

Chemistry 210

Exam 3

Be sure to put your name on each page. This page can be removed from your exam so that you will have a Periodic Table handy throughout the exam, it does not need to be turned in. Show all your work for problems which require any sort of calculation, no credit will be given for answers without work shown. If you have shown a significant amount of work or multiple drawings for a problem, draw a box around what you consider your final answer.

Avogadro's Number = 6.022×10^{23} units/mol

$32.00^\circ\text{F} = 0.000^\circ\text{C} = 273.15\text{K}$

Density of Water = $1.000^{\text{g}}/\text{mL}$

$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K} = 8.314 \text{ J}/\text{mol}\cdot\text{K}$

$PV = nRT$

$\Delta T_{\text{fp/bp}} = k_{\text{fp/bp}} \cdot m \cdot i$

For water: $k_{\text{fp}} = -1.86^\circ\text{C}/m$
 $k_{\text{bp}} = 0.512^\circ\text{C}/m$

$P_1 = X_1 P_1^\circ$

$\Pi = MRTi$

$C_1 V_1 = C_2 V_2$

Quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Integrated Rate Laws:

0th order $[A]_t = -kt + [A]_o$

1st order $\ln[A]_t = -kt + \ln[A]_o$

2nd order $1/[A]_t = kt + 1/[A]_o$

$k = Ae^{-E_a/RT}$

$$\ln(k) = \left(\frac{-E_a}{R} \right) \left(\frac{1}{T} \right) + \ln(A)$$

$$\ln\left(\frac{k_1}{k_2} \right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{conjugate base}]}{[\text{conjugate acid}]} \right)$$

$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$

$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K^\circ$

$K^\circ = e^{(nF/RT) E^\circ_{\text{cell}}}$

$F = 96485 \text{ J}/\text{V}\cdot\text{mol of electrons}$

$\Delta G^\circ = \Delta H^\circ_{\text{system}} - T\Delta S^\circ_{\text{system}}$

$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT \ln K^\circ$

$\Delta G = \Delta G^\circ + RT \ln Q$

$F = 96485 \text{ C}/\text{mol electrons}$

$1A = 1C / \text{sec}$

1 H 1.0079																	2 He 4.0026				
3 Li 6.941	4 Be 9.0122															5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305															13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80				
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29				
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)				
87 Fr (223)	88 Ra 226.03	89 Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)	114		116							

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.94	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (258)	101 Md (258)	102 No (259)	103 Lr (260)

1. Complete each row of the following tables for aqueous solutions at 25°C (4pts per box):

$[\text{H}_3\text{O}^+]$	$[\text{OH}^-]$	pH	pOH	Acidic, Basic or Neutral?
1.62×10^{-9}	6.19×10^{-6}	8.792	5.208	Basic
4.81×10^{-5}	2.08×10^{-10}	4.318	9.682	Acidic

Conjugate Acid	K_a @ 25°C	Conjugate Base	K_b @ 25°C
H_2SO_3	1.7×10^{-2}	HSO_3^-	5.9×10^{-13}
$\text{HC}_6\text{H}_6\text{O}_6^-$	1.6×10^{-12}	$\text{C}_6\text{H}_6\text{O}_6^{2-}$ (ascorbate ion)	6.3×10^{-3}

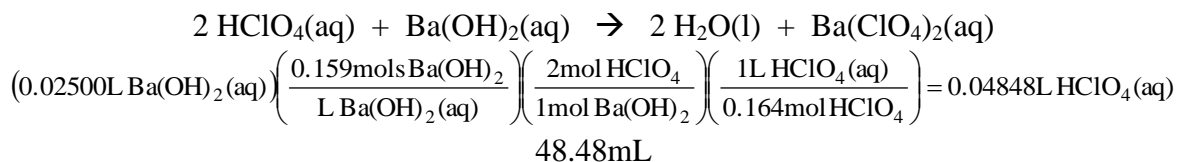
2. A labmate has prepared a sulfate/hydrogen sulfate buffer solution at pH=2.03, but does not write much information down in a lab notebook. You know that the concentration of the buffer is 0.73M and $\text{p}K_b=12.08$ for $\text{SO}_4^{2-}(\text{aq})$. Is the concentration of conjugate acid higher in this buffer or is the concentration of conjugate base in this buffer higher? Over what pH range would sulfate/hydrogen sulfate make an effective buffer? Explain your answers. (12pts)

From the given $\text{p}K_b$ for SO_4^{2-} , we can calculate the $\text{p}K_a$ for HSO_4^-

$$\text{p}K_a\{\text{HSO}_4^-\} = 14 - 12.08 = 1.92$$

Since the pH of the buffer is higher (more basic) than the $\text{p}K_a$ of the conjugate acid, there must be a higher concentration of the conjugate base in this buffer. This system will make an effective buffer for pH's within 1 unit of the $\text{p}K_a$, 0.92 to 2.92

3. How much 0.164M $\text{HClO}_4(\text{aq})$ must be added to 25.00mL of 0.159M $\text{Ba}(\text{OH})_2(\text{aq})$ to reach the equivalence point? What is the pH of this solution at the equivalence point? Explain. (12pts) {Note: $\text{Ba}(\text{OH})_2$ is a strong base.}



Since this is a strong acid/strong base titration, the equivalence point should be neutral, pH = 7

4. You have prepared a buffer solution by combining 0.476mols of nitrous acid (HNO_2 , $K_a = 4.6 \times 10^{-4}$) and 0.397mols of sodium nitrite in enough water to make 500.0mL of solution. What is the pH of this buffer solution? (12pts)

Plugging in to the Henderson-Hasselbalch equation...

$$\text{pH} = 3.337 + \log \left\{ \frac{0.397 \text{mols NO}_2^-(\text{aq})}{0.476 \text{mols HNO}_2(\text{aq})} \right\} = 3.26$$

5. What is the expected pH of a 0.914M aqueous solution of ammonium bromide? ($K_b(\text{NH}_3) = 1.76 \times 10^{-5}$) (15pts)

Set up a table of initial/ Δ / @ Equilibrium concentrations, calculate K_a of $\text{NH}_4^+(\text{aq})$ from the K_b of $\text{NH}_3(\text{aq})$, make some simplifying assumptions, and we should get down to:

$$\begin{aligned} 5.68 \times 10^{-10} &= x^2 / 0.914 \\ x &= 2.28 \times 10^{-5} = [\text{H}_3\text{O}^+] \\ \text{pH} &= 4.642 \end{aligned}$$

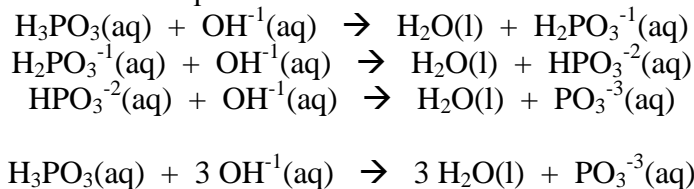
6. What is the K_b of a weak base if 500.0mL of a solution containing 0.241mol of the base and 0.209mol of its conjugate acid has a pH of 8.337? Over what pH range would this conjugate acid/ conjugate base pair make an effective buffer? (15pts)

Plugging in to the Henderson-Hasselbalch equation...

$$\begin{aligned} 8.337 &= \text{p}K_a + \log \left\{ \frac{0.241 \text{mols conj. base}}{0.209 \text{mols conj. acid}} \right\} \\ \text{p}K_a &= 8.275 \rightarrow \text{p}K_b = 14 - 8.275 = 5.725 \\ \text{Effective buffer} &\text{ within 1 unit of } \text{p}K_a \text{ of the conjugate acid, } 7.275 \rightarrow 9.275 \end{aligned}$$

7. You are going to use a titration to determine the concentration of an unknown phosphorous acid solution (H_3PO_3 , $\text{p}K_a = 1.29$). The base you have chosen to use is 0.796M sodium hydroxide.
- a. Write out the chemical equations for the step-wise deprotonation/neutralization of phosphorous and the overall/net chemical reaction. (7pts)

Plugging in to the Henderson-Hasselbalch equation...



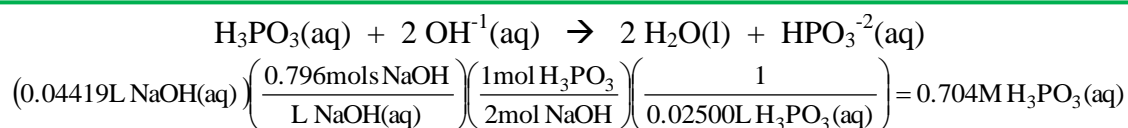
- b. Someone left your pH probe laying on the bench and it has dried out. After a short search, you have found the following three visual indicators: Thymolphthalein (TP, endpoint pH range = 9.5-10.5); Phenol red (PR, endpoint pH range = 6.8-8.3); Bromophenol Blue (BPB, endpoint pH range = 3.1-4.6). Which of these visual indicators would be useful in your titration? Explain your choice(s). (6pts)

Strong base/weak acid, the equivalence point should be basic, but *which* equivalence point? {There are 3 of them...} Given the very low $\text{p}K_a$, the pH of the first equivalence point should be fairly acidic, so BPB is probably a good indicator for the 1st equivalence point. The second equivalence point should be somewhere around neutral (about 4-5 units higher than the first...), so PR is probably an OK indicator for the 2nd equivalence point. The third equivalence point should be another 4-5 units higher than the second, so TP might be an OK indicator for the 3rd equivalence point.

(#7 continued)

- c. Sketch the titration curve you would expect for this titration, labeling all equivalence points and phosphorous acid-based species present in each portion of the curve. (7pts)

- d. As you are about to start your titration, a package arrives with a new pH probe, so you decide to use the pH probe to monitor your titration. You find that 25.00mL of phosphorous acid requires 44.19mL of sodium hydroxide to reach the second equivalence point. What is the concentration of the phosphorous acid solution? (10pts)



- e. How much sodium hydroxide solution would be required to reach the first equivalence point in part “d”? How much sodium hydroxide solution would be required to reach the third equivalence point in part “d”? Explain your answer. (6pts)

Each equivalence point is an equal step, so the volume of NaOH(aq) required to reach each equivalence point is the same. If it took 44.19mL to reach the 2nd equivalence point, then it would have taken $\{44.19/2\}=22.10\text{mL}$ to reach the first. To reach the 3rd equivalence point, we need 3 times as much NaOH(aq) as it took to reach the 1st, $\{22.10 \times 3\} = 66.29\text{mL}$