1) a) salicylic acid

i) This is a good model for NOM because it has the two most common functional groups of NOM, the phenolic group and the carboxyl group. It also has the aromatic character of a lot of NOM.

ii) The carboxylic acid group is a stronger acid and will deprotonate first, so the $pK_a = 3.1$ corresponds to ii.

b) 

- hemimellitic acid
- versus trimesic acid.

The carboxylic acid groups in trimesic acid are more separated and consequently more independent than those in hemimellitic acid. This suggests that trimesic acid has $pK_a = 3.12$, $pK_{a2} = 4.10$, and $pK_{a3} = 5.18$.

The carboxyl group is slightly electron withdrawing, and when the carboxyl groups are closer together, then the first deprotonation results in a conjugate base that is stabilized by the nearby other groups. This suggests that hemimellitic acid has a lower first $pK_a$ than trimesic acid has. So hemimellitic acid has $pK_{a1} = 2.86$, $pK_{a2} = 4.30$, $pK_{a3} = 6.28$.

Subsequent deprotonation is less favorable because the carboxylate anionic groups are not electron withdrawing. There may also be steric effects from proximate anionic groups.
2) Prepare pH 6 solution with $10^{-3}$ M total MES from: water, 0.1 M HMES, 0.1 M NaOH.

\[
\text{HMES} = \text{H}^+ + \text{MES}^- \\
K_a = 10^{-6.15} = \frac{[\text{H}^+] [\text{MES}^-]}{[\text{HMES}]} \quad \text{M NaOH}
\]

Species: $\text{H}^+$, $\text{OH}^-$, $\text{HMES}$, $\text{MES}^-$, $\text{Na}^+$

Components: $\text{H}^+$, $\text{MES}^-$, $\text{Na}^+$ (not necessary, but can be helpful)

a) Write the tableau and then find the recipe that would provide the answer.

<table>
<thead>
<tr>
<th></th>
<th>$\text{H}^+$</th>
<th>$\text{MES}^-$</th>
<th>$\text{Na}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}^+$</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{OH}^-$</td>
<td>-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{HMES}$</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$\text{MES}^-$</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Na}^+$</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$[\text{HMES}]_T$</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Na} \text{MES}]_T$</td>
<td>-1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{TOT} &= [\text{H}^+] - [\text{OH}^-] + [\text{HMES}]_T - [\text{NaOH}]_T \\
\text{TOTMES} &= [\text{MES}^-] + [\text{HMES}]_T = 10^{-3} \text{ M} = [\text{HMES}]_T + [\text{NaMES}]_T \\
\text{TOTNa} &= [\text{Na}^-] = [\text{NaMES}]_T + [\text{NaOH}]_T
\end{align*}
\]

\[
\begin{align*}
\text{At pH} 6, \quad [\text{H}^+] &= 10^{-6}, \quad [\text{OH}^-] &= 10^{-8} \\
\text{TOT} &= 10^{-6} - 10^{-8} + 5.86 \cdot 10^{-4} = 5.86 \cdot 10^{-4} \text{ M}
\end{align*}
\]

Need to get this TOT and TOTMES = $10^{-3}$ M.

Add all MES as HMES $[\text{HMES}]_T = 10^{-3}$ M, then $[\text{NaMES}]_T = 0$.

\[
\begin{align*}
\text{TOT} &= 5.86 \cdot 10^{-3} \text{ M} - 10^{-3} - [\text{NaOH}]_T \\
[\text{NaOH}]_T &= 4.14 \cdot 10^{-4} \text{ M}
\end{align*}
\]

Make by adding

\[
\begin{align*}
10 \text{ mL 0.1 M HMES solution} \\
0.414 \text{ mL 1 M NaOH solution} \\
989.6 \text{ mL H}_2\text{O}
\end{align*}
\]

b) Alternatively, add $[\text{HMES}]_T = 5.86 \cdot 10^{-4}$ M and $[\text{NaMES}]_T = 4.14 \cdot 10^{-4}$ M, which provides $\text{TOT} = 5.86 \cdot 10^{-4}$ M and TOTMES = $10^{-3}$ M.

These recipes result in the same mole balance equations so they are equivalent.

Recipe: $4.14 \text{ mL 0.1 M NaMES solution} \\
5.86 \text{ mL 0.1 M HMES solution}$
$3) \quad \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{CO}_2^{2-} \quad K = 10^{-3.50} \quad pK_a = 3.50 \quad \text{p. 149}$

$$\frac{[\text{CO}_2\text{(aq)}]}{[\text{H}_2\text{CO}_3\text{aq}]} = 707 \quad \text{p. 149}$$

$\text{CO}_2\text{(aq)}$ is present at a greater concentration
4) Problem 6 in Chapter 3

\[ HX \rightleftharpoons H^+ + X^- \quad K_{o1} = \frac{[H^+][X^-]}{[HX]} \quad [H^+]_T = 4 \times 10^{-3} M, \quad pH = 2.5 \]

What pH of solution \( [NaX]_T = 4 \times 10^{-3} M \)

Write charge balance and mole balances for first solution

\[ \text{TOT} X = [H^+] + [X^-] = 4 \times 10^{-3} \]

\[ \text{charge balance: } \quad [H^+] = [X^-] + [H_2O] \quad \text{reg} \text{ of } pH \ 2.5 \]

\[ [H^+] = \frac{4 \times 10^{-3}}{(4 \times 10^{-5})} \quad \text{reg} \text{ of } pH \ 2.5 \]

\[ \frac{[H^+]^2}{K_a} + [H_2O] = 4 \times 10^{-3} \]

\[ \frac{[H^+]^2}{K_a} + 4 \times 10^{-3} = 4 \times 10^{-3} \sqrt{K_a} = 4 \times 10^{-3} \]

\[ K_a = \frac{[H^+]^2}{(4 \times 10^{-5} - [H^+]^2)} = \frac{10^{-5}}{(4 \times 10^{-5} - 10^{-7})} = 0.0119 = 10^{-1.92} \]

Solution of NaX

\[ \text{TOT} X = [X^-] + [H^+] = 4 \times 10^{-3} M \quad \text{TOT} Na = [Na^+] = 4 \times 10^{-3} M \]

\[ \text{charge balance: } \quad [H^+] + [Na^+] = [OH^-] + [X^-] \quad [X^-] = \frac{\text{TOT} X}{[Na^+] / K_a + 1} \]

\[ [H^+] + 4 \times 10^{-3} = \frac{10^{-14}}{[H^+]} + \frac{4 \times 10^{-3}}{(4 \times 10^{-3}) / (10^{-14})} \]

will result in a cubic equation, that can be solved.

Alternatively substitute \( \text{TOT} X - [H^+] = [X^-] \) into charge balance

\[ [H^+] + [Na^+] = [OH^-] + \text{TOT} X - [H^+] \quad [Na^+] = \text{TOT} X = 4 \times 10^{-3} \]

\[ [H^+] + [H^+] = [OH^-] \]

because \( HX \) is a fairly strong acid, \( NaX \) is a weak base and we can probably assume \( \text{TOT} X - [H^+] \approx \text{TOT} X \)

\[ \frac{[H^+]^2}{K_a} \approx \frac{[H^+]^2}{4 \times 10^{-3}} \quad [H^+] = 0.33 \text{ M} \]

\[ 10^{-14} = 1.33 \times 10^{-14} \quad \text{reg of } pH 7.06 \]

\[ \text{check assumption } \quad [HX] = \frac{[H^+]^3}{(1 + 10^{14} / 10^{7.06})} = 2.9 \times 10^{-8} \ll [X^-] \checkmark \]
8) Problem 2 from Chapter 4

Citric acid system

\[ \begin{align*}
    K_{a1} &= 10^{-3.13} = \frac{[H_2C_2O_4^2^-][H^+]}{[H_2C_2O_4]^+} \\
    K_{a2} &= 10^{-4.72} = \frac{[HC_2O_4^-][H^+]}{[H_2C_2O_4]^+} \\
    K_{a3} &= 10^{-6.33} = \frac{[C_2O_4^{2-}][H^+]}{[HC_2O_4^-]} \\
\end{align*} \]

a) \[ \alpha_0 = \frac{[H_2C_2O_4]}{[H_2C_2O_4]^+} \text{ TotCit} = [H_2C_2O_4] + [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}] \\
\]

\[ \alpha_0 = \left( 1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a2}K_{a3}}{[H^+]^2} + \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3} \right)^{-1} \]

\[ \alpha_1 = \frac{[H_2C_2O_4]}{[H_2C_2O_4]^+} = \left( \frac{[H^+]^2}{K_{a1}} + 1 + \frac{K_{a2}}{[H^+]^2} + \frac{K_{a2}K_{a3}}{[H^+]^4} \right)^{-1} \]

\[ \alpha_2 = \frac{[HC_2O_4^-]}{[H_2C_2O_4]^+} = \left( \frac{[H^+]^2}{K_{a2}} + \frac{[H^+]^2}{K_{a3}} + 1 + \frac{K_{a3}}{[H^+]^4} \right)^{-1} \]

\[ \alpha_3 = \frac{[C_2O_4^{2-}]}{[H_2C_2O_4]^+} = \left( \frac{[H^+]^3}{K_{a1}K_{a2}K_{a3}} + \frac{[H^+]^2}{K_{a2}K_{a3}} + \frac{[H^+]}{K_{a3}} + 1 \right)^{-1} \]

b) \begin{align*}
    \text{H}_2\text{C}_2\text{O}_4^+ \text{ dominant } &\quad \text{pH} < 3.13 \\
    \text{H}_2\text{C}_2\text{O}_4^- \text{ dominant } &\quad 3.13 < \text{pH} < 4.72 \\
    \text{HC}_2\text{O}_4^- \text{ dominant } &\quad 4.72 < \text{pH} < 6.33 \\
    \text{C}_2\text{O}_4^{2-} \text{ dominant } &\quad \text{pH} > 6.33 \\
\end{align*}

\[ \text{pH} 7.5 \]

\[ \alpha_0 = \left( \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3} \right)^{-1} = \frac{[H^+]^3}{10^{-7.94} (1 + 10^{4.37} + 10^{7.15} + 10^{8.32})^{-1}} \]

\[ \alpha_1 = \left( \frac{K_{a2}K_{a3}}{[H^+]^2} \right)^{-1} = \frac{[H^+]^2}{10^{-4.85}} \]

\[ \alpha_2 = \left( \frac{K_{a3}}{[H^+]^2} \right)^{-1} = \frac{[H^+]^3}{10^6} \]

\[ \alpha_3 = (1)^{-1} = 1 \]

\[ \frac{[\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]} = 10^{4.85} = 10^{4.17} = 14.8 \text{, so might also consider } [\text{HC}_2\text{O}_4^-] \text{ forms} \]
$\text{5c) (continued) TOTCl}^+ = 0.1 \text{ M}$

\[
\text{log} \left[H_3\text{Cl}^-\right] = 13.18 - 3\text{pH}
\]

\[
\text{log} \left[H_2\text{Cl}^+\right] = 10.05 - 2\text{pH}
\]

\[
\text{log} \left[H\text{Cl}^2-\right] = 5.33 - \text{pH}
\]

\[
\text{log} \left[C\text{li}^2+\right] = 1.01
\]

**d)** see attached plot

d) see attached plot

d) see attached plot

e) i) $\left[H_3\text{Cl}^-\right]_T = 0.1 \text{ M}$

charge balance: $\left[H^+\right] = \left[OH^-\right] + \left[H_2\text{Cl}^+\right] + 2\left[H\text{Cl}^2-\right] + 3\left[C\text{li}^3-\right]

intersection $i)$ $\left[H^+\right] = \left[H_2\text{Cl}^+\right]$, $\text{pH} \approx 2.1$

ii) $\left[N_0\text{HCl}^-\right]_T = 0.1 \text{ M}$, as in i) $\text{TOTCl}^+ = \left[H_3\text{Cl}^-\right] + \left[H\text{Cl}^2-\right] + 2\left[H\text{Cl}^2-\right] = 10^{-1} \text{ M}$

now $\text{TOTNa} = \left[N_0\right] = 0.2 \text{ M}$

charge balance: $\left[N_0\right] + \left[H^+\right] = \left[OH^-\right] + \left[H_2\text{Cl}^+\right] + 2\left[H\text{Cl}^2-\right] + 3\left[C\text{li}^3-\right]$

from chart in region where $\left[N_0\right] = 2\left[H\text{Cl}^2-\right] + 3\left[C\text{li}^3-\right]$

(see plot of LHS and RHS)

looks like intersection of $\approx 5.7$
The intersection is hard to see because the LHS and RHS lines are so flat where they cross.

An improved estimate can be gained by eliminating the major terms from the charge balance by combination of mass and charge balance.

By looking at plots, we see that \( \text{HCl}^2^- \) and \( \text{Na}^+ \) are dominant charge balance

\[
\begin{align*}
[\text{Na}^+] + [\text{H}^+] - [\text{OH}^-] - [\text{H}_2\text{Cl}^-] - 2[\text{HCl}^2^-] - 3[\text{Cl}^-] &= 0 \\
+ 2 \times \text{TOT} \text{Cl}^+ \\
2[\text{H}_3\text{Cl}^-] + 2[\text{H}_2\text{Cl}^-] + 2[\text{HCl}^2^-] + 2[\text{Cl}^-] &= 0.2 \text{ M} \\
- \text{TOT} \text{Na} & \quad = -0.2 \text{ M}
\end{align*}
\]

\[
[\text{H}^+] - [\text{OH}^-] + 2[\text{H}_3\text{Cl}^-] + [\text{H}_2\text{Cl}^-] - [\text{Cl}^-] = 0
\]

Now eliminate minor terms in above equation (minor because of where they are on log \( \text{pH} \) plot in \( \text{pH} \) range of interest)

\[
[H_2Cl^-] - [Cl^-] = 0
\]

\[
[H_2Cl^-] = [Cl^-]
\]

Intersection at \( \text{pH} \approx 5.5 \)

or consider reactions

\[
[H_2Cl^-] = \frac{[\text{HCl}^2^-][\text{H}^+]}{K_{a2}} = \frac{K_{a2} [\text{HCl}^2^-]}{[\text{H}^+]}
\]

\[
[H^+]^2 = K_{a2} K_{a3}
\]

\[
[H^+] = \left( \frac{-4.72 - 6.33}{10} \right)^{0.5} - 5.53
\]

\[
\text{pH} = 5.53 , \quad \text{pH} = \frac{pK_{a2} + pK_{a3}}{2}
\]

\[\text{iii)} \ [\text{Na}_2\text{Cl}^-] = 0.05 \text{ M} \quad + [\text{NaH}_2\text{Cl}^+] = 0.05 \text{ M}
\]

Note \( \text{TOT} \text{Cl}^+ = [\text{Na}_2\text{Cl}^-] + [\text{NaH}_2\text{Cl}^+] = 0.1 \text{ M} \) \( \text{TOT} \text{Na} = 3 [\text{Na}_2\text{Cl}^-] + [\text{NaH}_2\text{Cl}^+] = 0.2 \text{ M} \) same as in part ii;)

No equations or mass balances have changed, so systems ii and iii are equivalent.

\[\text{pH} = 5.53\]
LogC-pH for Na-Citrate System
TOTCit = 0.1 M; TOTNa = 0.2 M

For parts ii and iii

Cations:
- [H^+]
- [OH^-]
- [H3Cit]
- [H2Cit^-]
- [HCit2^-]
- [Cit3-]
- [Na^+]

Anions:
- LHS
- RHS