2019 SSSS: Acton-Boxborough Regional High School – Chemistry Lab Test
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50 MINUTES, FIVE DOUBLE-SIDED PAGES OF NOTES

**Physical Properties (138 points):**

**Fill in the Blank (1 point each, 10 points total)**

1) A material that, when stressed, does not deform before it breaks, is said to be **brittle**.

2) The type of magnetism that a refrigerator magnet exhibits is called **ferromagnetism**.

3) The property of two substances, often liquids, to dissolve in each other and form a homogenous mixture in all proportions is called **miscibility**.

4) When the solid and liquid forms of a substance exist together, and the vapor pressure of the liquid is greater than that of the solid, then the phase change that will occur is **freezing**.

5) **Answers may vary; e.g. nitric acid (HNO₃)** (either name or formula) is one example of a ternary acid.

6) The density of water reaches a maximum at 4 °C.

7) The physical property of **ductility** is often characterized by the ability of the substance to be stretched into a wire.

8) The solubility of a gas **increases** (increases / decreases) with increasing pressure and **decreases** (increases / decreases) with increasing temperature.

9) 1.00 g of helium gas consists of **1.50 * 10²³** He atoms.

10) Aqueous potassium permanganate gives the solution a **purple** color.
Open Response and Calculations (128 points)

1) Match each of the following descriptions to one of the four types of crystalline solids. (6 points)

   (a) ionic      (b) metallic      (c) covalent network      (d) covalent molecular

   • Brittle, non-conductive solid at STP, but highly conductive when heated to temperatures above 801 °C. \( a \)
   • Very high hardness and thermal conductivity. Will only sublime, not melt, when exposed to high temperatures at atmospheric pressure. \( c \)
   • Melting point of 30 °C at standard pressure. As a liquid, very viscous and nonvolatile. Non-directional bonding. \( b \)
   • Conducts electricity as both a solid and a liquid. Malleable and ductile. \( b \)
   • White, crystal solid with a melting point of 78.2 °C. However, is extremely volatile and sublimes easily at room temperature. Directional bonding. \( d \)
   • Little to no electronegativity difference between atoms. Sublimation point is 3642 °C at standard pressure; will only melt at pressures of 100 atm or higher. \( c \)

2) Predict the products of the following chemical reactions, or write NR if no reaction occurs. Balance all equations where necessary. (6 points)

   (a) \( 2 \text{KClO}_3(s) \) + heat \( \rightarrow \) \( 2 \text{KCl} + 3 \text{O}_2 \)

   (b) \( \text{Ag}(s) \) + \( \text{HNO}_3(aq) \) \( \rightarrow \) \( \text{NR} \)

   (c) \( \text{NaNO}_3(aq) \) + \( \text{MgSO}_4(aq) \) \( \rightarrow \) \( \text{NR} \)

3) You are investigating the properties of a concentrated solution over a wide range of varying temperatures. Should you use molarity or molality as a measurement for the solution concentration? Explain. (4 points)

   - **molality**
   - Molarity is per unit volume of solution (while molality is per unit mass of solvent), and volume varies depending on temperature, so molality will not remain constant over a wide range of temperatures.
4) When calcium sulfate dihydrate (also known as gypsum) is heated at temperatures of 100 °C to 150 °C, it decomposes into calcium sulfate hemihydrate (also known as plaster of Paris). The hemihydrate does not appreciably decompose into the anhydrous form until temperatures as high as 170 °C to 180 °C.

- 30.0 g of gypsum are heated at 140 °C to be decomposed into plaster of Paris. After heating for 15 minutes, the remaining mass of the solid is 28.3 g. Calculate the percent yield of water for this reaction. (6 points)

\[ \text{Percent yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100 \]

\[ \text{Percent yield} = \frac{28.3}{\text{Theoretical yield}} \times 100 \]

\[ \text{36\%} \]

- What is one reason that could account for the fact that the percent yield is not 100%? (2 points)

\[ \text{was not heated long enough to remove all the water from the dihydrate} \]

5) A 0.488-\text{m} solution of a salt containing chromium and nitrate ions has a boiling point of 101.00 °C. What is the oxidation number of chromium in this salt? (5 points)

\[ +3 \]

6) Solid potassium hydroxide is gradually dissolved in 460 mL of 0.15-\text{M} calcium perchlorate. Will potassium perchlorate \((K_{sp} = 1.2 \times 10^{-4})\) or calcium hydroxide \((K_{sp} = 1.3 \times 10^{-6})\) precipitate first? What mass of potassium hydroxide must be added so that this precipitate begins to form? Assume that the potassium hydroxide has a negligible effect on the volume of the solution. (8 points)

\[ \text{potassium perchlorate \((KClO_4)\) precipitates first} \]

\[ 0.010 \text{ grams of potassium hydroxide (KOH) must be added} \]
7) The international prototype kilogram, abbreviated the IPK, is a cylinder manufactured from a platinum-iridium alloy with a mass of exactly one kilogram. Both the height and the diameter of the cylinder measure 38.94 mm. If the density of platinum is 21.45 g/cm³ and the density of iridium is 22.56 g/cm³, calculate the mass percentage of each metal in the alloy. (8 points)

\[90.0\% \text{ platinum, } 10.0\% \text{ iridium}\]

8) Order the following sets of compounds from lowest to highest melting/boiling point. (12 points)

- H₂O
- CH₃OH
- CH₃CH₂OH
- C₃H₈

CH₃H₈
- CH₃OH
- CH₃CH₂OH
- H₂O

- CH₄
- CH₃F
- CH₃Cl
- CH₃Br

CH₄
- CH₃F
- CH₃Cl
- CH₃Br

- CaCl₂
- NaCl
- CaO
- Na₂O

CaCl₂
- NaCl
- Na₂O
- CaO

- CH₃OH
- CH₃CH₂CH₂OH
- CH₃OCH₃
- HO–CH₂CH₂–OH

CH₃OCH₃
- CH₃OH
- CH₃CH₂CH₂OH
- HO–CH₂CH₂–OH
9) The graph depicts the temperature of a sample of water when heat is supplied at a constant rate:

\[ \text{line on graph: +2} \]

From 40 °C to 100 °C, draw a line that represents the change in temperature of a sample of liquid carbon tetrabromide of equal mass when heat is added at the same rate. Explain why, on a molecular level, the line for carbon tetrabromide is different than the line for water at these temperatures. You can assume that carbon tetrabromide does not undergo any phase changes in this temperature range. (7 points)

- carbon tetrabromide is nonpolar, unlike water, which is polar and exhibits hydrogen bonding
- weaker intermolecular forces in CBr₄ (only London Dispersion) → lower specific heat, temperature rises more quickly than in water, where heat is consumed to break hydrogen bonds
(explanation: +5)

10) Erythrose is an organic molecule with the appearance of a light yellow syrup when isolated, first extracted from rhubarb plants in 1849. It contains the elements carbon, hydrogen, and oxygen.

- Complete combustion of erythrose with 3.00 g of oxygen gas yields 4.13 g of carbon dioxide and 1.69 g of water vapor. What is the empirical formula of erythrose? (4 points)

\[ \text{CH}_2\text{O} \]

- Erythrose is a non-ionizing, nonvolatile solute when dissolved in water. 15.0 g of erythrose is dissolved in 90.0 g of water, and the new freezing point of the solution is −2.58 °C. What is the molecular formula of erythrose? (5 points)

\[ \text{C}_4\text{H}_8\text{O}_4 \]
11) For each row, circle the element that best fits the description: (6 points)

- Most conductive
- Least reactive
- Largest atomic radius
- Greatest first ionization energy
- Most malleable
- Lowest melting point

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Ag</th>
<th>Si</th>
<th>Ne</th>
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<tbody>
<tr>
<td>Most conductive</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Least reactive</td>
<td>Li</td>
<td>Cu</td>
<td>Zn</td>
<td>Pb</td>
</tr>
<tr>
<td>Largest atomic radius</td>
<td>K</td>
<td>Ca</td>
<td>Cr</td>
<td>Xe</td>
</tr>
<tr>
<td>Greatest first ionization energy</td>
<td>Br</td>
<td>Zn</td>
<td>Kr</td>
<td>Hg</td>
</tr>
<tr>
<td>Most malleable</td>
<td>Au</td>
<td>Rb</td>
<td>Ni</td>
<td>Sn</td>
</tr>
<tr>
<td>Lowest melting point</td>
<td>Be</td>
<td>Ga</td>
<td>Fe</td>
<td>Ti</td>
</tr>
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</table>

12) An element exhibits the following characteristics. Identify whether each is a physical or chemical property and give the identity of the element. (This is like a knockoff version of Chem Clue!) (5 points)

- Exists most stably as a pure element  
  Physical  Chemical
- Exists in the gaseous form at atmospheric pressure  
  Physical  Chemical
- Non-toxic to human cells  
  Physical  Chemical
- Approximately as soluble in water as oxygen gas  
  Physical  Chemical
- Low thermal conductivity  
  Physical  Chemical
- Decay product of radioactive potassium  
  Physical  Chemical

Identity of the element: Argon (Ar)

13) What is the identity of a diatomic gas with a density of 0.00169 g/mL at STP? Points will not be awarded for guessing without work shown. (6 points)

fluorine gas (F₂)
14) The $K_{sp}$ value for barium hydroxide is $5.0 \times 10^{-3}$. What is the pH of a saturated solution? (6 points)

13.33

15) 7.75 L of water is necessary to dissolve 1.00 g of strontium fluoride. What volume of 0.025-$M$ sodium fluoride is needed to dissolve 1.00 g of strontium fluoride? Assume negligible change to the volume of the solution upon dissolving. (8 points)

1150 liters

16) An aqueous solution containing 75.0 g of water has a freezing point of ~25.6 °C. How much water must be added so that the solution boils at 102.40 °C? (6 points)

145 grams

17) A solution contains an unknown dissolved metal cation to be identified. Qualitative analysis produces the following observations in separate samples of the solution:

- Addition of HCl produces no observable reaction
- Addition of NaOH produces a blue precipitate
- Addition of H$_2$S in acidic solution produces a black precipitate that burns blue–green
- Addition of Na$_2$CO$_3$ produces a green precipitate
- Addition of solid iron causes the cation to precipitate as metal
- Addition of solid silver produces no observable reaction

Identify the cation dissolved in the solution. (4 points)

$Cu^{2+}$
18) The following equation shows the equilibrium between two complex cobalt ions:

\[ \text{Co(H}_2\text{O)}_{6}^{2+}(aq) + 4\text{Cl}^{-}(aq) \rightleftharpoons \text{CoCl}_4^{2-}(aq) + 6\text{H}_2\text{O}(g) \]

The \text{Co(H}_2\text{O)}_{6}^{2+}(aq) is pink, while the \text{CoCl}_4^{2-}(aq) is blue. The following graph depicts two different possible absorption spectra that vary with the equilibrium in the solution:

- The absorption spectrum labeled A shows the absorption of the solution when cooled to its freezing point, while the absorption spectrum labeled B shows its absorption when heated to its boiling point. Is the forward reaction endothermic or exothermic? Explain. (6 points)

  - the reaction is endothermic
  - absorption spectrum A (absorbs green light maximally) is \text{Co(H}_2\text{O)}_{6}^{2+}(aq) (pink)
  - absorption spectrum B (absorbs red light maximally) is \text{CoCl}_4^{2-}(aq) (blue)
  - adding heat shifts towards B, meaning more \text{CoCl}_4^{2-}(aq) is produced
  - by LeChatelier’s Principle, the forward reaction producing \text{CoCl}_4^{2-}(aq) is endothermic

- If the absorption spectrum of a beaker containing these ions was intermediate between A and B, which spectrum, A or B, would it resemble more if... (4 points)

  - CoCl$_4^{2-}$ was added?  $\mathbf{A}$  $\mathbf{B}$
  - hydrochloric acid was added?  $\mathbf{A}$  $\mathbf{B}$
  - silver nitrate was added?  $\mathbf{A}$  $\mathbf{B}$
  - the solution was diluted?  $\mathbf{A}$  $\mathbf{B}$
19) Consider the following vapor pressure diagram for pure water:

On the graph, draw the curve that represents the vapor pressure of an aqueous solution. (2 points)

20) Consider the following unlabeled phase diagram of an unknown substance:

- Label the three states of matter in the diagram. (3 points)
- Draw new curves to show the change in the phase diagram when a substance is dissolved in this solvent. (3 points)
- Given that you know it is either one or the other, does this phase diagram represent the properties of water or benzene (C₆H₆)? What feature allows you to tell, and why is this feature different between the two different solvents? (6 points)
  - water, because the solid/liquid line (fusio/freezing point) has a negative slope
  - the solid form is less dense than the liquid form because higher pressure favors the formation of the state that occupies the lowest volume, which in this case is liquid
  - water is polar and exhibits hydrogen bonding; as a solid, molecules lock into place, forming a crystal lattice structure that is less dense than liquid water due to holes
**Acids and Bases (137 points):**

**Multiple Choice (1 point each, 15 points total)**

_____ 1) An unknown solution is poorly conductive and forms bubbles when nickel is added. The solute is most likely:

a. a strong base  
b. a weak base  
c. a strong acid  
d. a weak acid

_____ 2) Which of the following is always true?

a. the conjugate of a strong acid is a strong base  
b. the conjugate of a strong acid is a weak base  
c. the conjugate of a weak acid is a strong base  
d. the conjugate of a weak acid is a weak base

_____ 3) Consider the following equation:

\[ \text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \]

This reaction is an example of all of the following EXCEPT:

a. hydrolysis  
b. deprotonation  
c. autoionization  
d. amphotericism

_____ 4) Which of the following acids has the highest \( K_a \) value?

a. HF  
b. HCl  
c. HBr  
d. HI

_____ 5) Consider the following reaction:

\[ \text{NH}_3(aq) + \text{HNO}_3(aq) \rightarrow \text{NH}_4\text{NO}_3(aq) \]

Is this considered a neutralization reaction?

a. yes, the product is neutral in solution  
b. yes, \( \text{NH}_3 \) accepts a proton from \( \text{HNO}_3 \)  
c. no, water is not a product  
d. no, \( \text{NH}_3 \) is not an Arrhenius base

_____ 6) A base is gradually added to a buffer solution. The buffer capacity is exceeded when:

a. all the buffering acid has reacted  
b. all the buffering base has reacted  
c. the concentrations of hydronium and hydroxide are equal  
d. the \( K_a \) of the added base is higher than the \( K_a \) of the buffering base
7) Which of the following compounds acts as a Brønsted-Lowry base but not as an Arrhenius base?

   a. H₂O  
b. BF₃  
c. NH₃  
d. LiOH

8) Which of the following compounds is most likely to act as a Lewis base?

   a. NH₄⁺  
b. BBr₃  
c. CO₂  
d. PCl₃

9) Which of the following is/are true of a solution formed by dissolving BaO in water?

   I. red litmus paper will turn blue
   II. blue litmus paper will turn red
   III. pH > pOH

   a. I only  
b. II only  
c. I and III  
d. II and III

10) Which description is true of a solution formed by dissolving SO₃ in water?

   a. strong conductor with a pH above 7
   b. strong conductor with a pH below 7
   c. weak conductor with a pH above 7
   d. weak conductor with a pH below 7

11) What type of solution is formed by dissolving KNO₂ in water?

   a. neutral  
b. acidic  
c. basic  
d. not enough information

12) What type of solution is formed by dissolving Sb₂O₃ in water?

   a. neutral  
b. acidic  
c. basic  
d. not enough information

13) Will a solution of sodium formate (NaCHO₂) be an effective buffer?

   a. yes, it produces acidic Na⁺ and basic CHO₂⁻  
b. yes, it produces acidic HCHO₂ and basic CHO₂⁻  
c. no, there is not enough acid  
d. no, there is not enough base

14) The pH of 12 M hydrochloric acid is:

   a. -1.38  
b. -1.08  
c. -0.78  
d. 0

15) 1.60 mL of 0.100 M sodium hydroxide is used to titrate 2.50 mL of oxalic acid. What is the concentration of the oxalic acid solution?

   a. 0.032 M  
b. 0.064 M  
c. 0.078 M  
d. 0.13 M
1. Solution:

(a) The $\text{KH}_2\text{PO}_4$ will have the greatest effect on the pH because the first dissociation of the acid produces the most $\text{H}_3\text{O}^+$ ions:

$$\text{H}_3\text{PO}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{PO}_4^{-}(aq) + \text{H}_3\text{O}^+(aq).$$

By Le Châtelier’s principle, adding more $\text{H}_2\text{PO}_4^-$ shifts the equilibrium to the left, decreasing the concentration of $\text{H}_3\text{O}^+$. The other two salts have a greater impact on the dissociations of $\text{H}_2\text{PO}_3^-$ and $\text{HPO}_2^-$, which account for a smaller portion of the $\text{H}_3\text{O}^+$ ions.

(b) In the same vein, the $\text{K}_3\text{PO}_4$ will have the least effect on the pH because the dissociation of $\text{HPO}_2^-$ accounts for the smallest portion of the $\text{H}_3\text{O}^+$ ions, so the change in pH caused by Le Châtelier’s principle will be small.

(c) The pH will increase because, by Le Châtelier’s principle, the equilibrium will shift to the left when a salt is added due to the common ion effect. $\text{H}_3\text{O}^+$ will be consumed to form more undissociated acid, so the pH will increase.

(d) The $K_a$ values will stay the same because equilibrium constants only change with temperature, not with changes in concentration.

(e) The concentration of $\text{PO}_3^{3-}$ will increase because, by Le Châtelier’s principle, adding $\text{KH}_2\text{PO}_4$ decreases the concentration of $\text{H}_3\text{O}^+$ in the dissociation of $\text{H}_2\text{PO}$:

$$\text{H}_2\text{PO}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{PO}_4^{-}(aq) + \text{H}_3\text{O}^+,$$

Adding $\text{KH}_2\text{PO}_4$ also increases the concentration of $\text{HPO}_2^{-}$:

$$\text{H}_2\text{PO}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HPO}_2^{-}(aq) + \text{H}_3\text{O}^+.$$  

These changes both increase the concentration of $\text{PO}_3^{3-}$ in the dissociation of $\text{HPO}_2^-$:

$$\text{HPO}_2^{-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{PO}_3^{3-}(aq) + \text{H}_3\text{O}^+.$$  

(f) The amphoteric species in solution are $\text{H}_2\text{O}$, $\text{H}_2\text{PO}_4^-$, and $\text{HPO}_2^-$ because all three are capable of both donating and accepting a proton. Adding $\text{K}_3\text{PO}_4$ does not change this.

2. Solution: Ammonium bicarbonate has the chemical formula $\text{NH}_4\text{HCO}_3$. The following reactions show the reactions of the added ions with water:

$$\text{HCO}_3^{-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq).$$

$$\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq).$$

(We can assume that the deprotonation of $\text{HCO}_3^{-}(aq)$ is negligible because it is such a weak acid.)

Both $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions are produced, so we must determine which one is produced in higher concentrations to tell whether the solution is acidic or basic. We can see that $K_b$ for $\text{NH}_3$ is greater than $K_a$ for $\text{H}_2\text{CO}_3$, so $K_a$ for $\text{NH}_4^+$ is less than $K_b$ for $\text{HCO}_3^-$ because the strength of an acid or a base varies inversely with the strength of its conjugate.

Thus, $\text{HCO}_3^-$ is stronger as a base than $\text{NH}_4^+$ is an acid, so more $\text{HCO}_3^-$ will react with water than $\text{NH}_4^+$. From the equations, we can see that this will yield more $\text{OH}^-$ than $\text{H}^+$, so the solution will be basic. Therefore, phenolphthalein will turn the solution pink.
3. **Solution:** Metal oxides are basic anhydrides that react with water to form metal hydroxides. Let M be the unidentified metal. The reaction with water is as follows:

\[
\text{M}_2\text{O}(s) + \text{H}_2\text{O}(l) \rightarrow 2\text{M}^+_{(aq)} + 2\text{OH}^-_{(aq)}.
\]

The pOH of the solution is 14.00 – 12.18 = 1.82, so the concentration of the hydroxide ions is:

\[
[\text{OH}^-] = 10^{-1.82} M = 0.015 M.
\]

Using the volume, we convert the concentration to number of moles:

\[
0.015 M \text{OH}^- \times 650 \text{ mL} = \frac{0.015 \text{ mol OH}^-}{1 \text{ L}} \times 650 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0098 \text{ mol OH}^-.
\]

We use stoichiometry to find the moles of M$_2$O reacted:

\[
0.0098 \text{ mol OH}^- \times \frac{1 \text{ mol M}_2\text{O}}{2 \text{ mol OH}^-} = 0.0049 \text{ mol M}_2\text{O}.
\]

The molar mass of the M$_2$O is:

\[
\text{MM} = \frac{0.92 \text{ g}}{0.0049 \text{ mol}} = 190 \text{ g/mol}.
\]

We find the molar mass of M:

\[2 \times \text{MM of M} + \text{MM of O} = \text{MM of M}_2\text{O}.
\]

\[2 \times \text{MM of M} = 190 \text{ g/mol} - 16.00 \text{ g/mol} = 170 \text{ g/mol}.
\]

\[
\text{MM of M} = \frac{170 \text{ g/mol}}{2} = 85 \text{ g/mol}.
\]

Using a periodic table, we can see that M is **rubidium (Rb)**.

4. **Solution:**

(a) We know sulfur, being in one of the upper periods of the periodic table, has a higher electronegativity than tellurium. This means that sulfur exerts a greater pull on electrons than tellurium, thus making the bond between the proton and the polyatomic anion more polar. A higher polarity means that it is easier for water, a polar solvent, to dissociate the solute. As a result, **HSO$_3^-$** deprotonates more easily and thus has a higher $K_a$ value.

**Note:** The rule of electronegativity does not apply to binary acids such as HF, HCl, HBr, and HI because the bond strength of those acids decreases sharply as the electronegativity difference decreases, so the more electronegative ones, such as HF, are actually weaker. However, in oxyacids, the hydrogen atom is always bonded to an oxygen atom, so electronegativity has no effect on the bond strength.)

(b) The oxygen atoms in an oxyacid pull on the electrons in the bond with hydrogen. Thus, a greater number of oxygen atoms around the central atom in the polyatomic anion increases the electronegativity difference within the acid. An increased electronegativity difference makes it easier to be dissociated in water, so H$_3$AsO$_4$ is a stronger acid than H$_3$AsO$_3$. Since the strength of an acid is inversely related to the strength of its conjugate base, H$_2$AsO$_4^-$ is a weaker base than H$_2$AsO$_3^-$. Therefore, **H$_2$AsO$_3^-$** has a higher $K_b$ value.

(c) Since H$_2$S is a weak acid, HS$^-$ is a much weaker acid with an even lower $K_a$ but also a moderately effective base. Thus, HS$^-$ has a higher tendency to act as a **base** than as an acid, accepting more protons than donating.
5. **Solution:** Given the percent composition of pyruvate, our first step is to determine the empirical formula. Assuming that there are exactly 100 grams of pyruvate, we can calculate it as follows:

\[
\begin{align*}
41.39 \text{ g C} & \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.446 \text{ mol C}, \\
3.47 \text{ g H} & \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 3.44 \text{ mol H}, \\
55.14 \text{ g O} & \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.44 \text{ mol O}.
\end{align*}
\]

Thus, the empirical formula for pyruvate is \( \text{CHO}^- \).

Let A be the molecular formula for the pyruvate. Since pyruvic acid is an acid and pyruvate is a base, we can represent their reactions in water with the following equations:

\[
\begin{align*}
\text{HA}(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{A}^- (aq) + \text{H}_3\text{O}^+(aq), \\
\text{A}^- (aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{HA}(aq) + \text{OH}^-(aq).
\end{align*}
\]

Now, there are two ways to continue from here.

**Method 1:** This way is longer but more logical and more likely for one to think of while doing this problem. We can write the \( K_b \) expression of pyruvate as follows:

\[
K_b = \frac{[\text{HA}] [\text{OH}^-]}{[\text{A}^-]}.
\]

We know that pH + pOH = 14, so the pOH is 14 – 1.468 = 12.532. We use this to calculate the concentration of hydroxide ions:

\[
[\text{OH}^-] = 10^{-12.532} M = 2.94 \times 10^{-13} M.
\]

Since the dissociation of HA produced 0.0340 \( M \) of \( \text{H}_3\text{O}^+ \), we know that the equilibrium concentration of \( \text{A}^- \) is 0.0340 \( M \), formed by the dissociation of 0.0340 \( M \) of HA. We now set up a rice table to solve for the initial concentration of pyruvic acid using the given \( K_b \):

<table>
<thead>
<tr>
<th>R</th>
<th>A^-</th>
<th>HA</th>
<th>OH^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0 M</td>
<td>( x )</td>
<td>—</td>
</tr>
<tr>
<td>C</td>
<td>+0.0340 M</td>
<td>—0.0340 M</td>
<td>—</td>
</tr>
<tr>
<td>E</td>
<td>0.0340 M</td>
<td>( x - 0.0340 M )</td>
<td>( 2.94 \times 10^{-13} M )</td>
</tr>
</tbody>
</table>

We now substitute our values into the equation for \( K_b \) and solve:

\[
3.16 \times 10^{-12} = \frac{(x - 0.0340)(2.94 \times 10^{-13})}{0.0340}.
\]

\[
x - 0.0340 = \frac{(3.16 \times 10^{-12})(0.0340)}{2.94 \times 10^{-13}} = 0.365.
\]

\[
x = 0.365 + 0.0340 = 0.399 M.
\]

To calculate \( K_a \) for pyruvic acid, we substitute this value into the \( K_a \) expression:

\[
K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}.
\]
\[
K_a = \frac{(0.0340)(0.0340)}{0.399 - 0.0340}.
\]

\[
K_a = \frac{0.0340^2}{0.365} = 3.17 \times 10^{-3}.
\]

We use the initial concentration to calculate the initial number of moles of HA:

\[
0.399 M = \frac{0.399 \text{ mol}}{1 \text{ L}} \times 265 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.106 \text{ mol}.
\]

We can calculate the molar mass of pyruvic acid using the initial mass:

\[
MM = \frac{9.34 \text{ g}}{0.106 \text{ mol}} = 88.1 \text{ g/mol}.
\]

Since pyruvate is the conjugate base of pyruvic acid, it has one less H atom, so we must subtract to get the molar mass of pyruvate:

\[
MM = 88.1 \text{ g/mol} - 1.01 \text{ g/mol} = 81.7 \text{ g/mol}.
\]

We now calculate the formula factor of pyruvate:

\[
FF = \frac{\text{MM of Empirical}}{\text{MM of Molecular}}.
\]

MM of Molecular = 12.01 g/mol + 1.01 g/mol + 16.00 g/mol = 29.02 g/mol.

\[
FF = \frac{87.1 \text{ g/mol}}{29.02 \text{ g/mol}} = 3.00.
\]

The formula factor is 3, so the molecular formula of pyruvate is C\(_3\)H\(_3\)O\(_3\). Therefore, the chemical formula of pyruvic acid, which has one more H atom, is $\text{C}_3\text{H}_4\text{O}_3$ or $\text{HC}_3\text{H}_3\text{O}_3$.

**Method 2:** This way is significantly faster but also much less likely for one to think of. Observe the following relationship between the \(K_a\) of an acid and the \(K_b\) of the conjugate base:

\[
K_a \times K_b = \frac{[A^-][H_3O^+]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w = 1 \times 10^{-14}.
\]

Therefore, the \(K_a\) for pyruvic acid is:

\[
K_a = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{3.16 \times 10^{-12}} = 3.16 \times 10^{-3}.
\]

The concentration of hydronium ions is:

\[
[H_3O^+] = 10^{-1.468} M = 0.0340 M.
\]

By mole ratios, the concentration of the \(A^-\) is also 0.0340 M. We now set up a RICE table:

<table>
<thead>
<tr>
<th>R</th>
<th>HA</th>
<th>H(^+)</th>
<th>A(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>(x M)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>-0.0340 M</td>
<td>-0.0340 M</td>
<td>+0.0340 M</td>
</tr>
<tr>
<td>E</td>
<td>(x - 0.0340 M)</td>
<td>(0.0340 M)</td>
<td>(0.0340 M)</td>
</tr>
</tbody>
</table>
Using our calculated $K_a$ value, we solve for the initial concentration of pyruvic acid:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}.$$  

$$3.16 \times 10^{-3} = \frac{0.0340 \times 0.0340}{x - 0.0340}$$  

$$x - 0.0340 = \frac{0.0340^2}{3.16 \times 10^{-3}} = 0.366.$$  

$$x = 0.366 + 0.0340 = 0.400 \ M.$$  

Consult Method 1 to finish the problem from here.

6. Solution: Ammonium chloride dissociates in water by the following equation:

$$\text{NH}_4\text{Cl}_{(aq)} \rightarrow \text{NH}_4^{+}_{(aq)} + \text{Cl}^-_{(aq)}.$$  

Thus, one mole of ammonium chloride produces one mole of ammonium ions in solution.

We find the concentration of hydroxide ions in a solution with a pH of 9.00:

$$\text{pOH} = 14 - \text{pH} = 14 - 9.00 = 5.00.$$  

$$[\text{OH}^-] = 10^{-5.00} = 1.0 \times 10^{-5}.$$  

We now calculate the ratio of ammonia to ammonium chloride that we need for an initial pH of 9.00 using a RICE table:

<table>
<thead>
<tr>
<th></th>
<th>NH$_3$</th>
<th>NH$_4^+$</th>
<th>OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$x$</td>
<td>$y$</td>
<td>0 $M$</td>
</tr>
<tr>
<td>C</td>
<td>$-1.0 \times 10^{-5} \ M$</td>
<td>$+1.0 \times 10^{-5} \ M$</td>
<td>$+1.0 \times 10^{-5} \ M$</td>
</tr>
<tr>
<td>E</td>
<td>$x - 1.0 \times 10^{-5} \ M$</td>
<td>$y + 1.0 \times 10^{-5} \ M$</td>
<td>$1.0 \times 10^{-5} \ M$</td>
</tr>
</tbody>
</table>

Since the changes in the concentrations of NH$_3$ and NH$_4^+$ are so small, we can assume that they are negligible. With that assumption, we can find the ratio of NH$_3$ to NH$_4^+$:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}.$$  

$$1.8 \times 10^{-5} = \frac{(y)(1.0 \times 10^{-5})}{x}.$$  

$$y = \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-5}} = 1.8.$$  

$$y = 1.8x.$$  

We have determined that for every mole of NH$_4^+$, we must also have 1.8 moles of NH$_3$.

We now consider what happens when the lithium hydroxide is added. As it is a strong base, it will react with the acid in the buffer solution, which is NH$_4^+$. The neutralization reaction is as follows:

$$\text{NH}_4^+_{(aq)} + \text{LiOH}_{(aq)} \rightleftharpoons \text{NH}_3_{(aq)} + \text{H}_2\text{O}_{(l)} + \text{Li}^+_{(aq)}.$$  

We know that this is the neutralization reaction because NH$_4^+$, as a Brønsted-Lowry acid, undergoes neutralization by donating its proton to become its conjugate base, NH$_3$. We now use stoichiometry to determine the new concentrations of NH$_3$ and NH$_4^+$:

$$15 \text{ g LiOH} \times \frac{1 \text{ mol LiOH}}{23.95 \text{ LiOH}} = 0.63 \text{ mol LiOH}.$$  

5
\[ \frac{0.63 \text{ mol LiOH}}{2.5 \text{ L}} = 0.25 \text{ M LiOH}. \]

\[ [\text{NH}_3] = x + 0.25 \text{ M}, \quad [\text{NH}_4^+] = 1.8x - 0.25 \text{ M}. \]

Since the pH can change by no more than 0.30, the new pH after the neutralization should be 9.30. We find \([\text{OH}^-]\) at that pH:

\[ \text{pOH} = 14 - \text{pH} = 14 - 9.30 = 4.70. \]

\[ [\text{OH}^-] = 10^{-4.70} = 2.0 \times 10^{-5}. \]

We set up another RICE table to solve for \(x\):

<table>
<thead>
<tr>
<th></th>
<th>(\text{NH}_3)</th>
<th>(\text{NH}_4^+)</th>
<th>(\text{OH}^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>(x + 0.25 \text{ M})</td>
<td>(1.8x - 0.25 \text{ M})</td>
<td>0 M</td>
</tr>
<tr>
<td>C</td>
<td>(-2.0 \times 10^{-5} \text{ M})</td>
<td>(+2.0 \times 10^{-5} \text{ M})</td>
<td>(+2.0 \times 10^{-5} \text{ M})</td>
</tr>
<tr>
<td>E</td>
<td>(x + 0.25 \text{ M} - 2.0 \times 10^{-5} \text{ M})</td>
<td>(1.8x - 0.25 \text{ M} + 2.0 \times 10^{-5} \text{ M})</td>
<td>(2.0 \times 10^{-5} \text{ M})</td>
</tr>
</tbody>
</table>

We can once again assume that the changes in the concentrations of \(\text{NH}_3\) and \(\text{NH}_4^+\) are so small as to be negligible. We solve for \(x\), the initial concentration of \(\text{NH}_3\), using the \(K_b\) value:

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}. \]

\[ 1.8 \times 10^{-5} = \frac{(1.8x - 0.25 \text{ M})(2.0 \times 10^{-5})}{x + 0.25 \text{ M}}. \]

\[ (1.8 \times 10^{-5})x + 4.5 \times 10^{-6} = (3.6 \times 10^{-5})x - 5.0 \times 10^{-6}. \]

\[ 9.5 \times 10^{-6} = 1.8 \times 10^{-5}. \]

\[ x = \frac{9.5 \times 10^{-6}}{1.8 \times 10^{-5}} = 0.53 \text{ M NH}_3. \]

Finally, we know that the concentration of \(\text{NH}_4^+\) is \(1.8x\), which is:

\[ 1.8x = 1.8 \times 0.53 \text{ M} = 0.95 \text{ M NH}_4^+. \]

7. **Solution:**

(a) The autoionization of water is as follows:

\[ \text{H}_2\text{O}^{(l)} + \text{H}_2\text{O}^{(l)} \rightleftharpoons \text{H}_3\text{O}^{+ (aq)} + \text{OH}^{- (aq)}. \]

In pure water, the ratio of \(\text{H}_3\text{O}^+\) to \(\text{OH}^-\) is always 1 : 1, so pure water must always be neutral, even if the pH might seem to suggest otherwise. Furthermore, the fact that neither red nor blue litmus paper changes color shows that there is no excess of either \(\text{H}_3\text{O}^+\) or \(\text{OH}^-\) ions.

(b) From part (a), we know that the concentration of \(\text{OH}^-\) in pure water always equals the concentration of \(\text{H}_3\text{O}^+\), so pOH is equal to pH. Thus, the pOH of water at 85 °C is also 6.26.

(c) Since pH and pOH decrease with increasing temperature, the concentrations of \(\text{H}_3\text{O}^+\) and \(\text{OH}^-\) are increasing. With the equation for the autoionization of pure water in part (a), we can see that the equilibrium shifts to the right when temperature is increased. By Le Châtelier’s principle, heat must be a reactant of the equation, so the autoionization of water is endothermic.
8. Solution:

(a)  
- $\text{H}_3\text{PO}_4$: Yes, it is a weak acid.
- $\text{H}_2\text{SO}_4$: No, it is a strong acid.
- RbOH: No, it is a strong base.
- $\text{NH}_4\text{Br}$: Yes, it produces NH$_3$ (also written as NH$_4$OH), a weak base, and HBr, a strong acid.
- HClO$_4$: No, it is a strong acid.
- $\text{CH}_3(\text{CH}_2)_3\text{COOH}$: Yes, it has a covalent carboxyl group (–COOH), which is weakly acidic.
- CaCl$_2$: No, it produces HCl, a strong acid, and Ca(OH)$_2$, a strong base.
- KCH$_3$COO: No, it produces CH$_3$COOH, a weak acid, and KOH, a strong base.

(b) Weak acids remain mostly undissociated when dissolved and are therefore weakly conductive. Salts, on the other hand, ionize completely to produce solutions that are strong conductors. $\text{H}_3\text{PO}_4$ and $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ are weak acids, so they produce weakly conductive solutions. However, $\text{NH}_4\text{Br}$ is a salt, which means that it ionizes completely to become a strong conductor. While the solution is not strongly acidic, the many ions from the salt provide high conductivity.

9. Solution: The equation for the double displacement reaction in solution:

$$2\text{HCN}_{(aq)} + \text{Ba(OH)}_2_{(aq)} \rightarrow \text{Ba(CN)}_2_{(aq)} + 2\text{H}_2\text{O}_(l)$$

Using stoichiometry, we find the number of moles of hydrocyanic acid produced:

$$\frac{0.100 \text{ mol Ba(OH)}_2}{1 \text{ L}} \times 13.7 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{2 \text{ mol HCN}}{1 \text{ mol Ba(OH)}_2} = 0.00274 \text{ mol HCN}.$$  

Using the initial volume, the original concentration of HCN is:

$$\frac{0.00274 \text{ mol HCN}}{7.50 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.365 \text{ M HCN}.$$  

The dissociation equation for hydrocyanic acid is:

$$\text{HCN}_{(aq)} + \text{H}_2\text{O}_(l) \rightleftharpoons \text{CN}^-_{(aq)} + \text{H}_3\text{O}^+_{(aq)}.$$  

We can find $[\text{H}_3\text{O}^+]$ using the pH:

$$[\text{H}_3\text{O}^+] = 10^{-4.82} \text{ M} = 1.5 \times 10^{-5} \text{ M}.$$  

Since there is a 1 : 1 mole ratio, we know that $[\text{CN}^-]$ is equal to $[\text{H}_3\text{O}^+]$. Thus, the $K_a$ value is:

$$K_a = \frac{[\text{CN}^-][\text{H}_3\text{O}^+]}{[\text{HCN}]} = \frac{(1.5 \times 10^{-5})(1.5 \times 10^{-5})}{(0.365 - 1.5 \times 10^{-5})} = \frac{(1.5 \times 10^{-5})^2}{0.365}.$$  

$$K_a = 6.2 \times 10^{-10}.$$  

From here, we can continue in two ways, as we did in #5.
Method 1: This way takes longer but does not require the relationship between $K_a$ and $K_b$ if one does not know it. The reaction of the cyanide ion with water is as follows:

$$\text{CN}^-_{(aq)} + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}_{(aq)} + \text{OH}^-_{(aq)}.$$  

The number of moles of cyanide ions in the titrated solution is:

$$0.00274 \text{ mol HCN} \times \frac{1 \text{ mol Ba(CN)}_2}{2 \text{ mol HCN}} \times \frac{2 \text{ mol CN}^-}{1 \text{ mol Ba(CN)}_2} = 0.00274 \text{ mol CN}^-.$$  

The final volume of the solution is $7.50 \text{ mL} + 13.70 \text{ mL} = 21.20 \text{ mL}$, so the concentration of CN$^-$ is:

$$\frac{0.00274 \text{ mol CN}^-}{21.20 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.129 \text{ M}.$$  

Let $x$ be the concentration of CN$^-$ that reacts with water as shown, which is also the concentration of HCN and OH$^-$ produced. In order to use the $K_a$ value, we must use $[\text{H}_3\text{O}^+]$ instead of $[\text{OH}^-]$. Since $[\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$, we know that $[\text{H}_3\text{O}^+] = (1 \times 10^{-14})/x$. We set up a RICE table:

<table>
<thead>
<tr>
<th></th>
<th>HCN</th>
<th>CN$^-$</th>
<th>H$_3$O$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0 M</td>
<td>0.129 M</td>
<td>—</td>
</tr>
<tr>
<td>C</td>
<td>+x</td>
<td>−x</td>
<td>—</td>
</tr>
<tr>
<td>E</td>
<td>$x$</td>
<td>0.129 M − $x$</td>
<td>$(1 \times 10^{-14})/x$</td>
</tr>
</tbody>
</table>

Since we do not know the $K_b$ of CN$^-$, let us assume the 5% rule and check it at the end, because otherwise we have to use the quadratic formula and nobody likes that. We now solve for $x$ with $K_a$:

$$6.2 \times 10^{-10} = \frac{(0.129)(1 \times 10^{-14})/x}{x}.$$  

$$6.2 \times 10^{-10} = \frac{0.129 \times 10^{-14}}{x^2}.$$  

$$x^2 = \frac{0.129 \times 10^{-14}}{6.2 \times 10^{-10}}.$$  

$$x = 0.0014 \text{ M}.$$  

We check the 5% rule with the initial concentration of CN$^-$:

$$\frac{0.0014 \text{ M}}{0.129 \text{ M}} \times 100\% = 1.1\%. \quad 1.1\% < 5\%.$$  

Therefore, our assumption was valid. Whew. We calculate $[\text{H}_3\text{O}^+]$ and finally the pH:

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{0.0014} = 7.1 \times 10^{-12} \text{ M}.$$  

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(7.1 \times 10^{-12}) = \boxed{11.15}.$$  

Method 2: We established in #5 that $K_a \times K_b = K_w$. We use this solve for the $K_b$ value for cyanide:

$$K_a \times K_b = K_w$$  

$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}.$$  

The reaction of the cyanide ion with water is as follows:

$$\text{CN}^-_{(aq)} + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}_{(aq)} + \text{OH}^-_{(aq)}.$$

8
The number of moles of cyanide ions in the titrated solution is:
\[
0.00274 \text{ mol HCN} \times \frac{1 \text{ mol Ba(CN)}_2}{2 \text{ mol HCN}} \times \frac{2 \text{ mol CN}^-}{1 \text{ mol Ba(CN)}_2} = 0.00274 \text{ mol CN}^-.
\]

The final volume of the solution is 7.50 mL + 13.70 mL = 21.20 mL, so the concentration of CN\(^-\) is:
\[
\frac{0.00274 \text{ mol CN}^-}{21.20 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.192 \text{ M}.
\]

We now construct a RICE table to solve for [OH\(^-\)]:

<table>
<thead>
<tr>
<th></th>
<th>CN(^-)</th>
<th>HCN</th>
<th>OH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>0.129 M</td>
<td>0 M</td>
<td>0 M</td>
</tr>
<tr>
<td>C</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>E</td>
<td>0.129 M - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Given the low value of \(K_b\), we can assume that the decrease in [CN\(^-\)] is negligible. We solve for \(x\):
\[
K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}
\]
\[
1.6 \times 10^{-5} = \frac{x^2}{0.129}
\]
\[
x^2 = 2.1 \times 10^{-6}
\]
\[
x = 0.0014 \text{ M}.
\]

Knowing [OH\(^-\)], we calculate [H\(_3\)O\(^+\)] and finally the pH:
\[
[H_3O^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{0.0014} = 7.1 \times 10^{-12} \text{ M}.
\]
\[
pH = -\log[H_3O^+] = -\log(7.1 \times 10^{-12}) = 11.15.
\]

10. **Solution**: The equation for the dissociation of methyl orange is:
\[
HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq).
\]

The \(K_a\) expression for methyl orange is:
\[
K_a = \frac{[A^-][H_3O^+]}{HA}.
\]

We know that we will see a change in color from yellow to red when:
\[
\frac{[HA]}{[A^-]} = 10.
\]

This means that:
\[
\frac{[A^-]}{[HA]} = 10.
\]

The \(K_a\) expression for methyl orange is:
\[
K_a = \frac{[H_3O^+][A^-]}{[HA]}.
\]
We can substitute in order to find the concentration of $\text{H}_3\text{O}^+$ necessary to observe a change in color:

$$3.4 \times 10^{-4} = [\text{H}_3\text{O}^+] \times 10.$$  

$$[\text{H}_3\text{O}^+] = \frac{3.4 \times 10^{-4}}{10} = 3.4 \times 10^{-5}.$$  

The dissociation of selenic acid occurs in two steps:

$$\text{H}_2\text{SeO}_4(aq) + \text{H}_2\text{O}(l) \rightarrow \text{HSeO}_4^-(aq) + \text{H}_3\text{O}^+(aq),$$

$$\text{HSeO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{SeO}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq).$$

We must take into the account that both the first and second dissociations account for some of the $\text{H}_3\text{O}^+$ ions. Since selenic acid is a strong acid, we know that the first deprotonation occurs completely. Letting $x$ be the concentration of $\text{H}_3\text{O}^+$ from the first dissociation and $y$ be the concentration of $\text{H}_3\text{O}^+$ from the second dissociation, we set up a RICE table before and after the second dissociation:

<table>
<thead>
<tr>
<th>R</th>
<th>HSeO$_4^-$</th>
<th>SeO$_4^{2-}$</th>
<th>$\text{H}_3\text{O}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$x$</td>
<td>0 $M$</td>
<td>$x$</td>
</tr>
<tr>
<td>C</td>
<td>$-y$</td>
<td>$+y$</td>
<td>$+y$</td>
</tr>
<tr>
<td>E</td>
<td>$x - y$</td>
<td>$y$</td>
<td>$x + y$</td>
</tr>
</tbody>
</table>

We know that $[\text{H}_3\text{O}^+] = 3.4 \times 10^{-5}$, which means that:

$$x + y = 3.4 \times 10^{-5}.$$  

$$y = 3.4 \times 10^{-5} - x.$$  

We want to solve for $x$ to find the initial concentration of HSeO$_4^-$, which is equal to the original concentration of H$_2$SeO$_4$ because selenic acid is a strong acid. We use the given $K_a$ of HSeO$_4^-$ to solve for $x$:

$$K_{a2} = \frac{[\text{SeO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HSeO}_4^-]}.$$  

$$2.2 \times 10^{-2} = \frac{(y)(x + y)}{(x - y)}.$$  

When we substitute for $y$, we get:

$$2.2 \times 10^{-2} = \frac{(3.4 \times 10^{-5} - x)(3.4 \times 10^{-5})}{(2x - 3.4 \times 10^{-5})}.$$  

$$1.2 \times 10^{-7} - (3.4 \times 10^{-5})x = 1.2 \times 10^{-9} - (3.4 \times 10^{-5})x.$$  

$$2.2 \times 10^{-2} = (4.4 \times 10^{-2)x} + (3.4 \times 10^{-5})x = (4.4 \times 10^{-2)x} = 7.5 \times 10^{-7} + 1.2 \times 10^{-9}.$$  

$$x = 7.5 \times 10^{-7}.$$  

$$4.4 \times 10^{-7} = 1.7 \times 10^{-5} \text{ M} \text{H}_3\text{O}^+.$$  

This is the concentration of $\text{H}_3\text{O}^+$ produced by the first dissociation only, which occurs as follows:

$$\text{H}_2\text{SeO}_4(aq) + \text{H}_2\text{O}(l) \rightarrow \text{HSeO}_4^-(aq) + \text{H}_3\text{O}^+(aq).$$

Therefore, the initial concentration of H$_2$SeO$_4$ necessary is:

$$1.7 \times 10^{-5} \text{ M} \text{H}_3\text{O}^+ = \frac{1.7 \times 10^{-5} \text{ mol H}_3\text{O}^+}{1 \text{ L}} \times \frac{1 \text{ mol H}_2\text{SeO}_4}{1 \text{ mol H}_3\text{O}^+} = 1.7 \times 10^{-5} \text{ M} \text{H}_2\text{SeO}_4.$$

10
11. **Solution:** We have four equations: First we find the initial molarity of $\text{H}_3\text{O}^+$ using the pH:

$$[\text{H}_3\text{O}^+] = 10^{-2.29} \, M = 0.0051 \, M.$$  

We now find the initial concentration of the citric acid originally:

$$K_{a1} = 8.4 \times 10^{-4} = \frac{[\text{H}_2\text{A}^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{A}]} = \frac{0.0051 \times 0.0051}{x - 0.0052}$$

$$x = 0.036 \, M.$$  

We now find the molar mass of the added sodium dihydrogen citrate, which has one sodium atom in place of a hydrogen atom:

$$\text{MM} = 192 \, \text{g/mol} - 1.01 \, \text{g/mol} + 23.00 \, \text{g/mol} = 214 \, \text{g/mol}.$$  

We find the number of moles of NaH$_2$A:

$$0.11 \, \text{g NaH}_2\text{A} \times \frac{1 \, \text{mol NaH}_2\text{A}}{214 \, \text{g NaH}_2\text{A}} = 5.1 \times 10^{-4} \, \text{mol NaH}_2\text{A}.$$  

The dissociation of NaH$_2$A occurs as follows:

$$\text{NaH}_2\text{A}_{(aq)} \rightarrow \text{Na}^+_{(aq)} + \text{H}_2\text{A}^-_{(aq)}.$$  

We find the number of moles of $\text{H}_2\text{A}^-$:

$$5.1 \times 10^{-4} \, \text{mol NaH}_2\text{A} \times \frac{1 \, \text{mol H}_2\text{A}^-}{1 \, \text{mol NaH}_2\text{A}} = 5.1 \times 10^{-4} \, \text{mol H}_2\text{A}^-.$$  

We find the concentration of $\text{H}_2\text{A}^-$:

$$\frac{5.1 \times 10^{-4} \, \text{mol H}_2\text{A}^-}{55 \, \text{mL}} \times \frac{1000 \, \text{mL}}{1 \, \text{L}} = 0.0093 \, M \text{H}_2\text{A}^-.$$  

Since we are to assume that all $\text{H}_3\text{O}^+$ ions are produced by the first dissociation, our first step is to find the new concentration of $\text{H}_3\text{O}^+$. We draw a RICE table for the first dissociation:

<table>
<thead>
<tr>
<th></th>
<th>$\text{H}<em>3\text{A}</em>{(aq)}$</th>
<th>$\text{H}<em>2\text{O}</em>{(l)}$</th>
<th>$\text{H}<em>2\text{A}^-</em>{(aq)}$</th>
<th>$\text{H}<em>3\text{O}^+</em>{(aq)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R</strong></td>
<td>0.036 M</td>
<td>0.0093 M</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>$-x$</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td><strong>E</strong></td>
<td>0.036 M $-x$</td>
<td>0.0093 M $+x$</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Since the $K_a (8.4 \times 10^{-4})$ has an exponent of $-4$, we see that the 5% rule will not work here. (In fact, if you go ahead and make the assumption anyways, it comes out to be about 7% of the initial concentration, and the answer gets thrown off.) We must solve for $x$ using the quadratic formula:

$$K_a = \frac{[\text{H}_2\text{A}^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{A}]}.$$  

$$8.4 \times 10^{-4} = \frac{(x)(0.0093 + x)}{(0.036 - x)}$$  

$$3.0 \times 10^{-5} - (8.4 \times 10^{-4})x = 0.0093x + x^2.$$  

$$x^2 + 0.0101x - 3.0 \times 10^{-5} = 0.$$
\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}.
\]
\[
x = \frac{-0.0101 \pm \sqrt{1.02 \times 10^{-4} + 1.2 \times 10^{-3}}}{2}.
\]
\[
x = \frac{-0.0101 \pm 0.015}{2}.
\]
\[
x = -0.013 \text{ M}, 0.025 \text{ M}.
\]
We reject the negative root:
\[
x = 0.0025 \text{ M}
\]
Whew. Now, we can stop using the quadratic formula because the next two \( K_a \) values are low enough.

We draw another RICE table for the second dissociation:

\[
\text{H}_2\text{A}^-_{(aq)} + \text{H}_2\text{O}(_t) \rightleftharpoons \text{HA}^{2-}_{(aq)} + \text{H}_3\text{O}^+_{(aq)},
\]

<table>
<thead>
<tr>
<th>R</th>
<th>H(_2)A(^-)</th>
<th>HA(^{2-})</th>
<th>H(_3)O(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.0093 M + 0.0025 M</td>
<td>0</td>
<td>0.0025 M</td>
</tr>
<tr>
<td>C</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>E</td>
<td>(0.0118 \text{ M} - x)</td>
<td>(x)</td>
<td>0.0025 M + x</td>
</tr>
</tbody>
</table>

\[
K_{a2} = \frac{[\text{HA}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{A}^{2-}]}.
\]
\[
1.8 \times 10^{-5} = \frac{x(0.0025 + x)}{(0.0118 - x)}.
\]
\[
1.8 \times 10^{-5} = \frac{0.0025x}{0.0118}
\]
\[
x = 8.5 \times 10^{-5} \text{ M}.
\]

There are a lot of RICE tables here...

\[
\text{HA}^{2-}_{(aq)} + \text{H}_2\text{O}(_t) \rightleftharpoons \text{A}^{3-}_{(aq)} + \text{H}_3\text{O}^+_{(aq)},
\]

<table>
<thead>
<tr>
<th>R</th>
<th>HA(^{2-})</th>
<th>A(^{3-})</th>
<th>H(_3)O(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>8.5 \times 10^{-5} M</td>
<td>0</td>
<td>0.0025 M + 8.5 \times 10^{-5} M</td>
</tr>
<tr>
<td>C</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>E</td>
<td>8.5 \times 10^{-5} M - x</td>
<td>(x)</td>
<td>0.0025 M + x</td>
</tr>
</tbody>
</table>

\[
K_{a3} = \frac{[\text{A}^{3-}][\text{H}_3\text{O}^+]}{[\text{HA}^{2-}]}.
\]
\[
4.0 \times 10^{-6} = \frac{x(0.0025 + x)}{(8.5 \times 10^{-5} - x)}.
\]
\[
4.0 \times 10^{-6} = \frac{0.0025x}{8.5 \times 10^{-5}}
\]
\[
x = 1.4 \times 10^{-7} \text{ M}.
\]

Finally (wow, this is exhausting), we find the number of citrate ions:

\[
1.4 \times 10^{-7} \text{ mol} \frac{\text{mol}}{L} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{55 \text{ mL}}{6.022 \times 10^{23} \text{ ions}} = 4.6 \times 10^{15} \text{ ions}.
\]