

# CHEM 241 - EXAM 3 REVIEW GUIDE - KEY

## Chapters 10 and 11

### Chapter 10 (and part of Ch. 1) Introduction to Titrations and Acid-Base Titration

NOTE: Review your problem set and lecture notes; pay attention to sample and assigned problems

1. Distinguish between the terms *end point* and *equivalence point* of a titration.

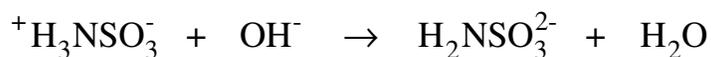
The **end point** of a titration refers to the stage in the titration when the indicator exhibits a color change, signaling the end of titration. This color change happens near the equivalence point.

The **equivalence point** of a titration is reached when the *number of moles of titrant* added corresponds exactly to the **number of moles of substance** being titrated according to the reaction stoichiometry

2. Explain the following: **See Chapter 10 lecture notes to help you with answers.**

- Problem 10-4. Sketch the general appearance of the curve for the titration of a weak acid with a strong base. Explain (in words) what chemistry governs the pH in each of the four distinct regions of the curve. See Chapter 10 Lecture Notes
- Problem 10-12. Sketch the general appearance of the curve for the titration of a weak base with a strong acid. Explain (in words) what chemistry governs the pH in each of the four distinct regions of the curve.
- Problem 10-13. Why is the equivalence-point pH necessarily below 7 when a weak base is titrated with strong acid? **The titration forms the conjugate acid,  $BH^+$ , of the weak base B.  $BH^+$  dissociates to form  $H^+$  (and B) hence a slightly acidic pH at the equivalence point.**
- Problem 10-19, Harris. Sketch the general appearance of the curve for the titration of a weak diprotic acid with NaOH. Explain (in words) what chemistry governs the pH in each distinct region of the curve.
- Problem 10-42. Cresol red has two transition ranges listed in Table 10-3. What color would you expect it to be at the following pH values? (a) 0; (b) 1; (c) 6; (d) 9
- Problem 10-43. Would the indicator bromocresol green, with a transition range of pH 3.8–5.4, ever be useful in the titration of a weak acid with a strong base? **No, because the pH at the equivalence point is slightly basic, whereas BCG changes color in acidic pH range.**

3. Problem 1-45, Harris: Sulfamic acid is a primary standard that can be used to standardize NaOH.

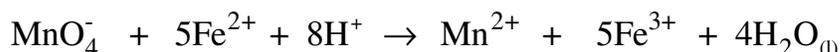


Sulfamic acid  
(MM 97.094)

What is the molarity of a sodium hydroxide solution if 34.26 mL react with 0.3337 g of sulfamic acid?

Let	HA = sulfamic acid
mol HA	$= \frac{0.3337 \text{ g}}{97.094 \text{ g}} \times 1 \text{ mol} = 3.4369 \times 10^{-3}$
mol $OH^-$	$= 3.4369 \times 10^{-3} \text{ mol HA} \times \frac{1 \text{ mol } OH^-}{1 \text{ mol HA}} = 3.4369 \times 10^{-3}$
$M_{NaOH}$	$= \frac{\text{mol } OH^-}{\text{vol. of } OH^-} = \frac{3.4369 \times 10^{-3} \text{ mol}}{0.03426 \text{ L}} \Rightarrow M_{NaOH} = 0.1003 \frac{\text{mol}}{\text{L}}$

4. (Adapted from Brown, Lemay and Bursten, 10<sup>th</sup> ed.) A sample of iron ore is dissolved in acid, and the iron is converted to Fe<sup>2+</sup>. The sample is then titrated with 47.20 mL of 0.02240 M KMnO<sub>4</sub> solution. The oxidation-reduction reaction that occurs during titration is as follows:



[NOTE: All the other species are in aqueous form.]

(a) How many grams of Fe were in the sample? **0.2952 g Fe**

(b) If the sample had a mass of 0.8890 g, what is the percentage of iron in the sample?

$$\begin{aligned} \text{mol MnO}_4^- \text{ titrant} &= 0.04720 \text{ L} \times \frac{0.02240 \text{ mol}}{\text{L}} \\ &= 1.0573 \times 10^{-3} \\ \text{mol Fe}^{2+} \text{ analyte} &= 1.0573 \times 10^{-3} \text{ mol MnO}_4^- \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4^-} \\ &= 5.2864 \times 10^{-3} = \text{mol Fe in sample} \\ \text{mass of Fe} &= 5.2864 \times 10^{-3} \text{ mol} \times \frac{55.845 \text{ g}}{1 \text{ mol}} = 0.29522 \text{ g} \\ \% \text{ Fe in sample} &= \frac{0.29522 \text{ g Fe}}{0.8890 \text{ g sample}} \times 100 = \mathbf{33.21\%} \end{aligned}$$

5. Problem 10-8, Harris. What is the pH at the equivalence point when 0.100 M hydroxyacetic acid is titrated with 0.0500 M KOH? (See HW Key)

**OMIT.** 6. Problem 10-9, Harris. Find the equilibrium constant for the reaction of MES (Table 8-2) with NaOH.

7. Problem 10-10, Harris. When 22.63 mL of aqueous NaOH were added to 1.214 g of cyclohexylaminoethanesulfonic acid (MM 207.29, structure in Table 8-2) dissolved in 41.37 mL of water, the pH was 9.24. Calculate the molarity of the NaOH. (See HW Key)

8. Calculate the pH of 25.00 mL solution of 0.125 M acetic acid ( $K_a = 1.75 \times 10^{-5}$ ) after the addition of each of the following volumes of 0.100 M KOH: 10.00 mL,  $V_{ep}$ , and 35.00 mL.

Analyte = 25.00 mL of 0.125 M HAC ( $K_a = 1.75 \times 10^{-5}$ )  
 Titrant = 0.100 M KOH  $pK_a = 4.757$   
 $\Rightarrow$  weak acid - strong base titration  
 First, calculate  $V_e$  so you'd know if you've gone beyond the equivalence point  

$$V_e = \frac{M_{HAC} V_{HAC}}{M_{OH^-}} = \frac{(0.125 M)(25.00 \text{ mL})}{0.100 M} = 31.25 \text{ mL}$$
  
 $V_e = 31.25 \text{ mL}$  of  $OH^-$  needed to reach the equiv. pt.

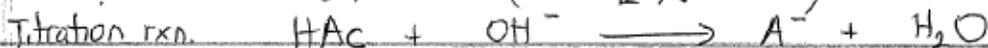
(a) Calc. pH when  $V_b = 10.00 \text{ mL}$

$\leftarrow$  before the equiv. pt. so you'll have a buffer; both HAC and  $Ac^-$  in solution

Strategy: Calc. mol  $OH^-$  added, mol HAC initially present and mol  $Ac^-$  formed. using a mole (or ICF) table

$$\text{mol } OH^- \text{ added} = \left(0.100 \frac{\text{mol}}{\text{L}}\right)(0.0100 \text{ L}) = 1.00 \times 10^{-3}$$

$$\text{mol HAC initially present} = \left(0.125 \frac{\text{mol}}{\text{L}}\right)(0.02500 \text{ L}) = 3.125 \times 10^{-3}$$



I mol	$3.125 \times 10^{-3}$	$1.00 \times 10^{-3}$	0
C	$-1.00 \times 10^{-3}$	$-1.00 \times 10^{-3}$	$+1.00 \times 10^{-3}$
F mol	$2.125 \times 10^{-3}$	0	$1.00 \times 10^{-3}$

Since we have a buffer, use the H-H eqn to calc. pH

$$pH = pK_a + \log \frac{[Ac^-]}{[HAC]} \quad \leftarrow \text{can use mole ratio}$$

$$pH = 4.757 + \log \left( \frac{1.00 \times 10^{-3}}{2.125 \times 10^{-3}} \right) \Rightarrow pH = 4.43$$

slightly acidic  $\leftarrow$   
 because  $[HAC] > [Ac^-]$

(b) Calc. pH when  $V_{OH^-} = V_e$  (i.e. at the equiv. pt.)

Note: Only  $Ac^-$  is left in solution since both HAc and  $OH^-$  are completely used up

Thus, the hydrolysis of  $Ac^-$ , a weak base, will det. pH

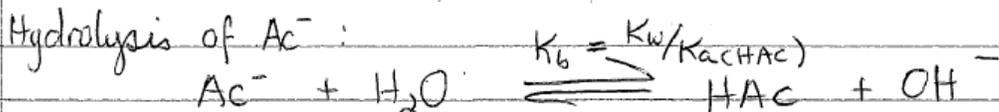
First, we need to calc.  $\Sigma Ac^-$  or  $F_{Ac^-}$

$$\text{mol } Ac^- \text{ formed} = \text{mol HAc initially present} = 3.125 \times 10^{-3} \quad (\text{part (a)})$$

$$\text{total vol. of solution} = \underset{\text{HAc}}{25.00 \text{ mL}} + \underset{= V_e}{31.25 \text{ mL}}$$

$$= 56.25 \text{ mL or } 0.05625 \text{ L}$$
$$F_{Ac^-} = \frac{3.125 \times 10^{-3} \text{ mol}}{0.05625 \text{ L}} = 5.55 \times 10^{-2}$$

Hydrolysis of  $Ac^-$ :



$$K_b = \frac{y^2}{F_{Ac^-} - y} \quad \text{where } K_b = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}}$$

$$= 5.714 \times 10^{-10}$$

$$5.71 \times 10^{-10} = \frac{y^2}{5.55 \times 10^{-2} - y} \quad \text{Assume } y \ll 5.55 \times 10^{-2}$$

$$y^2 = (5.71 \times 10^{-10})(5.55 \times 10^{-2}) \Rightarrow y = 5.634 \times 10^{-6}$$

But  $y = \Sigma OH^- = 5.634 \times 10^{-6}$

$pOH = 5.25$ ;  $pH = 8.75$  slightly basic since  $Ac^-$  is a weak base

9. Problem 10-19, Harris. Sketch the general appearance of the curve for the titration of a weak diprotic acid with NaOH. Explain (in words) what chemistry governs the pH in each distinct region of the curve.  
See lecture notes on titration of diprotic species.

## Chapter 11: EDTA TITRATIONS

1. Be able to explain each of the following terminologies: Back titration, blocking (of indicator), chelate, chelate effect, complexometric titration, direct titration, formation constant, metal ion indicator, multidentate ligand – see lecture notes on EDTA titrations

2. Problem 11-25. Calcium ion was titrated with EDTA at pH 11 using calmagite as indicator (Table 11-3). Which is the principal species of Calmagite at pH 11? What color was observed before the equivalence point? After the equivalence point? *We did this in class. See lecture notes.*
3. Problem solving (see lecture notes on water hardness (as  $\text{CaCO}_3$ ) determination).
4. Problem 11-31. How many milliliters of 0.0500 M EDTA are required to react with 50.0 mL of 0.0100 M  $\text{Ca}^{2+}$ ? With 50.0 mL of 0.0100 M  $\text{Al}^{3+}$ ?

WORK: EDTA forms a 1:1 metal-EDTA complex

$$V_{\text{EDTA}} = \frac{M_{\text{Ca}^{2+}} V_{\text{Ca}^{2+}}}{M_{\text{EDTA}}} = \frac{(0.0100 \text{ M})(50.0 \text{ mL})}{0.0500 \text{ M}}$$

$$V_{\text{EDTA}} = 10.0 \text{ mL}$$

*Same answer for aluminum*

Challenge question: 5. Problem 11-32. A 50.0-mL sample containing  $\text{Ni}^{2+}$  was treated with 25.0 mL of 0.0500 M EDTA to complex all the  $\text{Ni}^{2+}$  and leave excess EDTA in solution. The excess EDTA was then back-titrated, requiring 5.00 mL of 0.0500 M  $\text{Zn}^{2+}$ . What was the concentration of  $\text{Ni}^{2+}$  in the original solution?

Relationship

$$\text{moles of known excess of EDTA} - \text{moles of EDTA reacted with Ni}^{2+} = \text{mol unreacted or "excess" EDTA}$$

" mol  $\text{Zn}^{2+}$

$$\left(0.0500 \frac{\text{mol}}{\text{L}}\right)(0.0250 \text{ L}) - \text{mol of EDTA reacted with Ni}^{2+} = \left(0.0500 \frac{\text{mol}}{\text{L}}\right)(0.00500 \text{ L})$$

← switch around →

$$1.25 \times 10^{-3} - 2.50 \times 10^{-4} = \text{mol of EDTA reacted w/ Ni}^{2+}$$

$$= 1.00 \times 10^{-3} \text{ mol of EDTA reacted w/ Ni}^{2+}$$

Thus,  $M_{\text{Ni}^{2+}} = \frac{1.00 \times 10^{-3} \text{ mol}}{0.0500 \text{ L}}$  ← equal to mol EDTA (1:1 stoichiom.)

← volume of  $\text{Ni}^{2+}$  solution

$$M_{\text{Ni}^{2+}} = 2.00 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$