Time: 2½ hours

Chemistry 206
Final Examination

Feb. 5, 1999
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Family Name: ________________ First Name: ______________

ID No. ____________________ Major: ________________

Score: 1. 8.
2. 9.
3. 10.
4. 11.
5. 12.
6. 13.
7. 14.
15.

Data: Ka's at 25°C

	Ka_1	Ka_2	Ka_3	Ka_4
EDTA	1.0×10^{-2}	2.2×10^{-3}	6.9×10^{-7}	5.5×10^{-11}
H_3PO_4	1.1×10^{-2}	7.5×10^{-8}	4.8×10^{-13}	—
H_2CO_3	4.3×10^{-7}	4.8×10^{-11}	—	—

1. Which of the following expressions gives the hydronium ion concentration in an aqueous solution of 0.0100M Na_2H_2Y ?

a. $[H_3O^+] = (Ka_1Ka_2)^{½}$

b. $[H_3O^+] = (Ka_2Ka_3)^{½}$

c. $[H_3O^+] = \left\{\dfrac{Kw + Ka_3[H_2Y^{2-}]_0}{1 + [H_2Y^{2-}]_0 / Ka_2}\right\}^{1/2}$

d. $[H_3O^-] = \left\{\dfrac{Ka_3[H_2Y^{2-}]_0}{1 + [H_2Y^{2-}]_0 / Ka_2}\right\}^{1/2}$

e. $[H_3O^-] = \left\{\dfrac{Ka_2Ka_3[H_2Y^{2-}]_0}{Ka_3 + [H_2Y^{2-}]_0}\right\}^{1/2}$

f. $[H_3O^-] = \left\{\dfrac{Ka_2Kw + Ka_2Ka_3[H_2Y^{2-}]_0}{1 + [H_2Y^{2-}]_0}\right\}^{1/2}$

2. The total carbon dioxide content (HCO_3^- + CO_2) in a blood sample is determined by acidifying the sample and measuring the volume of $CO_2(g)$ evolved, which is then converted to concentration. The total concentration of CO_2 was determined to be 28.5 mmol per liter. The pH of blood sample at 37°C was measured to be 7.48. What are the concentrations of HCO_3^- and CO_2 in the blood ? For H_2CO_3 at 37°C: $pKa_1 = 6.10$, $pKa_2 = 10.32$

	$[CO_2]$, mmol/L	$[HCO_3^-]$, mmol/L
a.	1.28	25.0
b.	1.14	24.7
c.	1.1	27.4
d.	1.0	24.0
e.	18.0	1.38
f.	1.3	26.0
g.	1.0	20.0

Is this an effective buffering ratio ?

Buffer capacity will be weak towards strong acid or strong base ?

3. The pH of the blood in a healthy person remains remarkably constant at 7.35-7.45. From a physiological viewpoint, a change of ±0.3pH units is extreme. What maximum change in $[H_3O^+]$ will result from such fluctuation ?

Answer:

4. What weights of Na_2HPO_4 and NaH_2PO_4 would be required to prepare 1 liter of a buffer solution of pH 7.45 that has an ionic strength of 0.100 ?

	$W_{NaH_2PO_4}(g)$	$W_{Na_2HPO_4}(g)$
a.	1.92	4.10
b.	0.19	0.35
c.	1.92	3.46
d.	1.62	4.10
e.	3.50	1.92

5. a- Tris (hydroxymethyl) aminomethane {$(HOCH_2)_3CNH_2$-Tris, or THAM} is a weak base frequently used to prepare buffers in biochemistry. Its K_b is 1.2×10^{-6} ($pK_b = 5.92$). What weight of THAM must be taken with 100ml of 0.50M HCl to prepare 1L of a pH 7.40 buffer ?

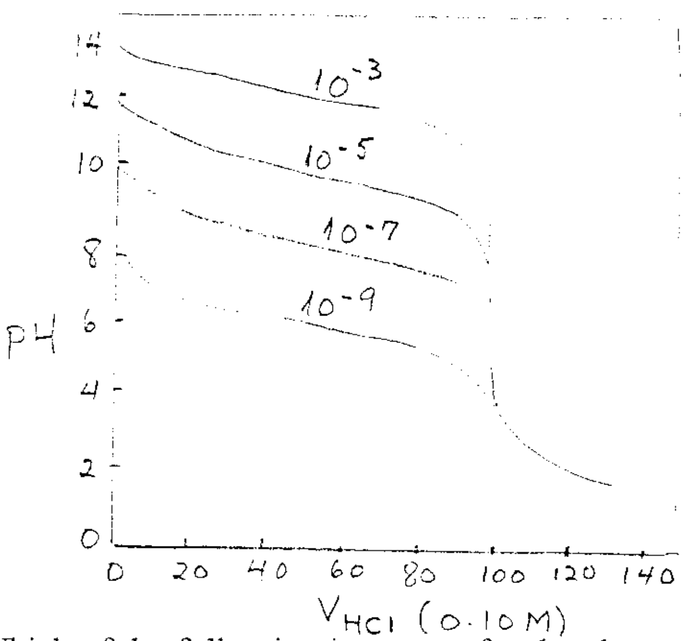
   a. 2.2 g
   b. 11.4 g
   c. 71.8 g
   d. 7.3 g
   e. 10.8 g

b. Give the Henderson-Hasselbalch equation for THAM / salt buffer:

c. Give one other important use for THAM:

d. Why is it useful for buffers in biochemistry ?

6.



Which of the following is correct for the above titration curves ?

a. The indicated numbers represent K_b's of different weak bases.
b. The numbers represent different concentrations of the same weak base.
c. The curve labelled 10^{-3} represents the titration of a 10^{-3}M strong base (monofunctional) with HCl.
d. None of the above is correct.

7. A mixture of NaOH and Na_2CO_3 is titrated with 0.250M HCl, requiring 26.2ml for the phenolphthalein end point and an additional 15.2ml to reach the methyl orange end point.
   PH transition intervals:
   MO 3.1-4.4
   Phenolphthalein 8.2-9.8

a. What is the system at the phenolphthalein end point ? MO end point ?

   Answer:

b. Calculate K_{b_1} for CO_3^{2-} :

   Answer:

c. Calculate the weight of NaOH and Na_2CO_3 in the mixture:

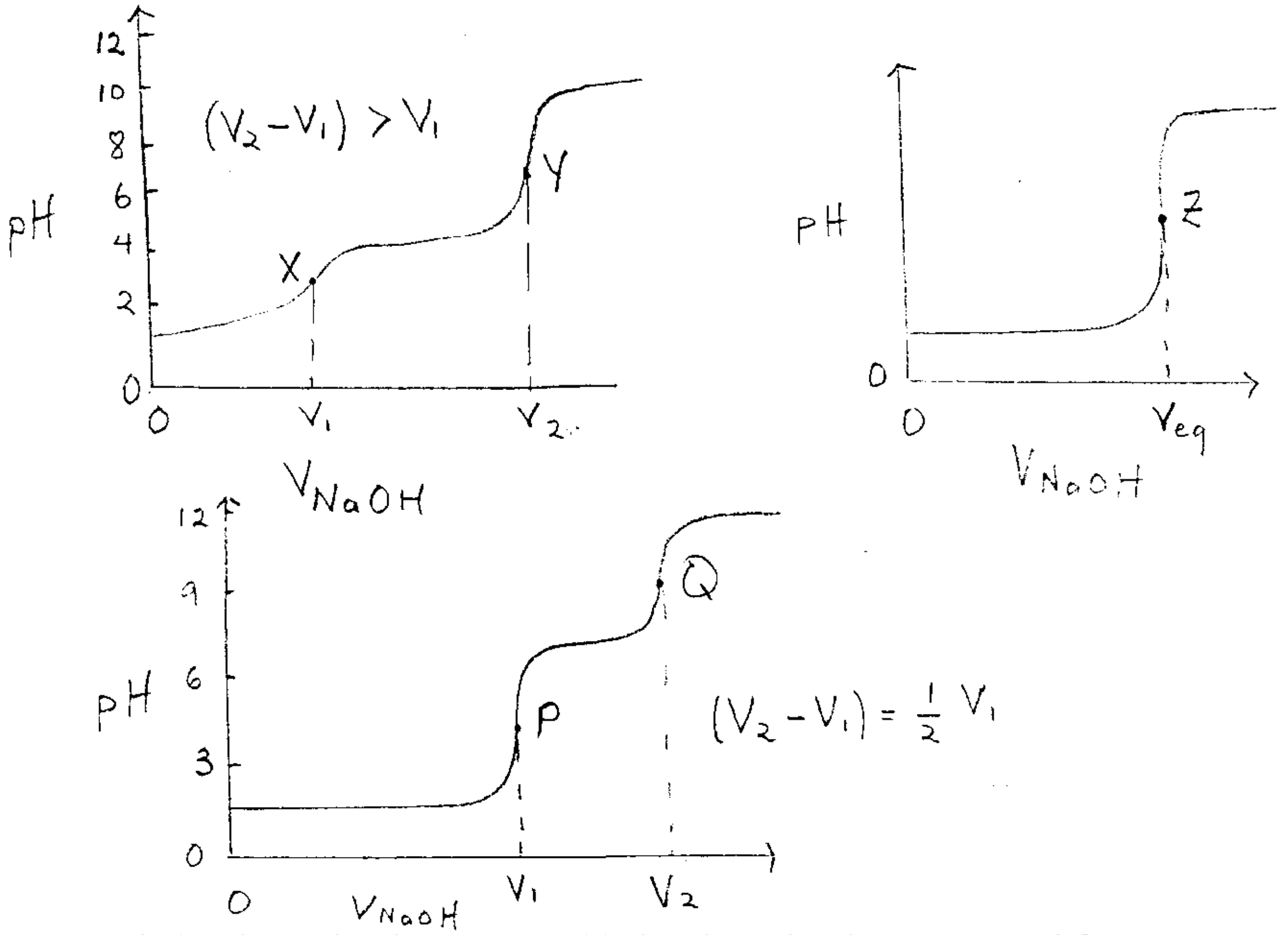
Answer: W_{NaOH} = $W_{Na_2CO_3}$ =

8. The following are the titration curves of:

A. H_2SO_4 (Ka of HSO_4^- = 1.2×10^{-2}) with strong base.

B. A mixture of 0.1 M HCl and 0.2 M HOAc (Ka = 1.8×10^{-5}) with strong base.

C. An equimolar mixture of HCl and H_3PO_4 with strong base.



a. Match the above titration curves with the given titrations A, B, and C.

b. Identify the systems at:

X: Y: P: Q:

9. Circle T for true and F for false:

T F a. Water is a leveling solvent for acids $HClO_4$, HNO_3, HI, HCl

T F b. Ethanol and methanol are amphiprotic solvents.

T F c. Glacial acetic acid is a leveling solvent for mineral acids.

T F d. Glacial acetic acid is a differentiating solvent for mineral acids.

T F e. Glacial acetic acid is an effective leveling solvent for bases.

T F f. An example of a an a protic solvent is CCl_4.

10. a. Calculate the fraction of Y^{4-} at pH 10 in 100 mL of 0.100 M EDTA solution:

Answer: $\alpha_4 =$

b. Calculate pCa at the equivalence point when 100 mL of 0.100 M Ca^{2+} is titrated at a constant pH of 10 with 0.100 M EDTA solution: K_f for $CaY^{2-} = 5.0 \times 10^{-10}$.

Answer: pCa =

K_f^1 = conditional formation constant for CaY^{2-} =

11. The Tl in a 9.76 g unknown sample was oxidized to the trivalent state and treated with excess Mg/EDTA solution, MgY^{2-}. Titration of the liberated Mg^{2+} required 13.34 mL of 0.03560 M EDTA.

a. Give the titration reaction:

Answer:

b. Give the final expression for the percentage of Tl as Tl_2SO_4 in the unknown sample. Mol. wt Tl_2SO_4 (504.8 g/mol); in the final expression, units should follow each number; No calculation is required!

Answer:

12. An EDTA solution was prepared by dissolving approximately 4g of $Na_2H_2Y \cdot 2H_2O$ (s) in approximately 1 L of H_2O. 50.00 mL aliquots of a standard that contained 0.7682 g of $MgCO_3$ per liter required an average of 42.35 mL of EDTA solution.

a. Calculate the molarity of the EDTA solution and give the numerical answer:

Answer: M_{EDTA} =

b. Titration of a 25.00 mL sample of mineral water at pH 10 required 18.81 mL of EDTA solution with Eriochrome black T used as indicator. Calculate total hardness of the mineral water as µg of $CaCO_3$ per mL water and give your numerical answer:

Answer:

c. How can hardness in Mg^{2+} be experimentally determined with one more experiment using the total hardness from above? Describe briefly; assume hardness is due to Ca^{2+} and Mg^{2+} only:

13 a. Give the balanced cell reaction for the following cell:

$Cu | Cu^{2+}$ (0.0601 M) || I^-(0.1350 M) , AgI (sat'd) | Ag

For the half-rxs:

$Cu^{2+} + 2e^- \rightleftharpoons$ $E_{cu} = +0.337$ V

$AgI (s) + e^- \rightleftharpoons Ag (s) + I^- (aq)$ $E°_{AgI/Ag} = -0.151$ V

Answer:

b. Calculate the theoretical cell potential for the cell in (a) and indicate whether the cell is galvanic or electrolytic as written:

Answer: E_{cell} =

c. What type of electrode is the cathode in (a)?
Can it be used as indicator electrode and for which ion?

Answer:

14. a. Calculate the numerical value of K_{eq} for the following unbalanced reaction:

$$V(OH)_4^+ + H_2SO_3 \rightleftharpoons SO_4^{2-} + VO^{2+} + H_2O$$

$E_V^\circ = 1.00$ V $\qquad E_S^\circ = 0.172$

Answer: $K_{eq} =$

b. Calculate E° for the process

$$AgIO_3\ (s) + e^- \rightleftharpoons Ag\ (s) + IO_3^-$$

Given: $Ag^+ (aq) + e^- \rightleftharpoons Ag\ (s) \qquad E^\circ_{Ag} = +0.799$ V
$Ksp\ (AgIO_3) = 3.1 \times 10^{-8}$

Answer: $E^\circ_{AgIO3} =$

15. Which of the following electrodes cannot be used as an indicator electrode?

a. Ag | AgCl (sat'd), KCl (sat'd) ||
b. Ag | AgCl (sat'd), Cl^- (xM) ||
c. M | M^{n+} (xM) ||
d. Hg(l) | HgY^{2-} (α_{HgY2-}), Y^{4-}(a) ||