PS 150 - ANSWERS

It is often helpful to devise a "pH line" for each family system encountered in problems such as these. By listing the formulas of the family members and the key data at various pH locations, one can better keep track of what is happening at various places within a titration (or in a problem).

For question 1 (and 2):
PHOSPHORIC ACID (OR PHOSPHATE) FAMILY

\[ \begin{align*}
\text{H}_3\text{PO}_4 & \quad pK_1 \\
\text{H}_2\text{PO}_4^- & \quad pK_2 \\
\text{HPO}_4^{2-} & \quad pK_3 \\
\text{PO}_4^{3-} & \quad \text{vs OH}^- \\
2.12 & \quad 7.21 & \quad 12.33
\end{align*} \]

\[ \frac{2.12 + 7.21}{2} = \frac{7.21 + 12.33}{2} = 9.77 \]

\[ \text{pH too high already, so no final e.p. here} \]

For question 3:
CITRIC ACID (OR CITRATE) FAMILY

\[ \begin{align*}
\text{H}_3\text{Cit} & \quad pK_1 \\
\text{H}_2\text{Cit}^- & \quad pK_2 \\
\text{HCit}^{2-} & \quad pK_3 \\
\text{Cit}^{3-} & \quad \text{vs OH}^- \\
3.08 & \quad 4.66 & \quad 6.40
\end{align*} \]

\[ \text{K's too close for intermediate e.p.'s} \]

For question 4a:
OXALIC ACID (OR OXALATE) FAMILY

\[ \begin{align*}
\text{H}_2\text{C}_2\text{O}_4 & \quad pK_1 \\
\text{HC}_2\text{O}_4^- & \quad pK_2 \\
\text{C}_2\text{O}_4^{2-} & \quad \text{vs OH}^- \\
1.27 & \quad 4.27 & \quad 1.27 + 4.27 = 5.54
\end{align*} \]

\[ \frac{1.27 + 4.27}{2} = 2.77 \]

\[ \text{start titration \quad 1st e.p. \quad 2nd e.p.} \]
For question 4b:

SUCCINIC ACID (OR SUCCINATE) FAMILY

\[
\begin{align*}
\text{H}_2\text{Suc} & \quad \text{PK}_1 & \quad \text{PK}_2 & \quad \text{Xs OH}^- \\
\text{HSuc}^- & \quad \text{Suc}^2- & \quad 4.19 & \quad 5.48 & \quad \text{K's too close for intermediate e.p.} \quad \uparrow \\
\text{start of} & \quad \text{titration} & \quad \text{e.p. here}
\end{align*}
\]

For question 4c:

HOAc SYSTEM (WITH EXTRA STRONG ACID, HCl)

\[
\begin{align*}
\text{xS H}_3\text{O}^+ & \quad \text{PK}_a & \quad \text{Xs OH}^- \\
\text{HOAc} & \quad \text{OAc}^- & \quad 4.74 & \quad \text{this will act as an e.p. after the strong acid is titrated} & \quad \text{e.p. here}
\end{align*}
\]

\[
\begin{align*}
\text{start of titration} & \quad \text{e.p. here}
\end{align*}
\]

For questions 5 (also applicable to 6):

CARBONIC ACID (OR CARBONATE) SYSTEM

\[
\begin{align*}
\text{xS H}_3\text{O}^+ & \quad \text{PK}_1 & \quad \text{PK}_2 & \quad \text{CO}_3^{2-} \\
\text{H}_2\text{CO}_3 & \quad \text{HCO}_3^- & \quad 6.37 & \quad 10.25 & \quad \text{which is (CO}_2\text{ and }\text{H}_2\text{O)} & \quad \text{2nd e.p.}
\end{align*}
\]

\[
\begin{align*}
6.37 + 10.25 & \quad 10.25 \quad \frac{10.25}{2} \quad = 8.31 \\
\text{start of titration} & \quad \text{1st e.p.}
\end{align*}
\]
1. For $H_3PO_4$, $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, $K_3 = 4.7 \times 10^{-13}$

$\text{Thus } pK_1 = 2.125, pK_2 = 7.21, pK_3 = 12.33$

a) Parent acid is $H_3PO_4$

b) Saltion is $PO_4^{3-}$

c) Intermediate salts include $H_2PO_4^-$ and $HPO_4^{2-}$

d) pH of soln. containing only $H_2PO_4^-$ = $\frac{1}{2}(pK_1 + pK_2)$

$= \frac{1}{2}(2.125 + 7.21) = 4.67$

pH of soln. containing only $HPO_4^{2-}$ = $\frac{1}{2}(pK_2 + pK_3)$

$= \frac{1}{2}(7.21 + 12.33) = 9.77$

2. Net rxn during titration:

$H_3PO_4 + 2\text{"NaOH" } \rightarrow \text{"Na}_2HPO_4" + 2H_2O$

Actual species involved in the net (major) reaction:

$H_3PO_4 + 2OH^- \rightarrow HPO_4^{2-} + 2H_2O$

At equivalence point, only $HPO_4^{2-}$ is abundant

a) pH of $HPO_4^{2-}$ solution = $\frac{1}{2}(pK_2 + pK_3) = 9.77$ (see prob. 1)

This pH applies, regardless of volume of solution.

b) $\text{Since the pK values differ by more than 3.0 units:}$

\begin{align*}
\text{pH} & \rightarrow 9.77 \quad \text{HPO}_4^{2-} \text{ present} \\
\text{Mw of } H_3PO_4 & \text{ is} \\
3H & = 3.024 \\
1P & = 30.974 \\
4O & = 63.997 \\
\text{97.995 g/mole } H_3PO_4
\end{align*}

\begin{align*}
\text{c) } 35.77 \text{ mL } \times \frac{0.1123 \text{ mmol NaOH}}{\text{mL}} \times \frac{1 H_3PO_4}{2 \text{ NaOH}} \times \frac{98.00 \text{ mg}}{1 H_3PO_4} \times \frac{1}{51347.8 \text{ mg}} \times 100 = 3.681 \% \text{ H}_3PO_4
\end{align*}
3. For $H_2$Cit, $K_1 = 8.3 \times 10^{-4}$, $K_2 = 2.2 \times 10^{-5}$, $K_3 = 4.0 \times 10^{-7}$

Thus $pK_1 = 3.08$, $pK_2 = 4.66$, $pK_3 = 6.40$

These $pK_a$ values do not differ by 3 units, therefore the intermediate equiv. pts will not be distinguishable.

Overall reaction occurring during titration:

$$H_2$Cit + 3 "NaOH" $\rightarrow$ "Na$_3$Cit" + 3 H$_2$O$

Overall net change in species during titration:

$$H_2$Cit + 3 OH$^-\rightarrow$ Cit$^{3-} + 3$ H$_2$O

5.0 mmoles of $H_2$Cit require 15.0 mmoles NaOH, to be changed to 5.0 Cit$^{3-}$. At the one (final) equiv. pt., where Cit$^{3-}$ occurs (now 5.0 mmoles of it), the equilibrum reaction

$$Cit^{3-} + H_2O \rightleftharpoons H$Cit$^{2-} + OH^-$$

It is the third proton which is moved in this equation.

$$K_w = \frac{K_b}{K_3} = \frac{[H$Cit$^{2-}][OH^-]}{[Cit^{3-}]}$$

$$[OH^-] = \frac{x}{5.0 + 15.0} = \frac{x}{20}$$

(Vol. of NaOH titrant required = 15.0 mmol NaOH x 1 mL = 150 mL) 0.1000 NaOH = 150 mL

$$\frac{1.00 \times 10^{-14}}{4.0 \times 10^{-7}} = \frac{(x)(x)}{(5.0/250)}$$

$x^2 = 5.0 \times 10^{-10}$

$x = 2.236 \times 10^{-5}$ [OH$^-] = 2.2 \times 10^{-5}$M, pH = 4.65, pH = 9.35
4. a) For \( \text{H}_2\text{C}_2\text{O}_4 \), \( pK_1 = 1.27 \), \( pK_2 = 4.27 \). The difference in \( pK \) values is 3.00 units.

A 5.0 mmol \( \text{H}_2\text{C}_2\text{O}_4 \) in 50.0 mL is being titrated with 0.2500 M \( \text{NaOH} \).

- The general shape of the titration curve indicates:
  - At the first equivalence point, \( pH = \frac{1}{2}(pK_1 + pK_2) \)
  - At the second equivalence point, where 5.0 mmol \( \text{C}_2\text{O}_4^{2-} \) now occurs, the volume of titrant needs to be determined.

\[
pH = \frac{1}{2}(1.27 + 4.27) = 2.77
\]

- Overall reaction is: \( \text{H}_2\text{C}_2\text{O}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} \)

- Overall change of species is: \( \text{H}_2\text{C}_2\text{O}_4 + 2\text{OH}^- \rightarrow \text{C}_2\text{O}_4^{2-} + 2\text{H}_2\text{O} \)

- Volume of titrant needed is: \( 5.0 \text{ mmol} \text{H}_2\text{C}_2\text{O}_4 \times \frac{2\text{NaOH}}{1 \text{H}_2\text{C}_2\text{O}_4} \times \frac{1 \text{ mL}}{0.2500 \text{ NaOH}} = 40 \text{ mL} \)

At the equivalence point, total volume of solution will be \( 50.0 \text{ mL} + 40 \text{ mL} = 90 \text{ mL} \)

At equilibrium at the equivalence point,

\[
\text{Kw} = K_b = \frac{[\text{HC}_2\text{O}_4^-][\text{OH}^-]}{[\text{C}_2\text{O}_4^{2-}]} \]

\[
\frac{[\text{OH}^-]}{[\text{HC}_2\text{O}_4^-]} = x = 5.4 \times 10^{-5}
\]

\[
[\text{C}_2\text{O}_4^{2-}] = \frac{5.0 \text{ mmol}}{90 \text{ mL}} = \frac{5.0}{90} \times 1.0 \times 10^{-14} = \frac{5.0}{90} \times \left(\frac{x}{x}\right) = \frac{5.0}{90} \times \left(\frac{5.4 \times 10^{-5} - x}{x}\right)
\]

\[
x^2 = 1.0 \times 10^{-11}
\]

\[
x = 3.2 \times 10^{-6}, \quad [\text{OH}^-] = 3.2 \times 10^{-6} \text{ M}, \quad p\text{OH} = 5.49, \quad \text{pH} = 8.51
\]
4. b) For H₂Succ (short for succinic acid), pK₁ = 4.19, pK₂ = 5.48
The difference in pK values is less than 3.0, so there will not be a stepwise equivalence point.

5.0 mmol H₂Succ in 50.0 mL is being titrated with 0.2500 M NaOH.

General shape of titration curve:

At the ultimate equivalence point, where 5.0 mmol Succ²⁻ will now occur, the volume of titrant needs to be determined:

Overall reaction is: H₂Succ + 2"NaOH" → "Na₂Succ" + 2H₂O
Overall change of species is: H₂Succ + 2OH⁻ → Succ²⁻ + 2H₂O

Vol. of titrant needed = 5.0 mmol H₂Succ x \( \frac{2 \text{NaOH}}{1 \text{H}_2\text{Succ}} \times \frac{1 \text{ml}}{0.2500 \text{M NaOH}} = 40 \text{ml} \)

At equivalence point, total volume of solution will be (50.0 mL + 40 mL) = 90 mL

At equilibrium at the equivalence point:

\[ \text{Succ}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{Succ}^{-} + \text{OH}^{-} \]

\[ K_b = \frac{K_w}{K_a} = \frac{[\text{Succ}^{-}][\text{OH}^{-}]}{[\text{Succ}^{2-}]} \]

\[ [\text{OH}^{-}] = x \]
\[ [\text{Succ}^{-}] = x \]
\[ [\text{Succ}^{2-}] = \frac{5.0 \text{ mmol}}{90 \text{ ml}} - x \approx \frac{5.0}{90} \]

\[ \frac{100 \times 10^{-14}}{3.3 \times 10^{-6}} = \frac{(x)(x)}{(5.0/90)} \]
\[ x^2 = 1.7 \times 10^{-10} \]
\[ x = 1.3 \times 10^{-5} \]

\[ [\text{OH}^{-}] = 1.3 \times 10^{-5} \text{ M}, \text{ pOH} = 4.89, \text{ pH} = 9.11 \]
4c) $5.0 \text{ mmol HCl} \Rightarrow \begin{cases} 
\text{H}_3\text{O}^+ & 5.0 \text{ mmol} \\
\text{Cl}^- & 5.0 \text{ mmol} 
\end{cases}$ all in 100.0 mL originally

$10.0 \text{ mmol HOAc} \Rightarrow \text{HOAc} 10.0 \text{ mmol}$

These acids are being titrated with 0.5000 M NaOH.

The strong acid, H$_3$O$^+$, will titrate first (being changed to H$_2$O); then the much weaker acid, HOAc, will react (being changed to OAc$^-$).

General shape of titr. curve

2nd e.p. where only OAc$^-$ occurs

1st e.p. where only HOAc occurs

Titration of H$_3$O$^+$

Titration of HOAc (twice as much of it)

At 1st e.p., 5.0 mmol NaOH has been added, to neutralize 5.0 mmol HCl.

Vol. of titrant = $\frac{5.0 \text{ mmol HCl}}{1 \text{ NaOH}} \times \frac{1 \text{ ml}}{1 \text{ HCl}} = 10 \text{ ml}$

The acid still present, unreacted by titrant, is the HOAc;

$\frac{10.0 \text{ mmol HOAc}}{110 \text{ ml volume}} = \frac{10.0 \cdot \text{ M HOAc}}{110}$

At equilibrium at 1st e.p.,

$\text{HOAc} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OAc}^-$

$K_a = \frac{[\text{H}_3\text{O}^+][\text{OAc}^-]}{[\text{HOAc}]}$

$[\text{H}_3\text{O}^+] = x$

$[\text{OAc}^-] = x$

$[\text{HOAc}] = \frac{10.0}{110} - x \approx \frac{10.0}{110}$

$1.8 \times 10^{-5} = \frac{(x)(x)}{(10.0/110)}$

$x = 1.28 \times 10^{-3}$

$[\text{H}_3\text{O}^+] = 1.3 \times 10^{-3}$

$\text{pH} = 2.89$

At 2nd e.p., 10.0 more mmol NaOH has been added, to neutralize 10.0 mmol HOAc

Vol. of titrant = $\frac{10.0 \text{ mmol HOAc}}{1 \text{ NaOH}} \times \frac{1 \text{ ml}}{1 \text{ HCl}} = 20 \text{ ml more}$

At equilibrium at 2nd e.p.

$\text{OAc}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HOAc}$

$K_b = \frac{K_w}{K_a} = \frac{[\text{OH}^-][\text{HOAc}]}{[\text{OAc}^-]}$

$[\text{OH}^-] = x$

$[\text{HOAc}] = x$

$[\text{OAc}^-] = \frac{10.0}{130} - x \approx \frac{10.0}{130}$
4. c) continued

\[
\frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{(x)(x)}{(10.0/130)}
\]

\[
x^2 = 4.27 \times 10^{-11}
\]

\[
x = 6.537 \times 10^{-6}
\]

\[
[OH^-] = 6.5 \times 10^{-6} \text{ M}; \quad pOH = 5.18; \quad pH = 8.82
\]

5. Analyte consists of

1.2 mmol Na₂CO₃ \( \Rightarrow \) Na⁺ (2.4 mmol) \[ CO_3^{2-} \text{ (1.2 mmol)} \]

FAMILY RELATIONSHIPS:

\| \text{H₂CO₃} \text{ "parent" acid } \text{ } \| \text{HCO₃⁻} \text{ intermediate } \text{ } K_1

\| \text{HCO₃⁻} \text{ "salt ion" } \text{ } \| \text{CO}_3^{2-} \text{ "salt ion" } \text{ } K_2

1.2 mmol NaHCO₃ \( \Rightarrow \) Na⁺ (1.2 mmol) \[ HCO₃⁻ \text{ (1.2 mmol)} \]

Titration with 0.1000 M HCl will first convert the \text{CO}_3^{2-} \text{ to HCO}_3⁻.

Net rxn: "Na₂CO₃" + "HCl" \( \rightarrow \) "NaHCO₃" + "NaCl"

Actual change: \text{CO}_3^{2-} + H⁺ \( \rightarrow \) HCO₃⁻ + H₂O

Continuing titration will convert all \text{HCO}_3⁻ \text{ to H₂CO₃}.

Net rxn: "NaHCO₃" + "HCl" \( \rightarrow \) "H₂CO₃" + "NaCl"

Actual change: \text{HCO}_3⁻ + H⁺ \( \rightarrow \) \text{H}_2\text{CO}_₃ + H₂O

Any further titration merely puts excess titrant (\text{H}⁺) in the soln.

a) At first e.p., the principal analyte species will be \text{HCO}_3⁻

(This includes the original 1.2 mmol \text{HCO}_3⁻ and 1.2 mmol \text{HCO}_3⁻ formed by the titration thus far, a total of 2.4 mmol \text{HCO}_3⁻ there.)

b) At second e.p., the principal analyte species will be \text{H}_2\text{CO}_₃

(which will be 2.4 mmol in quantity, formed from all the \text{HCO}_3⁻)

c) Only 1.2 mmol \text{H}⁺ was used to convert \text{CO}_3^{2-} \text{ to HCO}_3⁻

but 2.4 mmol \text{H}⁺ was required to convert \text{HCO}_3⁻ \text{ to H}_2\text{CO}_₃

\[ \text{inasmuch as both of the original solutes are now being reacted.} \]

d) Shape of titration curve:

NOTE: The curve begins nearly level, because you already have a mixture of conjugate species present: \text{CO}_3^{2-} \text{ and HCO}_3⁻

\[ \text{1st e.p., HCO}_3⁻ \text{ present} \]

\[ \text{pH} \quad \text{2nd e.p., H}_2\text{CO}_₃ \text{ present} \]

\[ \text{0} \quad 12 \quad 36 \quad \text{mL HCl} \]
5. e) At first e.p.,

\[ \text{HCO}_3^- \text{ is present and is an intermediate species} \]

\[ \begin{align*}
2 \text{K}_1 & = 4.3 \times 10^{-7} & \text{pK}_1 & = 6.37 \\
2 \text{K}_2 & = 5.6 \times 10^{-11} & \text{pK}_2 & = 10.25
\end{align*} \]

By the "intermediate" rule,

\[ \text{pH} = \frac{1}{2} (\text{pK}_1 + \text{pK}_2) \]

\[ = \frac{1}{2} (6.37 + 10.25) = 8.31 \]

f) At second e.p.,

\[ \text{H}_2\text{CO}_3 \text{ is present and is the "parent" acid} \]

\[ \text{H}_2\text{CO}_3 + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^- \]

The "first" proton is being moved in this reaction.

\[ \text{K}_1 = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \]

\[ \frac{[\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} = x \]

\[ \frac{[\text{H}_2\text{CO}_3]}{2.4 \text{ mmol H}_2\text{CO}_3} = \frac{x}{(100.0 \text{ mL} + 36.0 \text{ mL})} \approx \frac{2.4}{136.0} \]

\[ 4.3 \times 10^{-7} = \frac{(x)(x)}{(2.4/136.0)} \]

\[ x^2 = 7.6 \times 10^{-9} \]

\[ x = 8.7 \times 10^{-5} \]

\[ [\text{H}_3\text{O}^+] = 8.7 \times 10^{-5} \text{ M} \]

\[ \text{pH} = 4.06 \]

6. \( \text{MW Na}_2\text{CO}_3 = 106.0 \) and \( \text{MW NaHCO}_3 = 84.01 \)

At the first e.p., you have titrated just \( \text{Na}_2\text{CO}_3 \), converting it to \( \text{NaHCO}_3 \).

\[ \% \text{Na}_2\text{CO}_3 = 15.52 \text{ mL HCl} \times \frac{0.1189 \text{ HCl}}{1 \text{ mL}} \times \frac{1 \text{ Na}_2\text{CO}_3}{1 \text{ HCl}} \times \frac{100 \text{%}}{1250 \text{ mg Na}_2\text{CO}_3} = 15.65 \% \]

At the second e.p., you have titrated everything to the \( \text{H}_2\text{CO}_3 \) condition, but twice 15.52 mL HCl was used up for merely the reactions with \( \text{Na}_2\text{CO}_3 \). Therefore the net amount of titrant needed for just the original \( \text{NaHCO}_3 \) was 40.18 mL - \( 2 \times 15.52 \text{ mL} \) = 9.14 mL.

\[ \% \text{NaHCO}_3 = 9.14 \text{ mL HCl} \times \frac{0.1189 \text{ HCl}}{1 \text{ mL}} \times \frac{1 \text{ NaHCO}_3}{1 \text{ HCl}} \times \frac{84.01 \text{ mg}}{1 \text{ NaHCO}_3} \times \frac{100 \%}{1250 \text{ mg NaHCO}_3} = 7.30 \% \]