I. TITRATION OF WEAK ACID WITH STRONG BASE CONTINUED

25.0 mL of 0.10 M HCOOH with 0.15 M NaOH (Ka = 1.77 x 10^-4 for HCOOH)

3. \[ V = V_{eq} \] (Point S)
   At the equivalence point, the amount of NaOH added is equal to the amount of HCOOH. The pH is not 7 as it is for a strong acid and a strong base.

The pH is _______ 7 when a weak acid is titrated with a strong base.

The pH depends on the properties of the ____________ formed during the neutralization process.

HCOOH and NaOH form NaHCO_2 and H_2O.

Na\(^+\) has ______________________on pH and
HCO_2\(^-\) is a ______________________.

Thus at the equivalence point, the pH is >7.

Calculate the pH at the equivalence point

Calculate total volume at equivalence point

moles of HCOOH = \(2.5 \times 10^{-3}\) moles = moles of HCO_2\(^-\) formed = moles of OH\(^-\) added

\[
2.5 \times 10^{-3} \text{ moles of OH}^- \times \frac{1\text{L}}{0.15 \text{mol}} = 1.67 \times 10^{-2} \text{ L of NaOH added}
\]

Total volume = 0.0250 L + 0.0167 L = 0.0417 L

Molarity of HCO_2\(^-\)

\[
2.5 \times 10^{-3} \text{ moles of HCO}_2^- / (0.0417 \text{ L}) = 0.0600 \text{ M HCO}_2^-
\]
\[
\text{HCO}_2^{-} (\text{aq}) + \text{H}_2\text{O} (l) \rightleftharpoons \text{HCOOH} (\text{aq}) + \text{OH}^{-} (\text{aq})
\]

<table>
<thead>
<tr>
<th>initial molarity</th>
<th>change in molarity</th>
<th>equilibrium molarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO(_2)(^-)</td>
<td>-x</td>
<td>0.0600 -x</td>
</tr>
<tr>
<td>HCOOH</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>+x</td>
<td>+x</td>
</tr>
</tbody>
</table>

This is a \underline{strong base} problem. You can take it from here. Simplify if x is small compared to 0.0600 M. Calculate x, which is equal to [OH\(^-\)] = 1.83 x 10\(^{-6}\) M. Then calculate pOH = 5.74. From pOH, calculate pH. pH = 8.26 (which is >7)

\[4. \quad V > V_{eq}\] (Point E)

Beyond the equivalence point, NaOH is added to the solution of the conj. base HCO\(_2\)\(^-\).

Since HCO\(_2\)\(^-\) does not give rise to much OH\(^-\) in solution (1.83 x 10\(^{-6}\) M), the pOH and pH are determined by the amount of \underline{NaOH}.

This problem is similar to a strong base problem.

At 5.00 mL past the equivalence point

\[0.00500 \text{ L} \times 0.15 \text{ M} = 7.5 \times 10^{-4} \text{ moles excess OH}^{-}\]

\[7.5 \times 10^{-4} \text{ moles OH}^{-}/(\underline{\text{Volume of base added (mL)}}) = 0.016 \text{ M OH}^{-}\]

pOH = -log [0.016] = 1.79

pH = 12.21

\underline{IN THEIR OWN WORDS: THE IMPORTANCE OF pKa}

Samuel Thompson discusses his research on designing tools to track the movement of proteins in cells. Understanding the relationship between pKa and pH was critical to design a sensor that he hopes will be used to image proteins in diseased cells.

Samuel’s video can be found at: [http://chemvideos.mit.edu/all-videos/](http://chemvideos.mit.edu/all-videos/).

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MORE ABOUT pKₐ

Example 1. Consider a probe (HA) that only glows in the deprotonated state. The pKₐ of the probe is 10.0. Estimate how much of the probe will glow at pH of 7.4?

Example 2. Which structure would you predict the amino acid tyrosine to have at pH 7.4?

END OF EXAM 3 MATERIAL

II. INTRODUCTION TO OXIDATION-REDUCTION (REDOX) REACTIONS

Redox reactions are a major class of chemical reactions in which there is an exchange of electrons from one species to another.

For example, 2Mg (s) + O₂ (g) → 2MgO

Definitions

Oxidation:

Reduction:

Oxidizing agent:

Reducing agent:
Guidelines for Assigning Oxidation Numbers

1) In free elements, each atom has an oxidation number of zero. Example H₂

2) For ions composed of only one atom the oxidation number is equal to the charge on the ion. Thus Li⁺ has an oxidation number of +1. Group 1 and group 2 metals have oxidation numbers of +1 and +2, respectively. Aluminum has an oxidation number of +3 in all its compounds.

3) The oxidation number of oxygen in most compounds is -2. However, in peroxides such as H₂O₂ and O₂²⁻, oxygen has an oxidation state of -1.

4) The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds, such as LiH, NaH, CaH₂. In these cases, its oxidation number is -1.

5) F has an oxidation number of -1 in all its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in compounds (Ex. NaCl). However, when combined with oxygen (oxoacids), they have positive oxidation numbers (Ex. ClO⁻).

6) In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion.

Example NH₄⁺

<table>
<thead>
<tr>
<th>H is</th>
<th>N is</th>
<th>Sum is</th>
</tr>
</thead>
</table>

7) Oxidation numbers do not have to be integers. For example, the oxidation number of oxygen in superoxide O₂⁻¹ is ________

Examples:

- Li₂O
- PCl₅
- HNO₃
- N₂O

Disproportionation Reactions

A reactant element in one oxidation state is **both** oxidized and reduced.

NaClO \( \Rightarrow \) NaClO₃ + NaCl

Write the half reactions and determine the changes in oxidation state. Na⁺ is a spectator ion so:

\[ \text{ClO}^- \quad \Rightarrow \quad \text{ClO}_3^- \]
\[ \text{ClO}^- \quad \Rightarrow \quad \text{Cl}^- \]
III. BALANCING REDOX REACTIONS

A. BALANCE IN ACIDIC SOLUTION

\[ \text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+} \]

(1) Write two unbalanced half reactions for oxidized and reduced species.

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+} \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]

(2) Insert coefficients to make the number of atoms of all elements except oxygen and hydrogen equal on the two sides of each equation.

\[ 2\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]

(3) Add \( \text{H}_2\text{O} \) to balance oxygen.

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]

(4) Balance hydrogen with \( \text{H}^+ \).

\[ 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]

(5) Balance the charge by inserting electrons.

\[ 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]
(6) Multiply the half reactions so that the number of electrons given off in the oxidation equals the number of electrons accepted in the reduction.

\[ 6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O \]

\[ Fe^{2+} \rightarrow Fe^{3+} + e^- \]

(7) Add half reaction, make appropriate cancellations.

\[ 6e^- + 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 6e^- \]

**B. BALANCE IN BASIC SOLUTION.**

\[ Fe^{2+} + Cr_2O_7^{2-} \rightarrow Cr^{3+} + Fe^{3+} \]

Follow steps (1-7) to get your answer for acidic solution:

\[ 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} \]

(8) Then "adjust pH" by adding OH\(^-\) to both sides to neutralize H\(^+\).

\[ 14OH^- + 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 14OH^- \]

\[ OR \]

\[ 14H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 14OH^- \]

CANCEL

\[ 14H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 14OH^- \]

Thus:

\[ 7H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 14OH^- \]

**Summary**

**Acidic:** \[ 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \]

**Basic:** \[ 7H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 14OH^- \]