

7 (3 points). What is the ratio of $[A^-] / [HA]$ for a buffer solution of HA with a pH of 5 if the $pK_a = 7$ for HA?

- a. -2.0
 b. 0.01
c. 0.1
d. 100

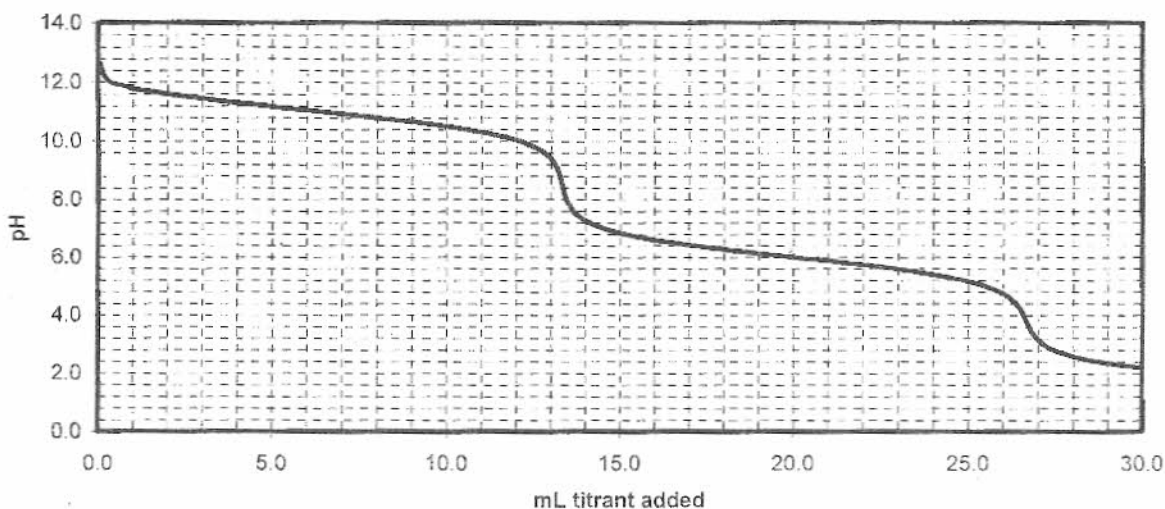
8 (2 points). When choosing a color indicator for an acid base titration, the pK_a of the indicator should match:

- a. the pK_b of the analyte.
b. the pH half way to the equivalence point.
c. the pK_a of the analyte.
 d. the pH at the equivalence point.

9 (3 points). What is the dominant form of aspartic acid (a triprotic acid (H_3A^+)) at a pH of 2.50 ($pK_{a1} = 1.990$, $pK_{a2} = 3.900$, $pK_{a3} = 10.002$)?

- a. H_3A^+ and H_2A are equal
b. H_3A^+
c. H_2A
d. H_2A and HA^- are equal

Refer to the titration curve below for questions 10 through 14.



10 (3 points). The titration curve shown above describes the:

- a. titration of a strong acid.
 b. titration of a weak diprotic base.
c. titration of a strong base.
d. titration of a weak diprotic acid.

11 (3 points). After 20.0 mL of titrant have been added, the solution represents a buffer between:

- a. A^{2-} and HA^-
 b. HA^- and H_2A
c. A^{2-} and H_2A
d. the solution is not a buffer.

12 (3 points). What is pK_{b2} for the acid or base being titrated in the figure?

- a. 3
b. 11

- c. 6
d. 8

13 (3 points). If the original formal concentration (before any titrant has been added) of weak base (A^{2-}) was 0.100 M in 10.0 mL of solution, what is the formal concentration of the intermediate form (HA^-) when the intermediate form is at its highest concentration during the titration?

- a. 0.100 M
b. 0.0426 M

- c. 0.0274 M
d. cannot be determined

14 (3 points). What is the pH at the first equivalence point?

- a. 11
b. 6

- c. 8.5
d. 4

Worked out Problems

It is your responsibility to work out your answers clearly. Unclear, or unreadable work will not be graded. If there is not enough space provided to show your work, continue on the back of the page and clearly mark the problem number. Be sure to show all of your work and report your final answer with the correct number of significant figures and **units**. A correct answer without work shown will not receive credit, and cannot receive partial credit. **Circle or draw a box around your final answer.**

Equations that may, or may not, be useful:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}, \text{ where } ax^2 + bx + c = 0$$

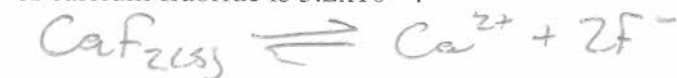
$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$[H^+] = \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$$

$$\log \gamma = \frac{-0.51z^2 \sqrt{\mu}}{1 + (\alpha \sqrt{\mu} / 305)}$$

$$\mu = \frac{1}{2} \sum_i c_i z_i^2$$

15 (6 points). What is the concentration of fluoride (F^-) in a saturated solution of CaF_2 ? The K_{sp} of calcium fluoride is 3.2×10^{-11} .



$$[Ca][F^-]^2 = 3.2 \times 10^{-11}$$

$$(x)(2x)^2 = 3.2 \times 10^{-11}$$

$$x = 2.0 \times 10^{-4}$$

$$[F^-] = 2x = \boxed{4.0 \times 10^{-4} M}$$

	Ca^{2+}	F^-
I	-	-
C	+x	+2x
E	x	2x

16 (6 points). Accounting for ionic strength, what is the equilibrium pH of a 0.100 M solution of the strong acid HCl? See the table below for activity coefficients (to receive full credit, show your work and circle the correct activity coefficient(s) that you use on the table below).

$$\text{ionic strength } (\mu) = 0.100$$

$$\text{pH} = -\log\{[\text{H}^+]_{\text{H}^+}\}$$

$$= -\log\{(0.100)(0.83)\} = \boxed{1.08}$$

Table 8-1 Activity coefficients for aqueous solutions at 25°C

Ion	Ion size (α , pm)	Ionic strength (μ , M)				
		0.001	0.005	0.01	0.05	0.1
Charge = ± 1						
H ⁺	900	0.967	0.933	0.914	0.86	0.83
(C ₆ H ₅) ₂ CHCO ₂ ⁻ , (C ₃ H ₇) ₄ N ⁺	800	0.966	0.931	0.912	0.85	0.82
(O ₂ N) ₃ C ₆ H ₂ O ⁻ , (C ₃ H ₇) ₃ NH ⁺ , CH ₃ OC ₆ H ₄ CO ₂ ⁻	700	0.965	0.930	0.909	0.845	0.81
Li ⁺ , C ₆ H ₅ CO ₂ ⁻ , HOC ₆ H ₄ CO ₂ ⁻ , ClC ₆ H ₄ CO ₂ ⁻ , C ₆ H ₅ CH ₂ CO ₂ ⁻ , CH ₂ =CHCH ₂ CO ₂ ⁻ , (CH ₃) ₂ CHCH ₂ CO ₂ ⁻ , (CH ₃ CH ₂) ₄ N ⁺ , (C ₃ H ₇) ₂ NH ₂ ⁺	600	0.965	0.929	0.907	0.835	0.80
Cl ₂ CHCO ₂ ⁻ , Cl ₃ CCO ₂ ⁻ , (CH ₃ CH ₂) ₃ NH ⁺ , (C ₃ H ₇)NH ₂ ⁺	500	0.964	0.928	0.904	0.83	0.79
Na ⁺ , CdCl ⁺ , ClO ₂ ⁻ , IO ₃ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , HSO ₃ ⁻ , H ₂ AsO ₄ ⁻ , Co(NH ₃) ₄ (NO ₂) ₂ ⁺ , CH ₃ CO ₂ ⁻ , ClCH ₂ CO ₂ ⁻ , (CH ₃) ₄ N ⁺ , (CH ₃ CH ₂) ₂ NH ₂ ⁺ , H ₂ NCH ₂ CO ₂ ⁻	450	0.964	0.928	0.902	0.82	0.775
⁺ H ₃ NCH ₂ CO ₂ H, (CH ₃) ₃ NH ⁺ , CH ₃ CH ₂ NH ₂ ⁺	400	0.964	0.927	0.901	0.815	0.77
OH ⁻ , F ⁻ , SCN ⁻ , OCN ⁻ , HS ⁻ , ClO ₂ ⁻ , ClO ₄ ⁻ , BrO ₃ ⁻ , IO ₄ ⁻ , MnO ₄ ⁻ , HCO ₂ ⁻ , H ₂ citrate ⁻ , CH ₃ NH ₂ ⁺ , (CH ₃) ₂ NH ₂ ⁺	350	0.964	0.926	0.900	0.81	0.76
K ⁺ , Cl ⁻ , Br ⁻ , I ⁻ , CN ⁻ , NO ₂ ⁻ , NO ₃ ⁻	300	0.964	0.925	0.899	0.805	0.755
Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , Tl ⁺ , Ag ⁺	250	0.964	0.924	0.898	0.80	0.75

a. Lanthanides are elements 57-71 in the periodic table.

17 (8 points). Ethylenediamine is a diprotic acid with $\text{pK}_{a1} = 6.848$, and $\text{pK}_{a2} = 9.928$. What is the equilibrium pH of a 0.855 M solution of the intermediate form of this acid?

$$K_1 = 10^{-6.848} = 1.42 \times 10^{-7}$$

$$F = 0.855 \text{ M}$$

$$K_2 = 10^{-9.928} = 1.18 \times 10^{-10}$$

$$K_w = 10^{-14}$$

$$[\text{H}^+] = \sqrt{\frac{(1.42 \times 10^{-7})(1.18 \times 10^{-10})(0.855 \text{ M}) + (1.42 \times 10^{-7})(10^{-14})}{(1.42 \times 10^{-7} + 0.855 \text{ M})}}$$

$$[\text{H}^+] = 4.09 \times 10^{-9}$$

$$\text{pH} = \boxed{8.39}$$

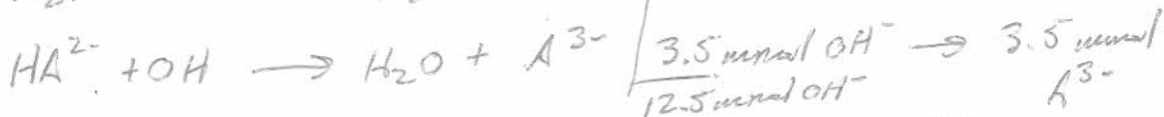
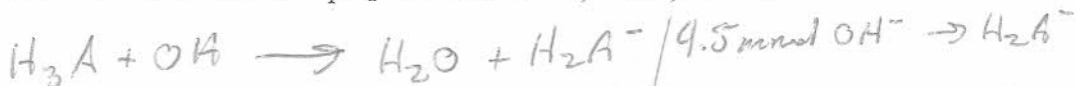
18 (4 points). For the solution described in question 17 (previous page), what is the equilibrium concentration of the acid form of ethylenediamine?



$$\frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} = 10^{-6.398}$$

$$[\text{H}_2\text{A}] = \frac{[\text{H}^+][\text{HA}^-]}{1.42 \times 10^{-7}} = \frac{(4.09 \times 10^{-9})(0.855)}{1.42 \times 10^{-7}} = \boxed{0.025 \text{ M}}$$

19 (12 points). What is the pH of the final combined solution at equilibrium when 75.0 mL of a solution containing 0.0600 M citric acid (H_3A) is mixed with 25.0 mL of 0.500 M NaOH? citric acid has pK_a values of 3.128, 4.761, and 6.396.



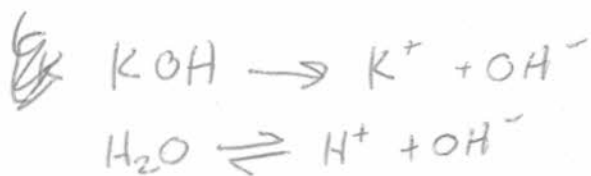
$$\frac{75.0 \text{ mL} \mid 0.0600 \text{ mmol H}_3\text{A}}{1 \text{ mL}} = \begin{array}{l} 4.5 \text{ mmol H}_3\text{A} \text{ converted to HA}^{2-} \\ -3.5 \\ \hline 1.0 \text{ mmol HA}^{2-} \text{ left over} \end{array}$$

$$\frac{25.0 \text{ mL} \mid 0.500 \text{ mmol}}{1 \text{ mL}} = 12.5 \text{ mmol OH}^-$$

buffer of A^{3-} and HA^{2-}

$$\text{pH} = 6.396 + \log \frac{3.5}{1.0} = \boxed{6.94}$$

20 (12 points). Use the systematic method to determine the equilibrium pH of a $8.85 \times 10^{-8} \text{ M}$ solution of strong base KOH. Report your answer to 3 significant digits.



charge

$$[\text{H}^+] + [\text{K}^+] = [\text{OH}^-]$$

mass

$$[\text{K}^+] = 8.85 \times 10^{-8} \text{ M}$$

equilibrium

$$[\text{H}^+][\text{OH}^-] = 10^{-14} \rightarrow [\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]}$$

unknowns

$$[\text{H}^+], [\text{OH}^-], [\text{K}^+]$$

solve:

$$[\text{H}^+] + 8.85 \times 10^{-8} = [\text{OH}^-]$$

$$[\text{H}^+] + 8.85 \times 10^{-8} = \frac{10^{-14}}{[\text{H}^+]}$$

$$[\text{H}^+]^2 + 8.85 \times 10^{-8} [\text{H}^+] - 10^{-14} = 0$$

$$[\text{H}^+] = \frac{-8.85 \times 10^{-8} \pm \sqrt{(8.85 \times 10^{-8})^2 - 4(1)(-10^{-14})}}{2}$$

$$\frac{-8.85 \times 10^{-8} \pm 2.19 \times 10^{-7}}{2}$$

$$[\text{H}^+] = 6.51 \times 10^{-8}$$

$$\text{pH} = \boxed{7.19}$$

21 (12 points). The acidic form of the common TRIS buffer (TRIS hydrochloride) has a molecular weight of 157.60 g/mole, and a pK_a of 8.07. What mass (g) of TRIS hydrochloride and what volume (mL) of 0.150M strong base is necessary to produce 250 mL of buffer at pH 8.30 and with total acid/base concentration of 0.0350 M ($[acid] + [base] = 0.0350$ M)?

$$250 \text{ mL} \left| \frac{0.0350 \text{ mmol}}{1 \text{ mL}} \right| \left| \frac{1 \text{ mol}}{1000 \text{ mmol}} \right| \left| \frac{157.60 \text{ g}}{1 \text{ mol}} \right| = \boxed{1.38 \text{ g}}$$

$$8.30 = 8.07 + \log \frac{\text{base}}{\text{acid}} \Rightarrow \frac{\text{base}}{\text{acid}} = 1.70$$

$$250 \text{ mL} \left| \frac{0.0350 \text{ mmol}}{1 \text{ mL}} \right| = 8.75 \text{ mmol} \Rightarrow \begin{cases} \text{base} + \text{acid} = 8.75 \text{ mmol} \\ \text{acid} = 8.75 - \text{base} \end{cases}$$

$$\frac{\text{base}}{8.75 - \text{base}} = 1.70$$

need 5.51 mmol of OH^-

$$\text{base} = 14.875 - 1.70 \text{ base}$$

$$\text{base} = 5.51 \text{ mmol}$$

$$\therefore \text{acid} = 3.24 \text{ mmol}$$



$$5.51 \text{ mmol} \left| \frac{\text{mL}}{0.150 \text{ mmol}} \right| = \boxed{36.7 \text{ mL}}$$