Key T2  mean±sd : 60±25  A ≥85; B≥ 75 ; C≥ 50 and D≥ 30  Highest = 98

1) Solution:
   a) we set up the overall species of H₃PO₄ :
      \[ \text{H}_3\text{PO}_4 \quad \text{H}_2\text{PO}_4^- \quad \text{HPO}_4^{2-} \quad \text{PO}_4^{3-} \]
   To have a pH = pK₃ , we need to add 2 \( \frac{1}{2} \) times the # moles of phosphoric acid initially present = 2.5 x (1.5mol) = \textbf{3.75 mol NaOH}.

   b) To get ionic strength, we of course need the individual ions and their concentrations.  The final solution will at least have the following species:
      \( \text{Na}^+, \text{H}_3\text{PO}_4, \text{H}_2\text{PO}_4^-, \text{HPO}_4^{2-} \), \( \text{PO}_4^{3-} \), \( \text{Cl}^- \), \( \text{H}^+ \) and \( \text{OH}^- \).
      Their individual concentrations are:
      
      \[ \text{# [Na}^+] = (1.0+3.75 \text{ mol})/1.0\text{L} = 4.75\text{M}; \quad [\text{Cl}^-] = 1.0 \text{ M}; \quad [\text{H}_3\text{PO}_4] \text{ very small}; \quad [\text{H}_2\text{PO}_4^-] \text{ very small}; \quad [\text{HPO}_4^{2-}] = 0.75 \text{ M}; \quad [\text{PO}_4^{3-}] = 0.75 \text{ M}; \quad [\text{H}^+] = 10^{-12.15} = 7.08 \times 10^{-13} \text{M (very small)}; \quad [\text{OH}^-] = 10^{-14.15} = 10^{-14.85} = 1.4 \times 10^{-7} \text{M (significant enough to mention)} \]

      so the ionic strength is: \( \mu = (1/2) \sum z_i^2 \)  
      \[ = (1/2) \left\{ [\text{Na}^+]^2 + [\text{H}_2\text{PO}_4^-]^2 + 2[\text{HPO}_4^{2-}]^2 + 3[\text{PO}_4^{3-}]^2 + [\text{Cl}^-]^2 + [\text{H}^+]^2 + [\text{OH}^-]^2 \right\} = \frac{1}{2} \left\{ 4.75^2 + 0 + 0.75^2 (4) + 0.75^2 (9) + 1.0 + 0 + 0.014 \right\} \]
      \[ = 1/2(4.75^2 + 0 + 0.75^2 (4) + 0.75^2 (9) + 1.0 + 0 + 0.014) = [1/2(5.514)] = 7.757 \text{ M} = \textbf{7.8 M} \]

   c) charge balance:  Here we equate + and – charges : line up the ions and multiply their concentrations by the magnitude of their charges: (the small concentrations are ignored):
      \[ [\text{Na}^+] + [\text{H}^+] = [\text{H}_3\text{PO}_4] + 2[\text{H}_2\text{PO}_4^-] + 3[\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] + [\text{Cl}^-] + [\text{OH}^-] \]
      \[ 4.75 + 0 = 0 + 2(0.75) + 3(0.75) + 1.0 + 0.014 = 4.764 \]
      so \( 4.8 \approx 4.8 \)

   d) 1.50 M = [H₃PO₄]ₐₑᵢₙ = [H₃PO₄] + [H₂PO₄⁻] + [HPO₄²⁻] + [PO₄³⁻]

2) Solution:  At the dilution given, DMG acts like a strong base:
      \[ \text{DMG} + 2 \text{H}_2\text{O} \rightarrow \text{DMG}^2+ + 2 \text{OH}^- \]
      \[ 5.0 \times 10^{-7} \quad \text{y} \]

      Water also supplies significant amounts of \( \text{OH}^- \) , so we let \( y = [\text{OH}^-] \) and from \( K_w \) equil:  
      \[ [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} = K_w = xy \quad \text{where} \ x = [\text{H}^+] \]

      We need another independent equation, so we use the charge balance equation:  
      \[ [\text{H}^+] + 2 [\text{H}_2\text{DMG}^2+] = [\text{OH}^-] \]
      or,  \( x + 2(5 \times 10^{-7}) = y \). Substitute for \( y \) and solve for \( x \):
      so: \( (x + 1.0 \times 10^{-6}) = 1.0 \times 10^{-14} \quad \Rightarrow \quad x^2 + 1.0 \times 10^{-6} \ x - 1.0 \times 10^{-14} = 0 \)

      \[ x = \{-1.0 \times 10^{-6} \pm \sqrt{(1.0 \times 10^{-6})^2 - 4(1)(-1.0 \times 10^{-14})}\} /2 = 9.902 \times 10^{-9} \]

      \( \text{pH} = -\log(9.902 \times 10^{-9}) = 8.00 \)

      The total \( [\text{OH}^-] = y = 1.0 \times 10^{-14} / x = 1.0 \times 10^{-14} / 9.902 \times 10^{-9} = 1.01 \times 10^{-6} \text{M} \)
      of that, only \( 9.902 \times 10^{-9} \text{ M is due to the water (it’s equal to the} [\text{H}^+] \text{ which is all from the self-ionization of water. So the} [\text{OH}^-] \text{ from water = 9.902 \times 10^{-9} x 100% / 1.01 \times 10^{-6} M} = \textbf{0.98%} \)
3) Solution: The overall “diagram” is:

\[
\begin{align*}
H_2C_2O_4 & \quad <\quad HC_2O_4^- \quad <\quad C_2O_4^{2-}
\end{align*}
\]

\[
\begin{align*}
1.27 & \quad 4.266
\end{align*}
\]

Initially we are here:

The substances are NaHC_2O_4 and Na_2C_2O_4: FW of NaHA = 23+1+24+64 = 112 g/mol (pK_a 's = 1.27, 4.266 ); FW of Na_2C_2O_4 = 46+24+64 = 134 g/mol

So that 0.350 g of NaHA = 3.125x10^{-3} mol (3.125 mmol) => [NaHA] = 0.0125 M

And 0.419 g Na_2A = 3.126x10^{-3} M;  => [Na_2A] = 0.0125 M

a) To reach the 1st e.p., we need to add exactly 3.125x10^{-3} moles of NaOH to neutralize the HA form: so , V_e = 3.125x10^{-3} moles / 0.200 M  = 0.0156 L = 15.6 mLs

b) pH values are:

i) At V_HCl = 0.00 mL, the pH will be equal to pK_2 = 4.266 (since there are equal amounts of the base and acid forms).

ii) At V_e, we have the intermediate form. We are at the isoionic point. The concentrations are not dilute, so we can use the approximation:

\[
\begin{align*}
\text{at V}_e = 15.6 \text{ mL}: \text{pH} = \frac{1}{2}(1.27+4.266) = 2.768 = 2.77
\end{align*}
\]

iii) At V=V_2e: we have a pure weak acid solution, we use K_{a1} equilibrium:

\[
\begin{align*}
H_2C_2O_4 & \quad <\quad H^+ + HC_2O_4^- \\
\text{n.b. } [HC_2O_4^-] & = (3.125 \text{ mmol x} 2) = 0.0468 \text{M}
\end{align*}
\]

\[
\begin{align*}
10^{-1.27} = x^2/(0.0468-x) \approx x^2/0.0468 \Rightarrow x = \sqrt{(0.0468(10^{-1.27}))} = 0.0501 = [H^+] \Rightarrow \text{pH}=1.30
\end{align*}
\]

\[
\begin{align*}
\text{or } x_{HA} & = 30.8 x_{H_2A} \text{; but we know that } x_{HA} + x_{H_2A} = 2(3.125x10^{-3}) \text{ mol} = 6.250 \text{ mmol} . \\
\text{That corresponds to the excess mmol HCl added after } V_e: \text{ so } V_{HCl,excess} = 0.1965 \text{mmol}/.220\text{M} = 0.98 \text{ mLs} \text{. That means we added } V_{HCl} = 15.6+0.98 = 16.58 \text{ mLs}.
\end{align*}
\]

4) Solution: a) use standard addition method:

\[
\frac{A_x}{A_{x+s}} = \frac{x}{(x+s)} \text{ where } A_x = \text{absorbance and } x = [\text{Cr}_2O_7^{2-}] \text{ in unknown, } s = [\text{Cr}_2O_7^{2-}] \text{ in standard.}
\]

\[
\begin{align*}
A_x & = -\log(0.4074) = 0.3900 \; ; \; A_{x+s} = -\log(0.4875) = 0.3120 \; ;
\end{align*}
\]

\[
\begin{align*}
\text{So: } \frac{0.3900}{0.3120} &= \frac{x}{(2/5)x+(3/5)(0.00100)} \\
0.500 x + 0.00075 &= x \Rightarrow 0.500 x = 0.00075 \Rightarrow x = 0.001500 \text{ M}
\end{align*}
\]

b) \[
\begin{align*}
A = \varepsilon cb & \Rightarrow \varepsilon = A/cb = 0.3900 / ((0.001500 \text{ M})(1 \text{ cm})) = 260 \text{ M}^{-1}\text{cm}^{-1}
\end{align*}
\]

c) \[
\begin{align*}
\% \text{ Cr} = (0.001500\text{M})(0.250\text{L})\text{(2 mol Cr/1 mol } \text{Cr}_2O_7^{2-})\text{(51.996g/mol)} \times 100\% / 0.500\text{g} = 7.80\% \text{ Cr}.
\end{align*}
\]
5) Solution: internal standard method.

Say \( x = 3.40 \text{ ppm Ba} \) and \( k_{\text{Ba}} = 0.250 \) => \( A_{\text{Ba},1} = (5.0/7.5)(3.40) = 2.27 \) 
\( A_{\text{Ba},2} = (5.0/7.5)(3.00) = 2.00 \) (x 1.5 evap factor for soln#2) = 3.00

And say \( k_{\text{F}} = 0.500 \) : \( A_{\text{F},1} = (2.5/7.5)(4.00\text{ppm})=1.33 \) and \( A_{\text{F},2} = 2.00 \)

Solution: use internal standard method:

\[
\frac{(I_x/I_s)_1}{(I_x/I_s)_2} = \frac{(5/7.5)x/ (2.5/7.5)s_1}{(7/9.5)x/ (2.5/9.5)s_2}
\]

\( (2.27/1.33) = (0.667)x/(0.333)(4.00) \) => 1.71 = 0.500x

\( (3.00/2.00) = (7.37)(3.00)/(2.63)(4.00) \) 1.50 2.10 => \( x = 4.79 \text{ ppm} \) > 2 ppm therefore: it’s over the regulation.

b) Absorption lines are broadened by:

(i) Heisenberg uncertainty principle \( \Delta E \Delta t \approx \hbar/4\pi \) so if \( \Delta t \) is small, \( \Delta E \) is the broadening

(ii) Doppler effect: gas molecules moving away from and toward an observer will shift the frequency of the light either up or down.

(iii) Pressure broadening: collisions between gas atoms broaden also the absorbance.

6) Solution: First things first:

\[ [\text{Ca}]^0 = M_{\text{EDTA}}V_{\text{EDTA}}/V_{\text{Ca}} = (0.104\text{M})(22.0)/(30.0) = 0.0763 \text{ M}; \]

\[ K_f' = a_{\text{Y4}}=K_f = (5\times10^{-4})(10^{0.69}) = 2.45 \times 10^{-7} \]

a) (i) here we are in a region before equivalence:

\[ [\text{Ca}] = [\text{Ca}]^0((22-18)/(22) ) (30/(30+18)) = 0.0763(4/22)(30/48)=8.67 \times 10^{-3} \]

\( p\text{Ca}= 2.06 \)

(ii) at \( V=Ve \), use \( K_f' \) equil: \( \text{Ca}^{+} + \text{Y} <=> \text{CaY} \)

\[ K_f' = 2.45\times10^{-7} \text{ so} \]

\[ x = .0440-x \]

\[ [\text{CaY}]=0.0763\text{M} (30/30+22)= 4.40\times10^{-2}\text{M} \Rightarrow x = \sqrt{(4.40\times10^{-2})/2.45\times10^{-7}} = 4.24\times10^{-5} \]

\( p\text{Ca}^{2+} = -\log [\text{Ca}^{2+}] = p\text{Ca}= 2.45\times10^{-7} \)

(iii) at \( V = 22.0 + 34.0 = 56.0 \text{ mLs}: \text{Ca}^{+} + \text{Y} <=> \text{CaY} \)

\[ K_f' = 2.45\times10^{-7} \]

\[ x = 0.0631+x \]

\( [\text{CaY}] = 0.0763 \text{M} (30/56)=0.0409 \text{ M} \]

\[ Y = (34.0)(0.104)/(56.0) = 0.0631 \text{ M} \]

\[ 2.45\times10^{-7} \approx .0409 /x(0.0631) \Rightarrow x = .0409/(2.45\times10^{-7}(0.0631)) = 2.64\times10^{-8} \text{ M}; \]

\( p\text{Ca}^{2+} = -\log [\text{Ca}^{2+}] = \text{pCa}= 7.578 \)

b) To show validity, \( K_f' > 10^{6}/F : 10^{6}/0.0763 = 1.3 \times 10^{7}. \) For that to be less than \( K_f' \), we can see that: \( K_f' = 2.45\times10^{-7} > 1.3 \times 10^{-7} \) ; so valid at pH 7.0

we can solve for \( a_4 \) at which it is not valid: \( \alpha_{\text{Y4}} = K_f'/K_f = (1.3 \times 10^{-7})/10^{10.69} =2.65\times10^{-4}. \)

That value is at a pH between 6 and 7. 

but at pH 6: \( K_f' = (2.3\times10^{-5})(10^{10.69}) = 1.12\times10^{6} < 1.3 \times 10^{7} \) hence roughly pH 6 and below, it’s no longer valid.

This buffer helps by setting the pH higher and thus increases \( a_4 \) and it also introduces \( \text{NH}_3 \) as an auxiliary complexing reagent to lower the chances of \( \text{Ca}^{2+} \) forming \( \text{Ca(OH)}_2 \) and precipitating out.