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Key to test #2 average \pm sdev = 50 ± 24 (Highest = 105 points/100 pts).

A = 80+, B = 70+, C = 45 +, D = 35+, F <35

1) a) $A = \epsilon cb$, $\epsilon = A/cb$; where $A = -\log T$; $T = \%T/100 = 31.6/100 = 0.316$

$A = -\log(0.316) = 0.500$

$$C = [\text{Cr}_2\text{O}_7^{2-}] = \frac{(2.60 \text{ g} \times (0.100/100)) \times (1 \text{ mol Cr}^{2+}/51.996 \text{ g}) \times (1 \text{ mol Cr}_2\text{O}_7^{2-}/2 \text{ mol Cr}^{2+})}{0.500 \text{ L}}$$

$$= 5.00 \times 10^{-5} \text{ M Cr}_2\text{O}_7^{2-}$$

$$\epsilon = A/cb = 0.500 / ((5.00 \times 10^{-5} \text{ M})(1 \text{ cm})) = 1.00 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1},$$

b) % Cr = 100% x g Cr/ g ore

$$= 100\% (.250 \text{ L})(1.00 \times 10^{-4} \text{ mol Cr}_2\text{O}_7^{2-}/\text{L})(2 \text{ mol Cr}/\text{mol Cr}_2\text{O}_7^{2-})(51.996 \text{ g/mol Cr}) / 1.30 \text{ g} = \mathbf{0.200\%}$$

or, you can also use ratios: (usually is less risky since you don't have to have to use ϵ)

note that $A_2 = -\log(.10) = 1.00$

$$\frac{A_2}{A_1} = \epsilon c_2 b / \epsilon c_1 b \Rightarrow (\%)_2 = (\%)_1 (A_2/A_1)(m_1/m_2)(V_2/V_1)$$
$$= (.100\%)(1.00/.500)(2.60 \text{ g}/1.30 \text{ g})(.250 \text{ L}/.500 \text{ L}) = \mathbf{0.200\%}$$

2) Internal standard method:

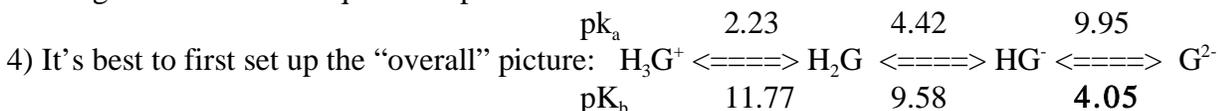
$$\frac{\{[X]/[S]\}_{\text{unk}}}{\{[X]/[S]\}_{\text{std}}} = \frac{\{I_x/I_s\}_{\text{unk}}}{\{I_x/I_s\}_{\text{std}}}$$

$$\frac{\{(1/4) \times (3/4)(100)\}}{\{(1/3)(250)/(2/3)(100)\}} = \frac{\{.465/.385\}_{\text{unk}}}{\{.885/.342\}_{\text{std}}}$$
$$= 1.208/2.588 = 0.4668 \quad \text{and so, } 2x/(3(250)) = .4668 \Rightarrow x = \mathbf{175 \text{ ppm Ca.}}$$

3) a) $[\text{Cl}^-] = (\text{mol Cl}^-)/(\text{vol Cl}^-) = (\text{total moles Ag}^+ \text{ added} - \text{moles Ag}^+ \text{ unreacted}) / \text{vol Cl}^-$
 $= \{(30.0 \text{ mL})(0.115 \text{ M}) - (0.205)(12.5 \text{ mL})\} / (50.0 \text{ mL}) = (3.450 - 2.563) / 50.0 = \mathbf{1.76 \times 10^{-2} \text{ M Cl}^-}$

b) $\text{Ag}^+ + \text{SCN}^- \rightarrow \text{AgSCN}$, $\text{SCN}^- + \text{Fe}^{3+} \rightarrow \text{FeSCN}^{2+}$ (red complex)

c) AgCl more soluble than AgSCN, so if you allow it to, AgCl will redissolve and form AgSCN unless you filter it out first before doing the backtitration. Silver ppt with Br⁻ and I⁻ are less soluble than AgSCN and don't require this precaution.



a) at $V_{\text{OH}} = 3 V_e$, we are at G^{2-} dominant and we use the K_{b1} equilibrium: $K_{b1} = 10^{-4.05} = 8.91 \times 10^{-5}$



$$8.91 \times 10^{-5} = x^2 / (.09412 - x) \approx x^2 / (.09412); \Rightarrow x = \sqrt{\{(0.09412)(8.91 \times 10^{-5})\}} = 0.00296 \text{ M} = [\text{OH}^-]$$
$$\text{pOH} = -\log(.00296) = 2.529; \text{pH} = 14 - \text{pOH} = \mathbf{11.47}$$

(how did we get $[\text{G}^{2-}] = 0.09412$? first, get V_e : Use $M_1 V_e = M_2 V_2$ (where "2" = H_3G^+ , etc)

$$\Rightarrow V_e = M_2 V_2 / M_1 = (.320 \text{ M})(20.0 \text{ mL}) / (0.400 \text{ M}) = 16.0 \text{ mL}$$

$$\text{where } [\text{G}^{2-}] = [\text{H}_3\text{G}^+]_o (\text{dilution factor}) = (M_2)(V_1 / (V_1 + 3V_e)) = (.320 \text{ M})(20.0 \text{ mL} / (20.0 + 3(16.0))) = 0.09412 \text{ M}$$

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b) @ $V = 36.0$, we are in the buffer region with HG^- and G^{2-} as the conjugates acid and base. The ratio of base to acid is $4\text{mL} / 12\text{mL}$; that is, $(36.0-32.0)/(48.0-36.0) = 4/12 = 1/3$ so, the $\text{pH} = \text{pK}_{a3} + \log([G^{2-}]/[HG^-]) = 9.94 + \log(1/3) = \mathbf{9.47}$

c) The isoelectric point needs to be reached. That means, we need to add enough so that we have a solution which is the equivalent of a pure H_2G solution. So, we must reach the first equivalence point, that is, add **16.0 mL**

d) For the graph, check your text book. It should show pH as the y-axis, and mL of OH^- added in the x-axis. The following values of pH are to be highlighted: pK_1 @ 2.23 (almost level region @ $1/2V_e=8\text{mL}$). Curve rises rapidly @ $V_e, 16.0\text{mL}$ and $\text{pH}=3.325$, curve almost level @ pK_{a2} or pH 4.42 @ $1.5 V_e$ i.e. 24 mL; curve rises rapidly @ $2V_e$, i.e. 32 mL and pH 7.19; curve almost level @ pK_{a3} , i.e. pH 9.95 @ $2.5 V_e$, i.e. 40 mL; curve rises rapidly at $3 V_e$, i.e. 48 mL, @ pH = 11.46 (we solved that in (a)).

5) a) First, decide which Gran Plot equation to use: it should be the one for a weak acid vs a strong base. If you inspect the equations given on page 1, you will see that it is $V_b 10^{-\text{pH}} =$

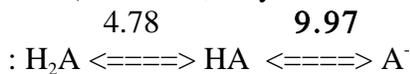
$$K_a (\gamma_B / \gamma_{HB^+}) (V_e - V_b) ;$$

Plot $V_b 10^{-\text{pH}}$ vs V_b that should result in a straight line of negative slope which crosses near the region of 16.5 – 17.0 mLs. By the way, the points are: $(V_b, V_b 10^{-\text{pH}})$: $(10.0\text{mL}, 7.31 \times 10^{-6})$ and $(15.0\text{mL}, 1.88 \times 10^{-6})$. We take $V_e = 17.0\text{mLs}$

From the V_e , solve for concentration: $M_1 V_e = M_2 V_2 \Rightarrow M_2 = M_1 V_e / V_2 = (.225)(17.0)/(25.0) = \mathbf{0.153\text{ M}}$

b) Note that the problem says that the activity coefficients are equal, not the activities. So, as stated in the lecture, we use the Gran Plot equation but let the $(\gamma_B / \gamma_{HB^+})$ term equal 1: so, the slope becomes K_a directly. Slope = $-K_a = \Delta y / \Delta x = (1.88 - 7.31) / (15.0 - 10.0) = -1.09 \times 10^{-6}$, so $K_a = 1.09 \times 10^{-6}$ and $\text{pK}_a = -\log(1.09 \times 10^{-6}) = \mathbf{5.963}$

c) Let's take an overview of aminophenol. In general, we can figure out that it is a diprotic weak acid (otherwise, why else do we use a strong base to titrate it and why else does it have 2 pK_a 's ?).



We see that to reach 9.97, one has to be exactly at $1.5 V_e$. That means $1.5 V_e = 18.0\text{mLs}$, or $V_e = 12.0\text{mL}$.

Using this V_e , we can calculate the concentration by $M_2 = M_1 V_e / V_2 = (.225\text{M})(12.0) / (20.0) = \mathbf{0.135\text{M}}$