

PART A (Titration) (10pts)

Draw a reasonable titration curve for the reaction of 200 ml 0.25M Pyruvic acid ($pK_a = 2.39$) with 0.10M Potassium hydroxide (assume totally soluble). Contrast this with the titration curve for a 0.25M Hydrochloric acid

Note the **THREE(3)** important pH's that help define the shape of this graph

GRAPH TO INCLUDE S shaped curve for weak acid with 3 key pH points at 0, 100 200mls of KOH

$$= 0.5 * (2.39 - \text{LOG}(0.25)) \quad 1.50$$

= Pyruvic Acid=1.50 and need 500 ml for equivalence (250 for $\frac{1}{2}$ equivalence)

$$\text{HCl} = \text{pH} = 0.602$$

$$\text{pH} = pK_a - \log\left(\frac{[\text{HA}]}{[\text{A}^-]}\right) = pK_a \quad 2.39 \quad (1/2 \text{ EQUIVALENCE})$$

$$\text{pH}(\text{salt}) = 7 + \frac{1}{2} (pK_a + \log[\text{A}^-]) = 7 + 0.5 * (2.39 + \text{LOG}((0.05/0.7))) \quad 7.62 \quad (\text{REMEMBER DILUTION for A})$$

PART B (Acid-Base Chemistry) (10x5=50 pts)

3) What is the pH of an aqueous solution of 0.747 M 2,3 dichloro-pyridine ($K_b = 1.288 \times 10^{-7}$)

(a weak base with the formula $\text{C}_5\text{Cl}_2\text{H}_5\text{N}$)

$$\text{BASE: } \text{pOH} = \frac{1}{2} (K_b - \log(0.747)) = 0.5 * (6.89 - \text{LOG}(0.747)) \quad 3.508 \rightarrow \text{pH} = 10.49$$

1) Using the fact that Acetic Acid $pK_a = 4.75$; show Three ways to construct a BUFFER solution at $\text{pH} = 4.75$ using the following: (Hint be careful all of the concentrations are not equal)

0.10M solution of Sodium Hydroxide
0.20M solution of Sodium Acetate
0.30M solution of Sodium Fluoride
0.30M solution of Hydrochloric Acid
0.20M solution of Hydrofluoric Acid
0.20M solution of Sodium Lactate
0.10M solution of Acetic Acid

2 volumes of 0.1 M HAc + 1 volume of 0.2 M NaAc
 3 volumes of 0.2 M NaAc + 1 volume of 0.3 HCl
 2 volumes of 0.1 M HAc + 1 volume of NaOH

2) Which of the following acids, if in solutions of equal concentration, is the MOST acidic?

- a) 0.1M octanoic acid $pK_a = 4.89$
- b) 0.1M uric acid, $pK_a = 3.89$
- c) 0.1M propanoic acid $pK_a = 4.86$

d) 0.1M acetic acid $pK_a=4.75$

e) All of these acids are equally acidic because they are all of equal concentration.

0.1M octanoic acid $pK_a=4.89$ least

0.1M uric $pK_a=3.89$ most

5) If the pH of a solution of NaF is adjusted with a strong acid or base. Using the fact that $pK_a(HF) = 3.17$; when is 40% of the total fluoride in the form of F^- ?

$$pH = pK_a - \log(0.60/0.40) = 2.99$$

4) How many milligrams of **Magnesium hydroxide**(Molar Mass=58.305) would be need to be added to one liter of solution (assume STRONG and it all dissolves) to give an aqueous solution with a pH of 10.00

$$\begin{aligned} pOH &= 14 - 10.73 & 3.27 \\ [OH] &= 10^{-4} & 0.0001 \\ \text{but } [Mg(OH)_2] &= 0.5[OH] = 5.0E-05 \\ & & 2.91E-3 \quad g \rightarrow 2.915 \text{ mg} \end{aligned}$$

7) What is the pH of a solution contains 0.402 M di-methylamine chloride and 0.389 M di-methylamine. ($pK_b(CH_3NH_2) = 3.21$)

pH of BASE BUFFER: $pOH = pK_b - \log([B]/[BH^+]) = 3.21 - \log(0.389/0.402) = 3.22 \rightarrow pH = 10.78$

8-9) A nitrous acid buffer is prepared by adding 150ml of 0.481 M nitrous acid ($pK_a = 3.35$) to 100 ml of 0.314 M sodium nitrite. What is the pH of this buffer?

$$= 3.35 - \log((0.15 \cdot 0.481)/(0.1 \cdot 0.314)) = 2.99$$

Now 100 ml of 0.2M sodium hydroxide is added, what is the final pH

$$= 3.35 - \log((0.15 \cdot 0.481 - 0.1 \cdot 0.2)/(0.1 \cdot 0.314 + 0.1 \cdot 0.2)) \quad 3.343709$$

10) What volume of a 0.25 M Sulfuric acid solution is required to titrate to equivalence 36.0 mL of a 0.225 M ammonium hydroxide ($pK_b = 4.75$) solution? **And** what is the resulting pH

$$MV = MV$$

$$(0.5) \cdot x = 0.225 \cdot 0.036 \quad 0.0162 \text{ L} \quad 16.2 \text{ ml}$$

Strong Acid/WEAK base \Rightarrow No excess Acid/Base and BUT contains Salt of Weak Base (Acidic)

$$\text{Molarity of } NH_4^+ = \text{moles of } NH_4 / (\text{Total Volume}) = (0.036 \cdot 0.225) / (0.0162 + 0.036) = 0.155 \text{ M}$$

$$pH = 7 - \frac{1}{2} \cdot (4.75 + \log(0.155)) = 5.03$$

6) Which of the following aqueous solutions are good buffer systems AND WHY!!?

0.45 M hydrocyanic acid + 0.22 M sodium hydroxide	YES(SB converts $HCN \Rightarrow CN^-$)
0.24 M nitric acid + 0.22 M potassium nitrate	NO(strong acid)

0.36 M potassium nitrate + 0.26 M barium sulfate	NO(both salts)
0.40 M sodium lactate + 0.47 M hydrofluoric acid	NO(needs conjugate pair)
0.31 M sulfuric acid + 1.24 M ammonia	YES(Half of the base will be converted to conjugate acid)
0.61 M ammonia + 0.034 M ammonium chloride	NO insufficient ammonium ion

POLYPROTONIC ACID TITRATION (10 pts)

Draw a rough titration curve for 500ml of 0.1M Phosphoric Acid with 0.1M Sodium Hydroxide.
Identify which forms of Phosphate are present at each of the Equivalence points!
 pK_a 's = 2.15, 7.2, 12.35

SOLUBILITY (5 pts)

What is the solubility in grams per liter of Sodium Phosphate if its $K_{sp} = 2.24 \times 10^{-26}$?

Part C. Consider the following Titration Conditions (8x5=40pts)

:

0.25 M ACID	0.35 M BASE	Equation/work	pH
35 ml Formic Acid (pKa=3.17)	25 ml of NaOH	moles of acid = MaVa 0.0088 moles of base = MbVb 0.0088 Total Volume= 0.060 L If Salt(WA/SB) 8.17	
50 ml HCl	50 ml NH ₃ (pK _b = 4.75)	moles of acid = MaVa 0.0125 moles of base = MbVb 0.0175 Total Volume= 0.100 LI WEAK Base (HH Eq) pH= 8.85	
50 ml Chloroacetic Acid (pKa=2.85)	15 ml Ca(OH) ₂	moles of acid = MaVa 0.0125 moles of base = MbVb 0.0105 Total Volume= 0.0650 L Weak Acid (HH Eq) pH= 3.57	
120 ml Nitrous Acid (pK _a)=3.35	40 ml NaOH	moles of acid = MaVa 0.030 moles of base = MbVb 0.014 Total Volume= 0.160 L WEAK Base (HH Eq) pH= 3.29	
35 ml of HCl	25 ml of Methylamine pK _b =3.34	moles of acid = MaVa 0.0075 moles of base = MbVb 0.0075 Total Volume= 0.060 ml Salt (WB/SA) 5.75	
No Acid	25 ml of Methylamine pK _b =3.34	moles of acid = MaVa 0.000 moles of base = MbVb 0.0088 Total Volume= 0.025 ml pH(WB alone)= 12.10	
20 ml of Cyanic Acid (HCNO) pKa = 3.46	No Base	moles of acid = MaVa 0.0088 moles of base = MbVb 0.000 Total Volume= 0.020 L pH(WA alone)= 2.03	
70ml of Sulfuric Acid	40 ml of NaOH	moles of acid = MaVa 0.035 moles of base = MbVb 0.014 Total Volume= 0.110 LI STRONG Acid Won pH= 0.72	

Part C. Consider the following Titration Conditions (8x5=40pts)

:

0.20 M ACID	0.40 M BASE	Equation/work	pH
40 ml Formic Acid (pKa)=3.17	20 ml of NaOH	moles of acid = MaVa 0.008 moles of base = MbVb 0.008 Total Volume= 0.060 L If Salt(WA/SB) 8.16	done
60 ml HCl	30 ml NH ₃ (pK _b = 4.75)	moles of acid = MaVa 0.0120 moles of base = MbVb 0.0120 Total Volume= 0.090 L Salt WEAK Base (HH Eq) pH= 5.06	done
50 ml Chloroacetic Acid (pKa=2.85)	12.5 ml Ca(OH) ₂	moles of acid = MaVa 0.0100 moles of base = MbVb 0.0100 Total Volume= 0.062.5 L Salt pH= 8.03	done
120 ml Nitrous Acid (pKa)=3.35	50 ml NaOH	moles of acid = MaVa 0.024 moles of base = MbVb 0.020 Total Volume= 0.160 L WEAK Base (HH Eq) pH= 4.05	done
20 ml of HCl	25 ml of Methylamine pK _b =3.34	moles of acid = MaVa 0.0040 moles of base = MbVb 0.0100 Total Volume= 0.060 ml HH (WB/SA) 10.84	done
No Acid	35 ml of Methylamine pK _b =3.34	moles of acid = MaVa 0.000 moles of base = MbVb 0.010 Total Volume= 0.025 ml pH(WB alone)= 12.13	done
30 ml of Cyanic Acid (HCNO) pKa = 3.46	No Base	moles of acid = MaVa 0.024 moles of base = MbVb 0.000 Total Volume= 0.020 L pH(WA alone)= 2.08	done
70ml of Sulfuric Acid	40 ml of Ba(OH) ₂	moles of acid = MaVa 0.014 moles of base = MbVb 0.032 Total Volume= 0.110 L STRONG Acid Won pH= 13.21	done