1a) If we are to ignore the second ionization, and we are told that $\text{H}_2\text{SeO}_4$ is strong acid (comparable to $\text{H}_2\text{SO}_4$) 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 $[\text{H}_3\text{O}^+]$ concentration. We can set up our I.C.F. table for the following reaction:

\[
\text{HSeO}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{SeO}_4^{2-} \quad K_{a2} = 1.2 \times 10^{-2}
\]

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<tbody>
<tr>
<td>x</td>
<td>0.175</td>
<td>-x</td>
<td>0.175-x</td>
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<tr>
<td>x</td>
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<td>+x</td>
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Setting up the equilibrium expression, we get (note we can NOT use the approximation, and must solve a quadratic):

\[
K_{a2} = 1.2 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{SeO}_4^{2-}]}{[\text{HSeO}_4^-]} = \frac{(0.175+x)(x)}{(0.175-x)}
\]

which leads to a value for $x = 0.011 \, M$, and a $[\text{H}_3\text{O}^+] = 0.186 \, M$.

2) We need to get a few pieces of data before we can really begin. The number of moles of quinidine is: $0.03385 \, g / 324.41 \, g / \text{mol} = 1.043 \times 10^{-4} \, \text{mol}$. The number of moles of HCl added is; $(0.00655 \, \text{L})(0.150 \, M) = 9.825 \times 10^{-4} \, \text{mol}$. 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: $9.825 \times 10^{-4} - 2.086 \times 10^{-4} = 7.739 \times 10^{-4} \, \text{moles}$, which would require $\frac{7.739 \times 10^{-4} \, \text{moles}}{0.0133 \, \text{mol/L}} = 58.19 \, \text{mL}$ 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 $1.043 \times 10^{-4} \, \text{mol}$ of $\text{QH}_2^{+2}$ (from the acidification step), and we need to provide, therefore, only $1.043 \times 10^{-4} \, \text{mol}$ of 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:
QH$_2^{2+}$ $\iff$ QH$^+$ $\iff$ Q

The first one is controlled by $K_{a2}$, and the second, by $K_{a1}$. (Since these are related through $K_a$, 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 p$K_b$ and get 7.70, which is the pH of the solution.

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

Here is our equilibrium:

NH$_3$ + H$_2$O $\iff$ NH$_4^+$ + OH$^-$.  

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

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)^2}{(0.87M)},$$

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 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 $977.18 \text{ g}$ of water ($= 0.97718 \text{ kg}$), and gives an apparent molality of $(0.87 + 0.00396) = 0.87396 \text{ m}$. Substituting this molality into $\Delta T_f = K_f m$, we get: $\Delta T_f = (1.858 \circ F/m)(0.87396 \circ C/m) = 1.624 \circ C$. Therefore, our freezing point is: $-1.624 \circ C$.

4) Since we are working with formic acid, we need a $K_a = 1.7 \times 10^{-4}$, so p$K_a = 3.77$. We need pH of 3.35, so: pH = p$K_a + \log(\frac{[CHO_2^-]}{[HCHO_2]})$ leads us to: 3.35 = 3.77 + $\log(\frac{[CHO_2^-]}{[HCHO_2]})$ or $-0.42 = \log(\frac{[CHO_2^-]}{[HCHO_2]})$. This leads to: $0.3802 = \frac{[CHO_2^-]}{[HCHO_2]}$. 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 NaOH solution we are given. We have 325 mL ($=0.325 \text{ L}$) 0.0857 M NaOH or $2.785 \times 10^{-2}$ moles OH$^-$ ion we need to neutralize, for which we will use $2.785 \times 10^{-2}$ moles of formic acid, or 1.2818 g of formic acid or 1.0507 mL. Call this volume1.

We now have $2.785 \times 10^{-2}$ moles of 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 HCHO$_2$ and CHO$_2^-$. As stated above, we have $2.785 \times 10^{-2}$ moles of NaCHO$_2$ in some unknown volume; we will also have a certain number of moles of HCHO$_2$ in the same unknown
volume!. From the ratio above \(0.3802 = \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]}\), we find we need an additional 7.325 \(\times\) \(10^{-2}\) moles \(\text{HCHO}_2\) or 3.3715 g which is 2.7635 mL. Call this volume_2. The total volume we need, therefore, is \(\text{volume}_1 + \text{volume}_2 = 1.0507 \text{ mL} + 2.7635 \text{ mL} = 3.8142 \text{ mL}\).