1a) If we are to ignore the second ionization, and we are told that H₂SeO₄ is strong acid (comparable to H₂SO₄) with a complete, first ionization, then the approximate hydronium ion concentration of a 0.175 M solution would be **0.175 M**.

b) We are told that we, in fact, can not ignore the second ionization, and therefore must calculate the [H₃O⁺] concentration. We can set up our I.C.F. table for the following reaction:

\[
\text{HSeO}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{SeO}_4^{2-}
\]

\[K_{a2} = 1.2 \times 10^{-2}\]

<table>
<thead>
<tr>
<th>I</th>
<th>0.175</th>
<th>0.175</th>
<th>0.0</th>
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</thead>
<tbody>
<tr>
<td>C</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>F</td>
<td>0.175 - x</td>
<td>0.175 + x</td>
<td>x</td>
</tr>
</tbody>
</table>

Setting up the equilibrium expression, we get (note we can NOT use the approximation, and must solve a quadratic):

\[K_{a2} = 1.2 \times 10^{-2} = \frac{[H_3O^+][SeO_4^{2-}]}{[HSeO_4^-]} = \frac{(0.175 + x)(x)}{(0.175 - x)}\]

which leads to a value for \(x = 0.011\) M, and a [H₃O⁺] = **0.186 M**.

2) We need to get a few pieces of data before we can really begin. The number of moles of quinidine is: \(\frac{0.03385 \text{g}}{324.41 \text{g/mol}} = 1.043 \times 10^{-4}\). The number of moles of HCl added is:

\((0.00655 \text{L})(0.150 \text{ M}) = 9.825 \times 10^{-4}\). The corresponding \(K_a\)'s are: \(K_{a1} = 2.5 \times 10^{-9}\); \(K_{a2} = 1 \times 10^{-4}\).

a) Every mole of quinidine uses two moles of HCl, so the number of moles of excess HCl is: 9.825 x 10⁻⁴ - 2.086 x 10⁻⁴ = 7.739 x 10⁻⁴ moles, which would require 7.739 x 10⁻⁴ moles / 0.0133 mol/L = **58.19 mL** of 0.0133 M NaOH to titrate.

b) We are now asked to figure out how much NaOH is needed for the reaction:

\[
\text{QH}_2^{2+} + \text{OH}^- \rightarrow \text{QH}^+ + \text{H}_2\text{O}
\]

We have only 1.043 x 10⁻⁴ moles of QH₂⁺² (from the acidification step), and we need to provide, therefore, only 1.043 x 10⁻⁴ moles OH⁻, so we need: \(\frac{1.043 \times 10^{-4} \text{mol}}{0.0133 \text{mol/L}} = **7.84 \text{mL}**\).

c) At the first equivalence point, we are looking at the following equilibria:
\[ \text{QH}_2^{2+} \leftrightarrow \text{QH}^+ \leftrightarrow \text{Q} \]

The first one is controlled by \( K_{a2} \), and the second, by \( K_{a1} \). (Since these are related through \( K_w \), we can also use \( K_{b1} \), and \( K_{b2} \)). At the midpoint of these equilibria, reactions both to the right and the left are operative, so we can (sort of) look at it as two separate application of a buffer system. Taking the geometric mean of the \( K_b \)'s, we get a value of \( 2 \times 10^{-8} \), which we can convert into a \( pK_b \) and get 7.70, which is the \( pOH \) of the solution. Subtracting this \( pOH \) from 14, we get \( pH = 6.30 \) (which probably makes a lot more sense than 7.70!)

3) We are given a \( pH \), and a density, and are asked to calculate the freezing point of 0.87 M \( \text{NH}_3 \) solution. The \( K_b \) for \( \text{NH}_3 \) is \( 1.8 \times 10^{-5} \).

Here is our equilibrium:

\[ \text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \]

Using our normal I.C.F. table, we come to the equilibrium expression (we can use the approximation):

\[ K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(x)^2}{(0.87 M)}, \]

which leads to an \( x = 3.96 \times 10^{-3} \) M.

We have been assuming one liter of solution, which has mass of 992 g (given the density as 0.992 g/mL). We have 0.87 moles \( \text{NH}_3 \), which leads to a mass of \((0.87 \text{ moles})(17.03061 \text{ g/mol}) = 14.82 \text{ g}\) for the ammonia. This mass of ammonia leaves 977.18 g of water (= 0.97718 kg), and gives an apparent molality of \((0.87 + 0.00396) = 0.87396 \text{ m}\). Substituting this molality into \( \Delta T_f = K_g m \), we get: \( \Delta T_f = (1.858 \degree \text{C/m})(0.87396 \text{ m}) = 1.624 \degree \text{C} \). Therefore, our freezing point is: \(-1.624 \degree \text{C}\).

4) Since we are working with formic acid, we need a \( K_a = 1.7 \times 10^{-4} \), so \( pK_a = 3.77 \). We need \( pH \) of 3.35, so: \( pH = pK_a + \log(\frac{[\text{CHO}_2^-]}{[\text{HCHO}_2^-]}) \) leads us to: 3.35 = 3.77 + 

\[ \log(\frac{[\text{CHO}_2^-]}{[\text{HCHO}_2^-]}) \text{ or } -0.42 = \log(\frac{[\text{CHO}_2^-]}{[\text{HCHO}_2^-]}). \]

This leads to: \( 0.3802 = \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2^-]} \). Formic acid has \( M_m = 46.0257 \) and a given density of 1.220 g/mL. To make the buffer, we need first to make the sodium salt of the formic acid, which we will do by the addition of pure formic acid to the \( \text{NaOH} \) solution we are given. We have 325 mL (=0.325 L) 0.0857 M \( \text{NaOH} \) or 2.785 x \( 10^{-2} \) moles \( \text{OH}^- \) ion we need to neutralize, for which we will use 2.785 x \( 10^{-2} \) moles of formic acid, or 1.2818 g of formic acid or 1.0507 mL. Call this volume \( 1 \).

We now have 2.785 x \( 10^{-2} \) moles of \( \text{NaCHO}_2 \).

The important thing to recognize at this point is that, although the total volume of the solution is unknown, it is quite possible to calculate concentrations of both \( \text{HCHO}_2^- \) and \( \text{CHO}_2^- \). As stated above, we have 2.785 x \( 10^{-2} \) moles of \( \text{NaCHO}_2 \) in some unknown volume; we will also have a certain number of moles of \( \text{HCHO}_2^- \) in the same unknown
volume!\). From the ratio above \(0.3802 = \frac{CHO_2}{HCHO_2}\), we find we need an additional

\[7.325 \times 10^{-2}\] moles HCHO₂ or 3.3715 g which is 2.7635 mL. Call this volume₂. The total
volume we need, therefore, is volume₁ + volume₂ = 1.0507 mL + 2.7635 mL = \textbf{3.8142 mL}.\]