EXPERIMENT 7

A STUDY OF AN ACID IONIZATION EQUILIBRIUM

PURPOSE:

1. To estimate the Acid-Ionization Constant (Ka) of acetic acid by conductivity testing comparisons.
2. To become familiar with the pH meter and pH measurements.
3. To determine the Acid-Ionization Constant (Ka) of acetic acid by pH measurements.
4. To examine the effect of dilution on the degree of ionization of acetic acid.

PRINCIPLES:

All acids (strong and weak) react with water to produce hydrogen ions. This process is referred to as **Acid Ionization** or **Acid Dissociation**.

Since all strong acids ionize completely in solution (100%), for solutions of strong acids, the concentrations of ions strong acids produce in solution are determined by the stoichiometry of the reaction and the initial concentration of the acid.

$$HCl(aq) \quad + \quad H_2O(l) \quad \longrightarrow \quad H_3O^+(aq) \quad + \quad Cl^-(aq)$$

Initial Concentration	0.10 M	excess	0	0
Final Concentration	0	excess	0.10 M	0.10 M

The situation is quite different for weak acids. Consider an aqueous solution of the weak acid, acetic acid ($HC_2H_3O_2$). When acetic acid is added to water, acetic acid ionizes only partially, and an equilibrium system is established, in which the molecules of acetic acid $HC_2H_3O_2$ are in equilibrium with the ions they produce by ionization (H^+ and $C_2H_3O_2^-$)

This equilibrium system, commonly referred to, as Acid Ionization Equilibrium, can be represented by the following equation:

$$HC_2H_3O_2(aq) \ + \ H_2O(l) \ \rightleftharpoons \ H_3O^+(aq) \quad + \quad C_2H_3O_2^-(aq)$$

Initial Concentration	0.10 M	excess	0	0
Change	- 0.0013 M	excess	+ 0.0013	+ 0.0013
Equilibrium Concentration	0.10 M	excess	0.0013 M	0.0013 M

As shown above, this equilibrium system strongly favors the reactants, as evidenced by the fact that in a solution of 0.10 M of acetic acid, only 1.3 % of the acetic acid molecules change into ions.

$$\% \ Ionization = \frac{\text{Number of molecules ionized}}{\text{Total number of molecules originally present}} = \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} \times 100 = \frac{0.0013 \ M}{0.10 \ M} \times 100$$

% Ionization = 1.3 %

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At the level of arithmetic, this implies that out of 100 molecules of $HC_2H_3O_2$, only one molecule breaks apart to produce one hydronium ion (H_3O^+) and one acetate ion ($C_2H_3O_2^-$)

Since acidity is associated with the concentration of hydronium ions $[H_3O^+]$ in the solution of an acid, the relative strength of various weak acids is judged by the concentration of the H_3O^+ they produce at a given concentration. The higher the extent of ionization of the weak acid, the more $[H_3O^+]$ are produced and the relatively stronger the weak acid is.

The extent to which weak acids ionize differ greatly among weak acids. In order to objectively judge the relative strength of weak acids, a constant Ka, Acid-Ionization Constant has been introduced.

Ka is in fact the equilibrium constant for the ionization of a weak acid and it has a specific numerical value for every weak acid.

To find Ka, consider the Acid Ionization Equilibrium of a weak acid:

$$HA(aq) \quad + \quad H_2O(l) \quad \rightleftharpoons \quad H_3O^+(aq) \quad + \quad A^-(aq)$$
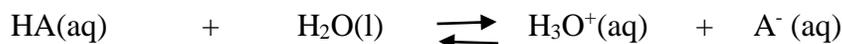
The corresponding equilibrium constant is:

$$Kc = \frac{[H_3O^+]\,[A^-]}{[HA]\,[H_2O]}$$

Assuming that this is a dilute solution and that the forward reaction occurs to only a small extent (as it is always the case for weak acids), the concentration of water can be considered constant. Rearranging the equation, with the aim to include the concentration of H_2O in the equilibrium constant, Kc, yields:

$$Kc \times [H_2O] = \frac{[H_3O^+]\,[A^-]}{[HA]\,[H_2O]} = \textbf{Ka} = \textbf{Acid – Ionization Constant}.$$

This expression indicates that for weak acids that are relatively highly ionized – that is few molecules of HA in solution – the value of Ka will be relatively large. A relatively small value of Ka indicates that the weak acid is only slightly ionized.

Ka of a weak acid can be determined experimentally by one of two methods:

1. **By conductivity testing comparison**.
   This method is based on the premise that two solutions that exhibit the same electrical conductivity also have the same concentration of ions. An estimate of the number of ions produced by the ionization of a weak acid ($HC_2H_3O_2$) of known concentration is determined by comparing the conductivity of the solution of the weak acid with the conductivity of a solution of a known concentration of a strong acid (HCl), which is completely ionized.
   Since the conductivity indicator used in this experiment provides only semi-quantitative data, this method yields only in a very approximate and estimated value for Ka.

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2. **By pH measurements**

In this method, the pH of a solution of weak acid of known concentration is determined experimentally with a pH meter. From the pH, the equilibrium concentration of the $[H_3O^+]$ and of the other ion being produced can be calculated.

Once the equilibrium concentrations of all species present in the equilibrium system are known, the Acid – Ionization Constant can be calculated.

Once the equilibrium concentrations of all species present in the acid ionization equilibrium of a weak acid are known, the degree (%) of ionization of a weak acid can be easily calculated.

By calculating the degrees (%) of ionizations for solutions of acetic acid of varying concentrations, it can be shown that the degree (%) of ionization of a weak acid, such as acetic acid, is greatly dependent on the concentration of the acid.

Part III of this experiment evaluates and interprets this dependence and examines the cause and effect of this relationship.

PROCEDURE:

PART I:
ESTIMATING THE ACID IONIZATION CONSTANT OF A WEAK ACID (Ka) BY CONDUCTIVITY TESTING COMPARISONS

1. **Preparing your Chemplate**

Your Chemplate should be clean, drained of water and reasonably dry.
Clean your Chemplate by rinsing it with tap water followed by three rinses with D.I water.
Drain off excess D.I water and blot it dry with tissue paper (Kimwipe if available)

2. **Preparing your equipment**

Check out a "Conductivity Tester Combo", composed of a Power Converter connected to a Conductivity Indicator.
Check your Conductivity Indicator and the electrodes in the same manner it was done in the previous experiment (Experiment # 6: Acid & Base Strength).
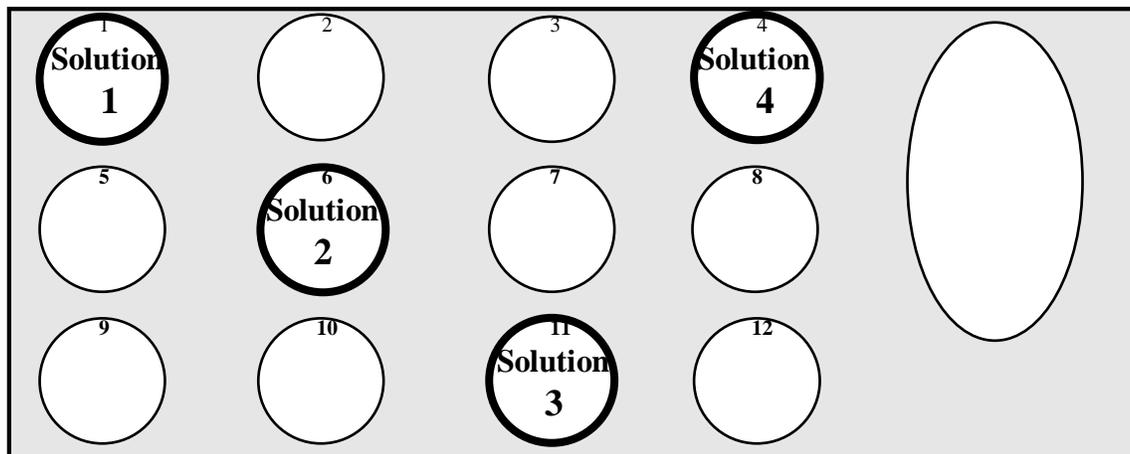
3. **Testing your solutions**

You will find available in the lab four solutions, which can be dispensed from dropper bottles.

- **Solution 1**: $HC_2H_3O_2(aq)$ (Acetic Acid)   **0.10 M**

- **Solution 2**:   **HCl(aq)**   (Hydrochloric Acid)   **0.10 M**

- **Solution 3**:   **HCl(aq)**   (Hydrochloric Acid)   **0.010 M**

- **Solution 4:**   **HCl(aq)**   (Hydrochloric Acid)   **0.0010 M**

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(a) Plan the depressions you are going to use for the conductivity testing of the four solutions. It is advisable to use depressions well separated from each other (as suggested below), to avoid cross contamination of the solutions, by accidentally overfilling the depressions

NOTE:

Record in your Lab Notebook the formula and the molarity of the solution you plan to place in each depression.

(b) Testing the conductivity of the solutions

- Fill the selected depressions completely (about 30 drops) with the solutions to be tested.
- Using the conductivity indicator, test the conductivity of each solution in the same manner as it was done in Experiment # 6.
    HINT: Cross-contamination caused by the electrodes is greatly minimized if the conductivity testing is done in the following order:

First:	Solution 1: $HC_2H_3O_2(aq)$	**0.10 M**
Second:	Solution 4: **HCl(aq)**	**0.0010 M**
Third:	Solution 3: **HCl(aq)**	**0.010 M**
Fourth:	Solution 2 **HCl(aq)**	**0.10 M** (highest concentration of ions)

Follow the same procedural guidelines that have been followed in Experiment # 6.

Record the response of the LED for each of the four solutions in your Lab Notebook.

Recall:

- ➢ Bright Light indicates Strong Conductivity   **(+)**
- ➢ Faint Light indicates Weak Conductivity   **(+/-)**
- ➢ No Light indicates a No Conductivity   **(-)**

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(c) Wrapping up PART I of the experiment

- Check with your instructor if your data is correct.
- Disconnect the Conductivity Tester Combo and return it in the same condition it has to been checked out. It is no longer needed for this experiment.
- Wash well your Chemplate (tap water followed by a few rinses of D.I water) and store it in your locker. It is no longer needed for this experiment.
- If time allows it, do some or all of the calculations for this part.

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PART II:
DETERMINING THE ACID IONIZATION CONSTANT OF A WEAK ACID (Ka) BY pH MEASUREMENTS

1. **Preparing the pH meter.**
   - ➢ Check out a pH-meter from your laboratory instructor.
     While you are preparing to use it, place it upright into a 250 mL Erlenmeyer flask.
   - ➢ Check out a small screwdriver from your laboratory instructor.
     You will use the screwdriver to calibrate your pH-meter.

The pH-meter

Description: A pH meter and its electrodes form a sensitive electrochemical device that will allow an accurate, reproducible, and reliable measurement of the pH of a solution. A pH meter is essentially a voltmeter that measures the voltage of an electric current flowing through a solution between two electrodes. There is a direct relationship between the voltage and the pH of a solution. As a result, the meter on the instrument is calibrated directly in pH units. You will be using a pH meter with a combination stick pH electrode, equipped with a screw-type connector for calibration.

Top View
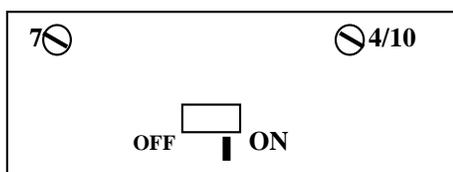
Front View
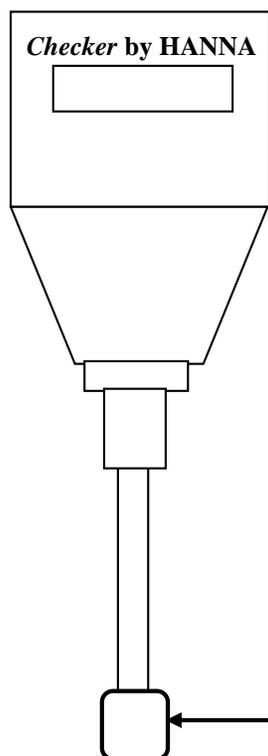
Protective cap

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Operating instructions for the pH meter

➢ Remove the protective cap and soak it in a D.I water by placing it into a 150 mL beaker filled with about 100 mL of D.I. water.
Place the beaker containing the cap in a secure location and ensure that the cap does not get lost. Be aware that if you lose the protective cap the pH meter becomes useless.

➢ Immerse the tip of the electrode (bottom 4 cm/1½") into a 150 mL beaker containing sufficient (**but not too much!)** water to cover the electrodes and dissolve the white crystals that may have deposited on the electrode during storage.
NEVER IMMERSE THE ELECTRODE UP TO THE CONNECTOR!
ALWAYS KEEP THE CONNECTOR CLEAN AND DRY!

➢ The electrode should always be kept in a solution, except when you are transferring it from one solution to another.

➢ When you transfer the combination electrode, you will want to avoid contaminating the solutions. During the transfer:

- Rinse the electrode with a stream of deionized water and catch the water in 250 mL beaker.
- Remove the excess water from the electrode with tissue paper (Kimwipe) before you immerse the electrode in the next solution.
- Do not touch the electrode with your hands
- Handle the electrode with care, since it is fragile

Calibrating the pH meter

➢ The pH meter must be **calibrated** with solutions whose pH values are known before you can measure with accuracy the unknown pH of a solution.
The solutions used for calibration are called **buffer solutions.**
Commonly three buffer solutions are used for calibration with the following
pH values: **pH = 4.0   pH = 7.0   pH = 10.0**
o The first calibration is always done with pH = 7.0 buffer
o The second calibration can be done with either pH = 4.0 buffer or pH = 10.0 buffer, depending on the character of the solution to be tested (acidic or basic)

➢ To calibrate the pH meter, you will need to use the buffer solution(s) whose pH value(s) is (are) in relatively close range with the assumed pH (acidic or basic) of your solution. In this experiment the pH-meter will be used to measure the pH of acidic solutions. As such, the pH-meter needs to be calibrated as follows:
o A first calibration with: pH = 7.0 Buffer
o A second calibration with: pH = 4.0 Buffer

➢ Label two short plastic text tubes with the pH of the buffer solutions they will contain.

➢ Fill two short, plastic test tube with about 8 mL of the respective buffer solutions, by dispensing the buffer solutions from the burets set up for this purpose in the lab.
Place the short, plastic test tubes containing the buffer solutions in the plastic test tube rack.

➢ Immerse the tip of the electrode (bottom 4 cm/1½) in the pH = 7.0 buffer solution

➢ Turn the pH meter "ON".

➢ Stir the pH = 7.0 buffer solution gently and allow the pH reading to stabilize.

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- ➢ Use a small screwdriver to adjust the pH 7 trimmer until the display reads "**7.01**" (or as close as possible to this value).
- ➢ Turn the pH meter "OFF".
- ➢ Remove the electrode from the pH= 7.0 buffer solution.
- ➢ Rinse the electrode with a stream of deionized water and catch the water in a beaker.
- ➢ Remove the excess water from the electrode with tissue paper (Kimwipe) before you immerse the electrode in the next solution.
- ➢ Immerse the tip of the electrode (bottom 4 cm/1½) in a sample of pH = 4.0 buffer solution.
- ➢ Turn the pH meter "ON".
- ➢ Stir the pH = 4.0 buffer solution gently and allow the pH reading to stabilize.
- ➢ Use a small screwdriver to adjust the pH 4/10 trimmer until the display reads "**4.01**" (or as close as possible to this value).
- ➢ Turn the pH meter "OFF".
- ➢ Leave the pH meter in the pH = 4.01 buffer solution, until you are ready to take the pH measurements of the solutions whose pH values will be measured..

2. Preparing the solutions for pH measurements

You will measure the pH of three solutions of acetic of varying concentrations.

Solution A	**HC₂H₃O₂(aq)**	**(Acetic Acid)**	**0.010 M**
Solution B:	**HC₂H₃O₂(aq)**	**(Acetic Acid)**	**0.10 M**
Solution C:	**HC₂H₃O₂(aq)**	**(Acetic Acid)**	**1.0 M**

- ➢ Take out three shell vials from your locker and label the shell vials with the respective formulas and concentrations of the solutions they will contain.
  NOTE: Only large lockers contain shell vials.
- ➢ Fill the three shell vials about 10 mL of the respective solutions, by dispensing the solutions A, B & C from the burets set up for this purpose in the lab.
- ➢ You may conveniently store the shell vials in your plastic test tube rack, along with the short plastic test tubes containing the two buffer solutions.

3. Taking the pH measurements

- ➢ Remove the electrode from the pH= 4.01 buffer solution.
- ➢ Rinse the electrode with a stream of deionized water and catch the water in a beaker.
- ➢ Remove the excess water from the electrode with tissue paper (Kimwipe) before you immerse the electrode in the solution whose pH is being measured.
  NOTE:
  To avoid contamination through the electrodes, when transferring the pH meter from one solution to the other, it is best to test the solutions in order of increasing concentration (from the most dilute to the most concentrated).

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Test First:

Solution A: $HC_2H_3O_2$(aq)   (Acetic Acid)   0.010 M

- o   Immerse the electrode (bottom 4 cm/1½) in Solution A
- o   Turn the pH meter "ON".
- o   Stir the electrode gently in the solution and allow the reading to stabilize. You should be able to read the pH of a solution about 10 seconds after the electrode has been immersed. The reading should be steady and not suddenly changing.
- o   Read and record the pH reading in your Laboratory Notebook.
- o   Turn the pH meter "OFF".
- o   Remove the electrode from Solution A.
- o   Rinse the electrode with a stream of deionized water and catch the water in a beaker.
- o   Remove the excess water from the electrode with tissue paper (Kimwipe) before you immerse the electrode in the next solution.

Test Second:

Solution B: $HC_2H_3O_2$(aq)   (Acetic Acid)   0.10 M

Repeat the same steps you have followed for taking the pH measurement of Solution A

Test Third:

Solution C: $HC_2H_3O_2$(aq)   (Acetic Acid)   0.010 M

Repeat the same steps you have followed for taking the pH measurement of the previous two solutions (A & B)

4.   **Wrapping up PART II of the experiment**

- •   **Storing the pH meter**
  - ➢   Turn the pH meter "OFF"
  - ➢   Remove the electrode from Solution C
  - ➢   Rinse the electrode with a stream of deionized water and catch the water in a beaker.
  - ➢   Remove the excess water from the electrode with tissue paper (Kimwipe).
  - ➢   Retrieve the protective cap from the 150 mL beaker and drain the water from inside the cap. Place a few drops of Storage Solution (available at the instructor's desk) in the protective cap of the pH meter. While keeping the pH meter in an upright position, snap the protective cap containing the storage solution onto the bottom of the pH meter.
  - ➢   Place the pH meter in an upright position in a 250 mL Erlenmeyer flask and store it in your locker (it will fit in large lockers only). You will use the pH meter again for several upcoming experiments.

- •   **Storing the two buffer solutions**
  - ➢   The plastic test-tubes containing the two buffer solutions should be kept in your locker (capped) for the next series of experiments. The test-tubes come with a cap and they should be well capped to preserve the contents. They fit only in the large lockers.

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PART III:
EFFECT OF DILUTION ON THE DEGREE OF IONIZATION OF ACETIC ACID

There is no experimental work in this part of the experiment.

If time allows, you may wish to work on this part of the experiment in class, taking advantage of the laboratory instructor's assistance. Alternatively, you may chose to complete the calculations and answer the questions at home.

The "Principles " section of this experiment outlines the basic concepts behind this part of the experiment and the tables given in the "Report Form" are almost self-explanatory.

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REPORT FORM

NAME: _____ Date: _____ Partner: _____

PART I:
ESTIMATING THE ACID – IONIZATION CONSTANT OF A WEAK ACID (Ka) BY CONDUCTIVITY TESTING COMPARISONS

WEAK ACID ($HC_2H_3O_2$)

	Molarity (M)	Electrical Conductance (+) or (+/-) or (-)
Solution 1	**0.10** **1.0×10^{-1}**	

STRONG ACID (HCl)

	Molarity (M)	Electrical Conductance (+) or (+/-) or (-)
Solution 2	**0.10** **1.0×10^{-1}**	
Solution 3	**0.010** **1.0×10^{-2}**	
Solution 4	**0.0010** **1.0×10^{-3}**	

OBSERVATIONS:

1. What is the effect of decreasing the concentration of the strong acid [HCl(aq)] on the electrical conductivity of its solution?

2. What is the relationship between the **number of ions** in an aqueous solution and the **electrical conductivity** of the solution?

3. What is the concentration of the **strong acid [HCl(aq)]** that exhibits the same electrical conductivity as the **0.10 M solution of the weak acid [$HC_2H_3O_2$(aq)]?**
   HCl(aq) _____ M

4. How do you account for the fact that two acids (strong and weak) of different concentrations exhibit the same electrical conductivity?

5. If two solutions of two different acids and of two different concentrations exhibit the same electrical conductivity, what is the relationship between the **concentrations of their ions** in their respective solutions?

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CONCLUSION:

1. **An aqueous solution of HCl _____ M has** _____

   (greater, about the same, lower)

   **(the) same concentration of ions as a solution of HC₂H₃O₂(aq) _____ M**

CONCENTRATION OF IONS

Solutions	Concentration of Solution (M)	Electrical Conductivity (+) OR (+/-) OR (-)	[H₃O⁺] (M)
HCl(aq)			
HC₂H₃O₂(aq)			

2. It is now possible to estimate the Acid Ionization Constant (Ka) of **HC₂H₃O₂ (aq)** by:
   - Constructing an Equilibrium Table for the Acid Ionization Equilibrium of the weak acid, and
   - Using the concentration data obtained from conductivity comparisons.

Acid Ionization Equilibrium Equation:

[ ] + [ ] ⇌ [ ] + [ ]

Initial Conc: [ ]   excess   [ ]   [ ]

Change: [ ]   excess   [ ]   [ ]
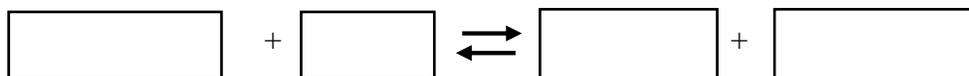
Equil. Conc: [ ]   [ ]   [ ]

Calculate the estimated value of Ka for **HC₂H₃O₂** from the equilibrium concentrations.

$$Ka = \frac{[H^+]\,[HC_2H_3O_2^{\,-}]}{[HC_2H_3O_2]} = \frac{(\quad)\,(\quad)}{(\quad)} \approx$$

Ka (HC₂H₃O₂) estimated: [ ]

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PART II:
DETERMINING THE ACID - IONIZATION CONSTANT OF A WEAK ACID (Ka) BY pH MEASUREMENTS.

$HC_2H_3O_2$

Solution	$[HC_2H_3O_2]$ M	Measured pH	$[H^+]$ M	$[HC_2H_3O_2{}^-]$ M	Ka
A	1.0 M				
B	0.010 1.0×10^{-2}				
C	0.0010 1.0×10^{-3}				

AVERAGE:

CALCULATIONS:
Calculations for Ka(A):
Acid Ionization
Equilibrium
Equation:

Initial
Conc:

Change:

Equilibrium
Conc:
Please show calculations below:

Ka(A):   (Enter this value in the table above)

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Calculations for Ka(B):

Acid Ionization
Equilibrium
Equation:

Initial
Conc:

Change:

Equilibrium
Conc. :
Please show calculations below:

Ka(B): [_____]   **(Enter this value in the table above)**

Calculations for Ka(C):
Acid Ionization
Equilibrium
Equation:

Initial
Conc:

Change:

Equilibrium
Conc:
Please show calculations below:

Ka(C): [_____]   **(Enter this value in the table above)**

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Conclusions:

PART I:

The experimentally estimated value for Ka of HC$_2$H$_3$O$_2$(aq) determined in PART I (conductivity comparison testing) is:

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Ka =
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PART II

The experimentally determined average value for Ka of HC$_2$H$_3$O$_2$(aq) obtained in PART II (pH measurements) is:

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Ka =
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PART III:

EFFECT OF DILUTION ON THE DEGREE OF IONIZATION OF A WEAK ACID [$HC_2H_3O_2(aq)$]

Using the concentration of [H^+] obtained by pH measurements for solutions of acetic acid of known concentration, the percentage ionization of the solutions of the weak acid (**$HC_2H_3O_2$**) of varying decreasing concentrations can now be calculated.

Ka = _____ [determined experimentally in PART II (pH measurements)]

Concentration of $HC_2H_3O_2(aq)$	pH (experimental)	[H^+] = [$C_2H_3O_2^-$]	% Ionization = $\dfrac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$ x 100
1.0 M			
0.10 M 1.0×10^{-1} M			
0.010 M 1.0×10^{-2} M			
0.0010 M 1.0×10^{-3} M	4.38 (given)		

CONCLUSION:

What is the relationship between the concentration of a solution of a weak acid [**$HC_2H_3O_2(aq)$**] and its Degree (%) Ionization?

The _____ the concentration, (the more _____ the solution)
(lower/higher)   (dilute/concentrated)

_____ the Degree of Ionization.
(greater/smaller)

(a) **Provide a rationale for your stated conclusion above, by completing the Equilibrium Table that illustrates the Acid Ionization Equilibrium of $HC_2H_3O_2(aq)$, being gradually diluted (water added to the solution).**

Equation: [ ] + [ ] ⇌ [ ] + [ ]

Stress:……………………………........ [ ]

Shift:………………………………………….. [ ]

New Equilibrium…… [ ] ……. [ ] ……………… [ ] …… [ ]
(Increased or Decreased)

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(b) <u>Provide a rationale for your stated conclusion above by explaining it in terms of Le Chatelier's Principle.</u>