Name_____Lab Day_____Lab Time_____

Experiment 8 · Acid–base titration

Pre-lab questions

Answer these questions and hand them to the TF before beginning work.

(1) What is the purpose of this experiment?

_____

_____

(2) What is the molar concentration of H_3O^+ in a solution whose pH is equal to 2?

_____

_____

(3) You will titrate a solution of an unknown acid (HX(aq)) by adding NaOH(aq). Suppose that 25 mL of 0.5 *M* NaOH(aq) is needed to reach the equivalence point. How many moles of HX were present initially? Show the calculation.

(4) You will titrate acid solutions by adding 0.2–0.3-mL or 2–3-mL portions of NaOH(aq). When should you add the smaller volume?

_____

_____

(5) The concentration of an aqueous solution of NaOH cannot be accurately determined by dissolving a known mass of NaOH(s) in a known volume of water: Why?

_____

_____

Acid–base titration

Mathematical development

Acids and bases are indispensable fixtures of daily life. Acids can be recognized by their sharp taste. The tartness of lemon juice is caused by citric acid, the sourness of wine by tartaric acid and malonic acid. Bases, on the other hand, are characterized by a bitter taste. Moderately concentrated aqueous solutions of bases such as household ammonia ($NH_4OH(aq)$) exhibit a slimy, slippery feel. Many bases are physiologically active and acutely toxic. Cigarette smokers crave the "buzz" from the base nicotine. The sentence of execution exacted on the Greek philosopher Socrates (his crime was that of corrupting the young) consisted of his being forced to drink hemlock, which contains the deadly base coniine.

pK_a and pH

Acids and bases are partners. An acid, generically represented by HA, is a proton (H^+) donor, whereas a base, generically represented by B, is a proton acceptor. When acids and bases combine, they swap a proton:

$$HA + B \rightleftarrows A^- + HB^+$$

Strong acids (e.g., sulfuric acid) have a very pronounced tendency to transfer a proton to a base whereas weak acids (e.g., water) give up a proton much less readily. Acid strength is

quantified by measuring the equilibrium constant of the reaction of an acid with water, which acts as a base:

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

$$K_{eq} = K_a = \frac{[A^-(aq)][H_3O^+(aq)]}{[HA(aq)]}$$

This equilibrium constant (called the "acid-dissociation constant") is given the special symbol K_a. A strong acid exhibits a large value of K_a whereas the K_a of a weak acid is generally less than unity (1). Because acid strength varies over an enormous interval of more than 60 orders of magnitude, ranging from the "super acid" hydroiodic acid (HI, $K_a = 10^{11}$) to the exceedingly weak acid methane (CH_4, $K_a = 10^{-50}$), and because we like to avoid scientific notation, it is usual to refer to an acid's pK_a rather than to its K_a. The pK_a is related to the K_a by the definition

$$pK_a = -\log_{10} K_a$$

Thus, HI ($K_a = 10^{11}$) has a pK_a of –11, whereas CH_4 ($K_a = 10^{-50}$) has a pK_a of 50.

The practice of referring to an acid's pK_a rather than to its K_a is analogous to the custom of referring to the molar concentration of $H_3O^+(aq)$ by pH:

$$pH = -\log_{10} [H_3O^+(aq)]$$

A solution that is 1 *M* in $H_3O^+(aq)$ has a pH of zero, whereas a solution that is 10^{-14} *M* in $H_3O^+(aq)$ has a pH of 14.

The relationship between pH and pK_a is expressed by the Henderson–Hasselbalch equation (Eqn. 8-1):

$$\frac{[A^-(aq)]}{[HA(aq)]} = 10^{pH - pK_a} \qquad \text{(Eqn. 8-1)}$$

Eqn. 8-1 states that there is more HA(aq) than $A^-(aq)$ when pH < pK_a and more $A^-(aq)$ than HA(aq) when pH > pK_a. When

pH = pK_a, [HA(aq)] = [A^-(aq)] (see Figure 8-1 for a specific example of this behavior).

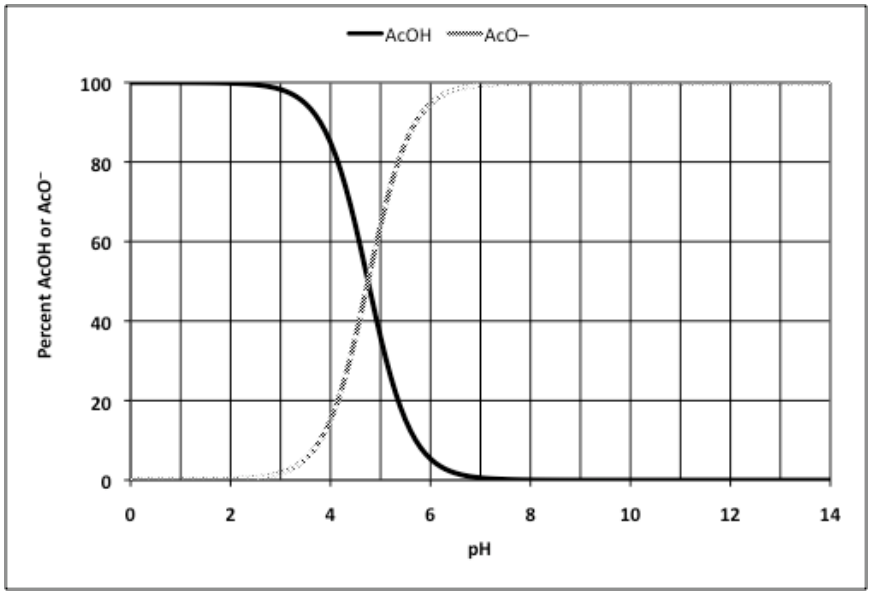
Acid–base titration curves

In this experiment you titrate an aqueous solution of an unknown acid (HX(aq)) by adding an aqueous solution of the base OH^-(aq); the balanced reaction is

$$HX(aq) + OH^-(aq) \rightleftarrows X^-(aq) + H_2O(l)$$

When the pH of the solution containing the unknown acid is plotted as a function of the volume of OH^-(aq) added, the data forms an acid–base titration curve. Such a curve has three regions: (1) a fairly flat "buffered" region at low pH; (2) a steep "equivalence point" region at intermediate pH; (3) a second fairly flat "unbuffered" region at high pH. Figure 8-2 shows the titration curve that results when a 25.00-mL sample containing 0.815 g of an unknown acid HX is titrated against 0.500 *M*

Figure 8-1 The relative amounts of acetic acid (abbreviated AcOH, pK_a = 4.75) and acetate ion (abbreviated AcO^-) as a function of pH as calculated by Eqn. 8-2. AcOH dominates when pH < 4.75 whereas AcO^- dominates when pH > 4.75. When pH = 4.75, there are equal amounts of AcOH and AcO^-.



NaOH(aq). Let's discuss the chemistry that takes place in each of these three regions and let's also demonstrate how the molar mass $\mathcal{M}$ and the pK_a of the unknown acid can be extracted from the data.

Buffered region at low pH

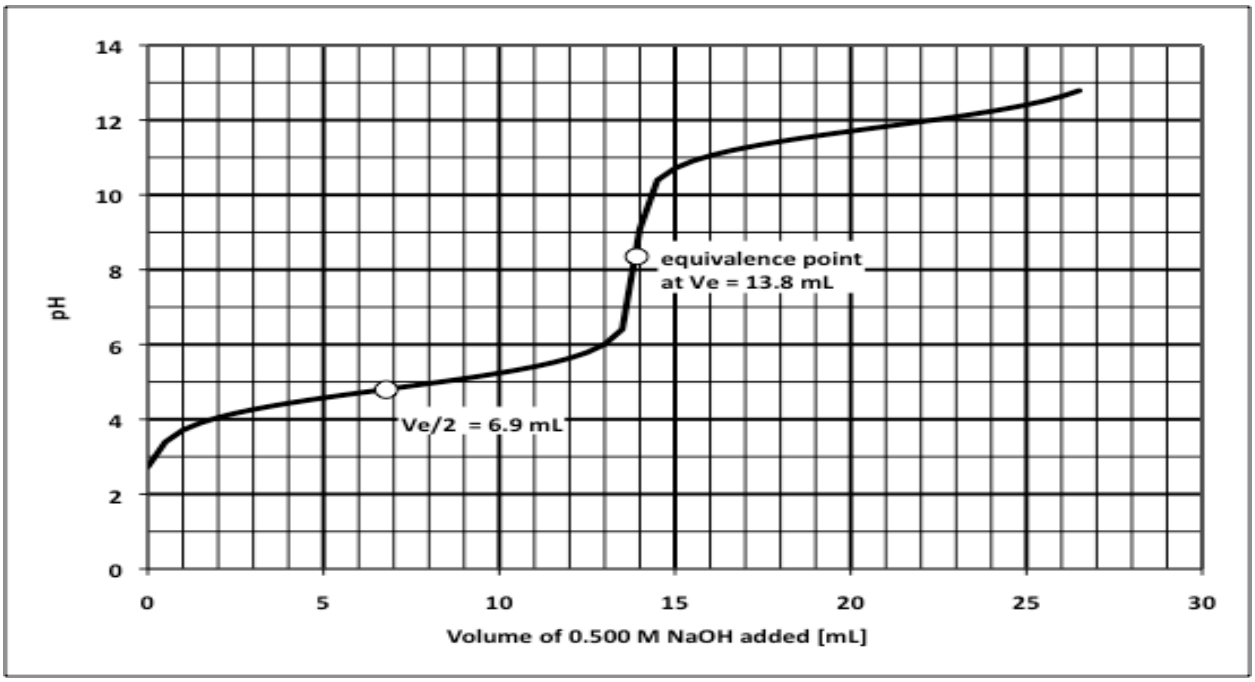
Even before any OH^-(aq) is added to the solution, some of the unknown acid reacts with water (a weak base) according to the balanced equation

$$HX(aq) + H_2O(l) \rightleftarrows X^-(aq) + H_3O^+(aq)$$

to the extent that the solution in Figure 8-2 exhibits a pH of 2.73, that is, $[H_3O^+(aq)] = 10^{-2.73}\ M = 1.87 \times 10^{-3}\ M$. When OH^-(aq) is added to the solution, the reaction

$$HX(aq) + OH^-(aq) \rightleftarrows X^-(aq) + H_2O(l)$$

Figure 8-2 Titration of 25.00 mL of a solution containing 0.815 g of an unknown acid HX against 0.500 *M* NaOH(aq). At the equivalence point (located at the midpoint of the steeply increasing region of the curve), the cumulative volume V_e of OH^-(aq) added contains as many moles of OH^- as there were moles of HX initially present. The pK_a of HX equals the pH at $V_e/2$.



begins to occur. The pH increases, but only modestly because the simultaneous presence of HX(aq) and X^-(aq) produces a buffer solution that resists changes in pH.

Equivalence point region at intermediate pH

Eventually so much OH^-(aq) is added to the solution that the supply of HX(aq) becomes exhausted and the buffering capacity of the solution collapses; thus, the pH rises sharply. At the equivalence point, which is located at the midpoint of the steeply increasing region of the titration curve, the cumulative volume V_e of OH^-(aq) added contains as many moles of OH^- as there were moles of HX initially present. In Figure 8-2 the equivalence point occurs when 13.8 mL of 0.500 *M* OH^-(aq) is added and the solution has a pH of 8.2.

Locating the equivalence point allows us to calculate the molar mass $\mathcal{M}$ and the pK_a of an unknown acid HX. The number of moles of OH^- needed to reach the equivalence point in Figure 8-2 is given by

$$\left(\frac{0.0138\ \text{L OH}^-}{}\right)\left(\frac{0.500\ \text{mol OH}^-}{\text{L OH}^-}\right) = 0.00690\ \text{mol OH}^-$$

implying that the 0.815 g of HX initially present corresponds to 0.00690 mol of HX. The molar mass of HX is thus

$$\frac{0.815\ \text{g HX}}{0.00690\ \text{mol HX}} = 118\ \text{g/mol}$$

Recall that Eqn. 8-1 says that [HX(aq)] = [X^-(aq)] when pH = pK_a. At the equivalence point (V_e), all of the HX initially present is depleted. When a volume of NaOH(aq) equal to $V_e/2$ is added, one-half of the unknown acid molecules initially present have reacted to form X^- but one-half still exists as HX. Thus, the p*Ka* of HX is equal to the pH of the solution at $V_e/2$. The pH at $V_e/2$ = 6.9 mL in Figure 8-2 is 4.8; thus, the pK_a of HX is 4.8.

Unbuffered region

Beyond the equivalence point, OH^- is being added to a solution that no longer contains any HX. The reaction

$$HX(aq) + OH^-(aq) \rightleftarrows X^-(aq) + H_2O(l)$$

no longer occurs and the increase in pH is attributable to simply adding OH^- (a strong base) to the solution.

Procedure

Preparation of $H_2C_2O_4$(aq)

Recording mass to two decimal places, weigh out about 3 g of oxalic acid dihydrate ($H_2C_2O_4{\cdot}2H_2O(s)$, $\mathcal{M}$ = 126.07 g/mol) onto a tared weighing boat. Transfer the $H_2C_2O_4{\cdot}2H_2O(s)$ to a 100-mL volumetric flask. Rinse the weighing boat and the neck of the flask with deionized water from a wash bottle; you want to get every last bit of $H_2C_2O_4{\cdot}2H_2O(s)$ into the volumetric flask. Fill the flask half-full with deionized water and swirl to dissolve the solid; this may take some time and extensive swirling. When the $H_2C_2O_4{\cdot}2H_2O(s)$ has completely dissolved, add water until the solution reaches the neck of the flask. Using a dropper carefully add more water until the bottom of the liquid level reaches the ring etched on the neck of the flask. Yes, if you pass the mark, you must discard the solution in a hazardous-waste container and begin again. Invert the flask several times to mix. Calculate the molarity of M_{H2C2O4} of oxalic acid in the solution.

Preparation of NaOH(aq)

Sodium hydroxide (NaOH(s), $\mathcal{M}$ = 40.00 g/mol) pellets pick up unknown amounts of water and carbon dioxide from the air. Thus, it is impossible to make up an NaOH solution of known concentration by simply weighing out the solid and dissolving it in water. The exact concentration of the NaOH solution is determined by titrating it against the $H_2C_2O_4$ (aq) solution you prepared.

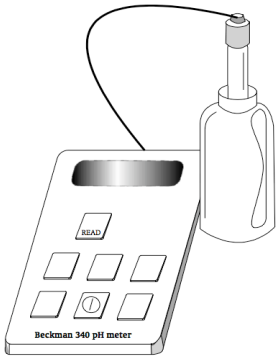


Figure 8-3 The Beckman 340 pH meter and its associated electrode.

Obtain a clean and dry plastic 500-mL screw-cap bottle. Weigh the bottle to two decimal places. Weigh out about 10 g of sodium hydroxide pellets; be sure to record the mass to two decimal places. Transfer the NaOH pellets to the plastic bottle and fill it with deionized water. Swirl and shake the bottle until the pellets are completely dissolved.

Measuring pH using the Beckman 340 pH meter

The progress of the acid–base titrations conducted in this experiment is monitored using the Beckman 340 pH meter (see Figure 8-3). Follow these steps to use the pH meter:

- Turn the power on.
- Push the "READ" button before taking a pH measurement.

The pH meter is connected to a fragile and expensive electrode that will probably be immered in a yellow or red buffer solution. **The electrode cannot ever be allowed to dry out!** Keep it immersed in the red or yellow buffer solution when not in use. **Do not drop the electrode, knock it against the walls or bottom of flasks, or use it as a stirrer!** The yellow or red buffer solution does not interfere with the experiment: any drops of the yellow or red buffer solution clinging to the electrode do not need to be knocked off the electrode before use.

Titration of NaOH(aq) against $H_2C_2O_4$(aq)

The exact concentration of the NaOH(aq) solution is now determined by titrating it against the $H_2C_2O_4$(aq) solution you prepared. Prepare a burette for NaOH(aq) solution and fill the prepared burette with that solution. Record the initial volume reading on the burette to two decimal places. Prepare a 25-mL volumetric pipette for $H_2C_2O_4$(aq) solution. Using a pipette pump, transfer exactly 25.00 mL of $H_2C_2O_4$(aq) solution into a clan and dry 125-mL Erlenmeyer flask., immerse the electrode in the $H_2C_2O_4$(aq) solution and record the pH.

Some of the pH measurements, especially the first few in the buffered region, are subject to drift. Although annoying, drift does not compromise the quality of the data as long as you observe a steady increase in pH as NaOH(aq) solution is added.

Open the stopcock and add 2–3 mL of NaOH(aq) solution to the $H_2C_2O_4$(aq) in the Erlenmeyer flask. Close the stopcock and swirl the solution. Record the pH and the volume reading on the burette to two decimal places. You should observe a modest pH increase of 0.1–0.2 units because you are in the buffered

region of the titration curve. Continue adding 2–3 mL of NaOH(aq), closing the stopcock, swirling the solution after each addition, recording pH and recording the volume reading on the burette.

Eventually, the addition of 2–3 mL of NaOH(aq) will cause the pH to increase by 0.5 units or more: you are entering the equivalence point region of the titration curve. Drastically decrease the volume of the NaOH(aq) additions to the solution in the Erlenmeyer flask: try adding no more than 0.2–0.3 mL, swirling, recording pH, and recording the volume reading on the burette as before.

If adding 0.2–0.3 mL of NaOH(aq) does not result in a pH increase of 0.5 units or more, you may have recorded an experimental artifact that we will call a "false jump": stop adding 0.2–0.3 mL of NaOH(aq) and go back to adding 2–3 mL of NaOH(aq), swirling, recording pH, and recording the volume reading on the burette as before. To repeat: **The only time the addition of 0.2–0.3 mL of NaOH(aq) is appropriate is after you see a pH jump of 0.5 unit or more. If the pH ever jumps by 0.5 unit or less, your next addition of NaOH(aq) should be 2–3 mL.**

Eventually, the addition of 0.2–0.3 mL NaOH(aq) will bring about a very large pH increase ($\geq$ 5 units): you have passed the equivalence point of the titration curve and are now in the unbuffered region. Once the equivalence point is exceeded, it's safe to go back to adding 2–3 mL of NaOH(aq), swirling, recording pH, and recording the volume reading on the burette. **Getting plenty of data beyond the equivalence point is critical to the success of the experiment.** Do not abandon the titration after you have passed the equivalence point.

Repeat the titration on a fresh 25.00-mL sample of $H_2C_2O_4$(aq). You want to calculate the molarity of NaOH(aq) from an average of at least two runs.

Calculating the molarity of NaOH(aq)

After completing the first titration of $H_2C_2O_4$(aq) against NaOH(aq), plot the data you just collected: you want to calculate the molarity of NaOH(aq). **Do not wait to prepare the plot at home after lab!** If the molarity of the NaOH(aq) is sig-

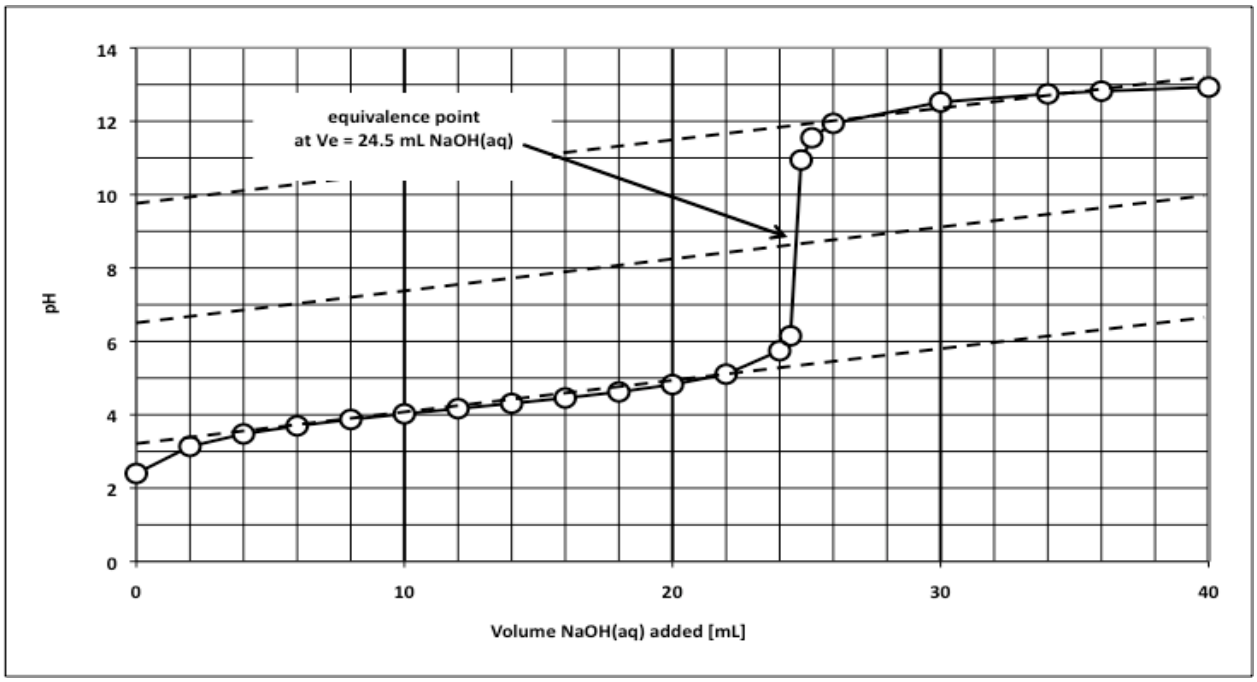
nificantly different from 0.5 *M*, you've done something wrong and remedial action must be taken immediately.

Plot the cumulative volume of NaOH(aq) added along the *x* axis and pH along the *y* axis. Connect the points; the plots should resemble Figure 8-4. Draw a line through the data points that lie on the gently sloping segments of the titration curve at low pH and at high pH. The two lines should ideally be parallel to each other. Now draw a third line parallel to and located midway between the first two. The point at which the center line intersects the titration curve corresponds to V_e, the volume of NaOH(aq) at the equivalence point. In Figure 8-4, V_e is equal to 24.5 mL.

Because two moles of NaOH are needed to react completely with one mole of $H_2C_2O_4$ according to the balanced equation

$$H_2C_2O_4(aq) + 2\,NaOH(aq) \rightarrow Na_2C_2O_4\,(aq) + 2\,H_2O(l)$$

Figure 8-4 Hypothetical data of the titration of 25.00 mL of 0.247 *M* $H_2C_2O_4$(aq) against 0.504 *M* NaOH(aq). Draw lines through the data points lying on the sloping segments of the titration curve at low pH and at high pH. Draw a third line parallel to and midway between the first two. The point at which the center line intersects the titration curve corresponds to V_e, the volume of NaOH(aq) at the equivalence point. In the figure, V_e is equal to 24.5 mL.



the molarity M_{NaOH} of NaOH(aq) is computed using the formula

$$M_{\mathrm{NaOH}} = \frac{2M_{\mathrm{H2C2O4}}V_{\mathrm{H2C2O4}}}{V_e} \qquad \text{(Eqn. 8-2)}$$

where M_{H2C2O4} is the molarity of the $H_2C_2O_4$(aq) solution, V_{H2C2O4} is the volume of $H_2C_2O_4$(aq) taken for titration (i.e., 0.02500 L if you follow instructions) and V_e is the volume in liters of NaOH(aq) required to reach the equivalence point.

Titration of an unknown acid

Weigh a plastic weighing boat to two decimal places. Recording mass to two decimal places, transfer 2–5 g of an unknown acid to the weighing boat. Be sure to record the code number of the unknown. Transfer the unknown acid to a 100-mL volumetric flask. Rinse the weighing boat and the neck of the flask with deionized water from a wash bottle; you want to get every last bit of unknown acid into the volumetric flask. Fill the flask half-full with deionized water and swirl to dissolve the solid; this may take some time and extensive swirling. When the the solid has completely dissolved, add water until the solution reaches the neck of the flask. Using a dropper carefully add more water until the bottom of the liquid level reaches the ring etched on the neck of the flask. Yes, if you pass the mark, you must discard the solution in a hazardous-waste container and begin again. Invert the flask several times to mix.

Using the same technique that you employed in the titration of NaOH(aq) against $H_2C_2O_4$(aq), titrate 25.00-mL samples of the unknown acid solution against NaOH(aq) at least twice. You want to calculate the molar mass $\mathcal{M}$ and the pK_a of the unknown acid from an average of at least two runs. Of course, perform the second titration on a fresh sample of the unknown acid solution. Don't forget to decrease the amount of NaOH(aq) added to the unknown acid solution as you approach the eqivalence point and be sure to record plenty of data after the equivalence point is exceeded. Also, be mindful of the annoying "false jump" phenomenon.

Data analysis

Employing the three-line technique described earlier to determine the molarity of NaOH(aq), for both of your runs in which you titrated the unknown acid solution find the volume V_e in liters of NaOH(aq) that corresponds to the equivalence point of the titration.

The unknown acid HX and NaOH react according to the balanced equation

$$\mathrm{HX(aq)} + \mathrm{NaOH(aq)} \rightarrow \mathrm{NaX(aq)} + \mathrm{H_2O(l)}$$

The number of moles n_{NaOH} of NaOH required to reach the equivalence point is thus given by

$$n_{\mathrm{NaOH}} = M_{\mathrm{NaOH}} V_e$$

where M_{NaOH} is the molarity of NaOH in units of moles per liter.

Because of the one-to-one stoichiometry of the reaction, n_{NaOH} is also equal to the number of moles of unknown acid in the 25.00-mL sample of unknown acid solution that you titrated. But recall, however, that the 25.00-mL samples of unknown acid solution represent only 1/4 of the 100-mL volume of unknown acid solution you prepared; thus, the total number of moles n_{HX} of HX you weighed out is given by

$$n_{\mathrm{HX}} = 4n_{\mathrm{NaOH}} = 4M_{\mathrm{NaOH}} V_e$$

Dividing the mass m_{HX} of unknown acid you dissolved by the total number of moles n_{HX} of unknown acid gives the molar mass $\mathcal{M}_{\mathrm{HX}}$ of the unknown acid. In summary, then,

$$\mathcal{M}_{\mathrm{HX}} = \frac{m_{\mathrm{HX}}}{4M_{\mathrm{NaOH}} V_e} \qquad \text{(Eqn. 8-3)}$$

To find the pK_a of the unknown acid, divide the volume V_e by two. The pH that the unknown acid solution exhibits at $V_e/2$ corresponds to the pK_a of the unknown acid.

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Lab report form **Page 1**

(I.A) Report the mass of $H_2C_2O_4{\cdot}2H_2O(s)$ ($\mathcal{M}$ = 126.07 g/mol) taken = _____ g

(I.B) Show the calculation of M_{H2C2O4}, the concentration of $H_2C_2O_4(aq)$ in units of mole per liter of the $H_2C_2O_4(aq)$ solution you prepared.

(I.C) Report the mass of NaOH(s) taken = _____ g

(II.A) On separate sheets, present plots of the data collected during the titrations of $H_2C_2O_4(aq)$ against NaOH(aq). Plot the cumulative volume of NaOH(aq) added along the *x* axis and pH along the *y* axis. Prepare a separate plot for each run. Give each plot a truly informative title (i.e., don't just call it "Run 1"), label the axes, and include appropriate units and divisions of those axes. Do not submit small plots: use a whole sheet of paper. Scale the horizontal and vertical axes so that the data points occupy most of the area of the plot. Draw the three lines needed to determine the equivalence point V_e (see Figure 8-4) and indicate the location of V_e on the plot.

(II.B) Report the molarity M_{NaOH} of NaOH(aq) calculated according to Eqn. 8-2 and the mean molarity of NaOH(aq).

$$M_{NaOH} = \frac{2M_{H2C2O4}V_{H2C2O4}}{V_e} \qquad \text{(Eqn. 8-2)}$$

Run	M_{H2C2O4} **[mol/L]**	V_{H2C2O4} **[L]**	V_e **[L]**	M_{NaOH} **[mol/L]**
1				
2				
			mean	

Name_____Lab Day_____Lab Time_____

Experiment 8 · Acid-base titration

Lab report form **Page 2**

(III.A) Report the code number of the unknown acid = _____

(III.B) Report the mass m_{HX} of unknown acid taken = _____ g

(IV.A) On separate sheets, present plots of the data collected during the titration of the unknown acid against NaOH(aq). Plot the cumulative volume of NaOH(aq) added along the *x* axis and pH along the *y* axis. Prepare a separate plot for each run. Give each plot a truly informative title (i.e., don't just call it "Run 1"), label the axes, and include appropriate units and divisions of those axes. Do not submit small plots: use a whole sheet of paper. Scale the horizontal and vertical axes so that the data points occupy most of the area of the plot. Draw the three lines needed to determine the equivalence point V_e (see Figure 8-4) and indicate the location of V_e on the plot. Indicate the pK_a of the unknown on the plot.

(IV.B) Report the molar mass $\mathcal{M}_{HX}$ of the unknown acid calculated according to Eqn. 8-3, the pK_a of the unknown acid, and the mean values of $\mathcal{M}_{HX}$ and pK_a.

$$\mathcal{M}_{HX} = \frac{m_{HX}}{4 M_{NaOH} V_e} \qquad \text{(Eqn. 8-3)}$$

Run	m_{HX} **[g]**	M_{NaOH} **[mol/L]**	V_e **[L]**	$\mathcal{M}_{HX}$ **[g/mol]**	pK_a
1					
2					
			mean		

Post-lab questions

(1) Circle the compound that most closely matches your unknown acid.

Acid	$\mathcal{M}$	pK_a	**Acid**	$\mathcal{M}$	pK_a
Boric acid	61.8	9.14	*trans*-Crotonic acid	86.1	4.69
Malic acid	134.1	3.40	Glutamic acid	147.1	4.25
L-Ascorbic acid	176.1	4.17	Potassium hydrogen phthalate	204.2	5.51
3-Iodobenzoic acid	248.0	3.80			