orange	3.1-4.4	Red to orange to yellow
Cangp red	3.0-5.0	Blue to red
Bromcresol green	3.8-5.4	Yellow to blue
Methyl red	4.4-6.2	Red to yellow
Bromcresol purple	5.2-6.8	Yellow to purple
Bromthymol blue	6.0-7.6	Yellow to blue
Thymol blue	8.0-9.6	Yellow to blue
Alizarin yellow R	10.0-12.0	Yellow to red
Indigo carmine	12.0-13.0	Blue to yellow

Table: Color changes and pH intervals of some important indicators

By matching the color of a suitable indicator in a solution of known pH with that in an unknown solution, one can determine the pH of the unknown.

The second method for the determination of pH involves an instrument called a pH meter/pH pen. The pH pen is designed so that the reading will directly furnish the pH of the solution. A pH pen gives much more precise measurement of pH than does a typical indicator, and is ordinarily used when an accurate determination of pH is needed.

INSTRUCTIONS FOR THE OPERATION OF A pH PEN

1. Check out a pH pen from the stockroom. The pH sensing electrode is made of glass and is therefore very fragile and expensive. You will be asked to pay for the electrode if you break it. Handle the electrode gently.

2. Rinse the tip of the pH pen with *tap* water and blot it gently with a Kimwipe. Do not use distilled water for rinsing the tip of the electrode. Distilled water will damage the electrode sensor.

3. Immerse the tip of the electrode in the solution to be measured to a depth of ~ 1-1.5 cm. Under no circumstances immerse it above the immersion level marked on the pH pen. Ask your instructor about the location of this mark.

4. The ON/OFF switch is located on top. Turn it ON only when you are taking readings. Do not leave it ON all the time for the sake of saving the battery inside it.
5. It takes about 5 seconds after turning it ON for the pH reading to be stable. There should be no drifting or fluctuation in reading after that. If there is any problem regarding the pH pen, report it to your instructor.

WEAK AND STRONG ACIDS AND BASES (THE STRENGTH OF ACIDS AND BASES)

Some acids and bases undergo substantial ionization in water and are called strong because of their essentially complete ionization in reasonably dilute solutions. Other acids and bases, because of their incomplete ionization (often only about 1% in a 0.1 M solution), are called weak. Hydrochloric acid, HCl, and sodium hydroxide, NaOH, are typical examples of a strong acid and a strong base, respectively. Acetic acid, $HC_2H_3O_2$, and ammonia, NH_3, are examples of a weak acid and a weak base.

A weak acid will ionize according to the following equilibrium equation:

$$HA\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+(aq) + A^-\ (aq)$$

The strength of an acid depends on its extent of ionization, that is, the number of moles of H^+ ions formed in the water per mole of original acid.

$$\boxed{\%\ \text{ionization} = \frac{[H^+]_{formed}}{M_{HA(\text{original acid concentration})}} \times 100}$$

PROCEDURE

Day 1

A. pH OF ACID, BASE AND SALT SOLUTIONS.

Use the pH pen to test samples of the solutions of acids, bases and salts listed in Table A on the report sheet. Set up a spot plate. Fill the wells of the spot plate (3/4 full) each with one of the solutions listed in part A of the report sheet. Rinse the tip of the pH pen with tap water between tests. Record the results.

After completing the pH measurements, comment on the pH of the salts as compared to the pH of the acids and bases tested. Are salt solutions always neutral?

B. DILUTING SOLUTIONS

In this part of today's experiment you will prepare 0.010 M and 0.0010 M solutions of HCl and NaOH needed for **part C** of the experiment.

STOPPER AND SAVE ALL SOLUTIONS PREPARED IN **PART B** TO BE USED FOR **PART C IN** NEXT LAB PERIOD.

1. Prepare a 0.010 M HCl solution

Show on the report sheet your calculation of the volume of 0.10 M HCl needed to make 20.00 ml of 0.010 M HCl solution. Ask your instructor to check it.

Use the solution from the Chem 111 reagent shelves that is labeled, 0.10 M HCl, and make the dilution as calculated using a 10 ml graduate cylinder. Mix well. Label and save the solution in a 25 ml Erlenmeyer flask. Some of it will be used for part 2 and the rest will be saved for **part C**

2. Prepare a 0.0010 M HCl solution

Use 4.00 ml of your 0.010 M HCl to prepare 0.0010 M HCl solution. What volume will you make? __________ ml

Mix the 0.0010 M HCl solution well. Label and save the solution. A portion of it will be used for part 3 and the rest will be saved in a 50 ml Erlenmeyer flask for **part C**

3. Measure the pH of your 0.0010 M HCl solution and calculate the $[H^+]$

Pour about 5 ml of your 0.0010 M HCl solution into one of the wells of a spot plate. Save the rest for use in **part C** of the experiment. Use the pH pen to measure the pH of the solution in the spot plate. Calculate from the measured pH the actual $[H^+]_{exp}$ of this solution. Calculate the theoretical, $[H^+]_{theo}$ of a 0.0010 HCl.

Calculate your percent error in preparing 0.0010 M HCl by dilution in terms of $[H^+]$.

$$\% \text{ error} = \frac{|[H^+]_{theo} - [H^+]_{exp}|}{[H^+]_{theo}} \times 100$$

4. Prepare 0.010 M NaOH solution

Use 0.10 M NaOH from the Chem 111 reagent shelves to prepare 20.00 ml of 0.010 M NaOH. Label and save the solution. A prtion of it will be used for part 5 and the rest will be saved in a 25 ml Erlenmeyer flask for **part C.**

5. Prepare 0.0010 M NaOH solution

Use your 0.010 M NaOH to prepare 20.00 ml of 0.0010 M NaOH solution. Label and save in a 25 ml Erlenmeyer flask for **part C** and **part E.**

Day 2

C. INDICATOR COLORS

Calculate the theoretical pH that corresponds to the listed concentrations of strong acids (HCl) and strong base (NaOH) in Table B on your report sheet.

It is recommended that you prepare all 24 solutions named in Table B on your report sheet in one lab period for the sake of comparing the developed color of the different indicators. The buffer solutions have been prepared and are on the Chem 111 reagent shelves. Set up three spot plates. Each spot plate will have a set of eight solutions. Each set will have a specific indicator. The wells should be ¾ filled with the solutions. Each set will have equal volumes of solutions. Do not measure the solutions with a graduate cylinder. You should be able to estimate equal amounts. Add one drop of the indicator named. Make sure all eight solutions have the same amount of drops of indicator. On the chart record the colors observed. From the constructed chart write down at what pH interval the indicators changed colors. **Show your result to your instructor and get approval**.

Save only the set of eight solutions containing **Orange IV** indicator. You will need this set for part C of the experiment. Dispose of the other two sets of solutions containing Methyl orange and alizarin yellow.

D. PERCENT OF IONIZATION OF A WEAK ACID

1. The 1.0 M and 0.10 M $HC_2H_3O_2$ solutions are on the Chem 111 reagent shelves. Put the 1.0 M $HC_2H_3O_2$ in one well of the spot plate (3/4 filled) and 0.10 M $HC_2H_3O_2$ in another well. Add one drop of Orange IV indicator to each solution.

2. Compare the color of the Orange IV indicator in the two wells with those of 0.10 M, 0.010 M, 0.0010 M HCl solutions and buffer 5 saved from part B. Hence, estimate the fractional pH of the 1.0 M and 0.10 M $HC_2H_3O_2$ solutions as 2.3 or 2.5, ..etc. **Get the approval of the instructor for the estimated pH.**

3. Calculate the corresponding $[H^+]$.

4. Complete the calculations in table part C on report sheet.

5. Get the approval of the instructor for the calculated % ionization.

E. CHOICE OF AN INDICATOR

Choose an indicator that will distinguish between 0.10 M NaOH and 0.0010 M NaOH. (First calculate the pH of each of these solutions of base. Show the setup on the report sheet.) **Get your instructor approval of your choice of the indicator**. Then, add the suggested indicator to samples of 0.10 M NaOH and 0.0010 M NaOH placed in the spot plate wells. **Show the two solutions to your instructor for approval**.

Report Sheet
pH and Its Measurements

Name______________
Last First

A. pH OF 0.10 M ACID, BASE, AND SALT SOLUTIONS

		Measured pH
Acids	$HC_2H_3O_2$	
	H_3BO_3	
	H_3PO_4	
Bases	$Ca(OH)_2$ (saturated, not 0.10 M)	
	$Mg(OH)_2$ (saturated, not 0.10 M)	
	NH_4OH	
Salts	Na_2HPO_4	
	$NaHSO_4$	
	NaH_2PO_4	
	Na_2CO_3	

Comment on the pH of salts in general. Are salt solutions always neutral?
____

B. DILUTING SOLUTIONS
Fill in the table below:

To make 20.0 ml of 0.010 M HCl, I will measure _____ ml of 0.10 M HCl and mix with distilled water to a total volume of __________ ml
Setup:

$M_{\text{before dilution}}$	$V_{\text{before dilution}}$	$M_{\text{after dilution}}$	$V_{\text{after dilution}}$
0.10 M HCl		0.010 M HCl	20.00 ml
0.010 M HCl	4.00 ml	0.0010 M HCl	
0.10 M NaOH		0.010 M NaOH	20.00 ml
0.010 M NaOH		0.0010 M NaOH	20.00 ml

Instructor's approval____________

What is theoretical $[H^+]$ of 0.0010 M HCl? $[H^+]_{theo}$=________M

Measured pH of 0.0010 M HCl solution: ___________

Calculate [H^+] from measured pH.
Setup:

[H+]$_{Meas}$= ________M
(correct sig figures)

Percent error in preparing 0.0010 M HCl by dilution of 0.10 M HCl
Setup: (Calculate from [H^+] concentration, not from pH)

% error= _________%
(correct sig figures)

C. INDICATOR COLORS

	0.10 M HCl	0.010 M HCl	0.0010 M HCl	Buffer pH=5	Buffer pH= 9	0.0010 M NaOH	0.010 M NaOH	0.10 M NaOH
pH (theoretical)								
Orange IV								
Methyl orange								
Alizarin yellow								

Indicators changed colors at the following pH intervals:

Orange IV _______________

Methyl orange ___________

Alizarin yellow___________

Instructor's approval for part C __________

D. PERCENT IONIZATION

Solution	Color of	pH estimated	$[H^+]$ calculated	% ionization
1.0 M $HC_2H_3O_2$	**Orange IV**			Setup:
0.10 M $HC_2H_3O_2$	**Orange IV**			Setup:

From your result above, fill-in the blanks:

What is the effect of dilution on the $[H^+]$ and percent ionization of a weak acid?

The more dilute the acetic acid solution the ___________ the [H+] and the _________
(higher, lower) (higher, lower)
the percent ionization.

Instructor's approval for part D_____________

E. CHOICE OF AN INDICATOR

From the table on page 2, choose an indicator that will distinguish between 0.10 M NaOH and 0.0010 M NaOH. (First calculate the pH of each of these solutions of base.)

pH of 0.10 M NaOH = __________

pH of 0.0010 M NaOH= __________

Indicator chosen_____________

Instructor's approval of chosen indicator ________

Now test the 0.10 M NaOH and 0.0010 M NaOH solutions that you prepared and saved from part B with the indicator chosen.

Color of your indicator in 0.10 M NaOH ________

Color of your indicator in 0.0010 M NaOH _______

Show the two solutions to your instructor for approval.

Instructor's approval _________

Exercise:

1. Refer to the table on page 2 for the color changes of indicators at different pH values. From the table we would expect the color of Orange IV indicator at pH 2 to be between red and yellow which is orange. What color would you expect of Bromcresol green at pH 4.6? ________________ Notice that only changes in color are given in the table. For methyl red the table says red color at pH 4.4, so all pH values less than 4.4 will produce red. It also lists yellow for pH 6.2, so all values higher than 6.2 will produce yellow. Notice that Thymol blue indicator changes color at two pH intervals.

Complete the table below:

Indicator	pH	Color
Orange IV	2	
Methyl red	5	
Bromthymol blue	7	
Cango red	2	
Thymol blue	10	
Thymol blue	1	
Bromcresol green	4	
Bromcresol purple	3	

2. What is the **pH** of a 0.0344 $\underline{M}$ KOH solution?
Setup:

1)Answer: _______________
(in correct number of significant figures)

3. a) What is the **theoretical** $[H^+]$ of a 0.00030 $\underline{M}$ HCl ?

a)Answer: _______________

(in correct number of significant figures)

b) The above 0.00030 $\underline{M}$ HCl solution was prepared in the lab by dilution. The pH of the solution was **measured** as 4.23. Calculate the $[H^+]$ from the **measured** pH.

b)Answer: _______________

(in correct number of significant figures)

c) Calculate the percent error in the measured $[H^+]$.

Setup:

c)Answer: _______________

(in correct number of significant figures)

4. What is the percent ionization for each of the following acids?

a) 0.022 $\underline{M}$ $HClO_2$ solution of pH= 3.88

Setup:

a)Answer: ______________%

(in correct number of significant figures)

b) 0.0027 $\underline{M}$ $HClO_2$ solution of pH= 4.70

Setup:

b)Answer: ______________%

(in correct number of significant figures)

5. fill in the blanks:

i) The percent of ionization _______________________ upon dilution.

(increases, decreases, or remains the same)

ii) The $[H^+]$ _______________________ upon dilution.

(increases, decreases, or remains the same)