

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, $k_{\text{fp}} = -1.86^\circ\text{C}/m$; $k_{\text{bp}} = 0.52^\circ\text{C}/m$

$P_1 = X_1 P_1^\circ$

$\Pi = MRTi$

$C_1 V_1 = C_2 V_2$

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 $1/[A]_t = kt + 1/[A]_o$

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

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

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

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

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

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

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

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

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

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

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

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

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

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?
3.44×10^{-9}	2.91×10^{-9}	5.464	8.536	Acidic
1.89×10^{-9}	5.28×10^{-9}	8.723	5.277	Basic

Conjugate Acid	K_a @ 25°C	Conjugate Base	K_b @ 25°C
H_2PO_3^-	2.90×10^{-7}	HPO_3^{2-}	3.45×10^{-8}
$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	1.23×10^{-4}	$\text{C}_6\text{H}_5\text{CO}_2^-$ (benzoate ion)	8.13×10^{-9}

2. A labmate has prepared a chlorite/chlorous acid buffer solution at pH=2.00, but does not write much information down in a lab notebook. You know that the concentration of the buffer is 1.25M and $\text{p}K_b=12.05$ for $\text{ClO}_2^-(\text{aq})$. 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 chlorite/chlorous acid make an effective buffer? Explain your answers. (10pts)

This problem *could* be solved by plugging in to the Henderson-Hasselbalch equation, but since it doesn't ask for a specific numerical amount of base, we can answer it a little more qualitatively. If $\text{p}K_b=12.05$ for chlorite ions, then $\text{p}K_a$ for chlorous acid must be $14-12.05=1.95$. If a buffer is prepared that has exactly equal amounts of chlorite and chlorous acid, the pH of the buffer should be equal to the $\text{p}K_a$ of chlorous acid. Since the pH of the buffer is *higher* than the $\text{p}K_a$ of chlorous acid, there must be more conjugate *base* in the buffer. A given weak conjugate acid/weak conjugate base pair can make an effective buffer within 1 pH unit of the $\text{p}K_a$ of the weak acid, so this buffer system *could* make an effective buffer over the range $0.95 \rightarrow 2.95$.

3. What is the concentration of lead(II) ions {Atomic # = 82} in a saturated solution of lead(II) phosphate? $\{K_{sp} = 7.97 \times 10^{-43}\}$ (10pts)

Set up a K_{sp} equilibrium problem...

	$\text{Pb}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons$	$3 \text{Pb}^{2+}(\text{aq}) +$	$2 \text{PO}_4^{3-}(\text{aq})$
Initial	----	0 M	0 M
Δ	----	+ 3x	+ 2x
@ Equilibrium	----	3x M	2x M

$$K_{sp} = [\text{Pb}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3x)^3(2x)^2 = 7.97 \times 10^{-43}$$

$$108x^5 = 7.97 \times 10^{-43}$$

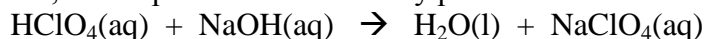
$$x = 1.49 \times 10^{-9}$$

$$[\text{Pb}^{2+}] = 3x = 3(1.49 \times 10^{-9}) = 4.47 \times 10^{-9} \text{ M}$$

$$[\text{PO}_4^{3-}] = 2x = 2(1.49 \times 10^{-9}) = 2.98 \times 10^{-9} \text{ M}$$

4. How many milliliters of 0.448M HClO₄(aq) must be added to 25.00mL of 0.591M NaOH(aq) to reach the equivalence point? What is the pH of this solution at the equivalence point? Explain. (10pts)

Strong acid/strong base titration, set it up like a stoichiometry problem...



$$(0.02500\text{L NaOH}(\text{aq})) \left(\frac{0.591\text{mols NaOH}}{1\text{mol NaOH}(\text{aq})} \right) \left(\frac{1\text{mol HClO}_4}{1\text{mol NaOH}} \right) \left(\frac{1\text{L HClO}_4(\text{aq})}{0.448\text{mols HClO}_4} \right) = 0.03298\text{L HClO}_4(\text{aq}) = 32.98\text{mL HClO}_4(\text{aq})$$

Since it's a strong monoprotic acid/strong monoprotic base titration, the equivalence point should be at pH=7

5. You have prepared a buffer solution by combining 0.316mols of nitrous acid (HNO₂, K_a = 4.6x10⁻⁴) and 0.385mols of sodium nitrite in enough water to make 500.0mL of solution. What is the pH of this buffer solution? (10pts)

Plugging in to the Henderson-Hasselbach equation...

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \right) = 3.337 + \log \left(\frac{0.385\text{mols NO}_2^- / 0.5000\text{L}}{0.316\text{mols HNO}_2 / 0.5000\text{L}} \right) = 3.423$$

6. What is the expected pH of a 0.784M aqueous solution of methyl amine? {K_b(CH₃NH₂) = 4.97x10⁻⁴}

Set up a K_b equilibrium problem...

	CH ₃ NH ₂ (aq) +	H ₂ O(l) ⇌	OH ⁻¹ (aq) +	CH ₃ NH ₃ ⁺ (aq)
Initial	0.784 M	----	0 M	0 M
Δ	-x	----	+ x	+ x
@ Equilibrium	(0.784 - x) M	----	x M	x M

$$K_b = [\text{OH}^-][\text{CH}_3\text{NH}_3^+] / [\text{CH}_3\text{NH}_2] = (x)(x) / (0.784 - x) = 4.97 \times 10^{-4}$$

Assuming "x" is much smaller than 0.784, the expression simplifies to"

$$(x)(x) / (0.784) = 4.97 \times 10^{-4}$$

$$x = 0.01974 = [\text{OH}^-] \rightarrow \text{pOH} = -\log(0.01974) = 1.705 \rightarrow \text{pH} = 14 - \text{pOH} = 14 - 1.705 = 12.295$$

7. What is the K_a of a weak acid if 500.0mL of a solution containing 0.229mol of the base and 0.216mol of its conjugate acid has a pH of 7.482? Over what pH range would this conjugate acid/ conjugate base pair make an effective buffer? (14pts)

Plugging in to the Henderson-Hasselbach equation...

$$7.482 = \text{pK}_a + \log \left(\frac{0.229\text{mols A}^- / 0.5000\text{L}}{0.216\text{mols HA} / 0.5000\text{L}} \right)$$

$$7.482 = \text{pK}_a + 0.025$$

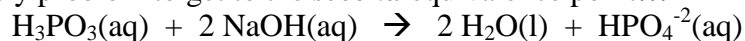
$$\text{pK}_a = 7.457, K_a = 3.49 \times 10^{-8}$$

$$\text{Effective buffer } 6.457 \rightarrow 8.457$$

8. You have titrated 25.00mL of 0.773M phosphorous acid solution with an unknown sodium hydroxide solution. You reach the second equivalence point when 44.17mL of base is added. What is the concentration of the original stock sodium hydroxide solution?

$$\{K_{a1}(\text{H}_3\text{PO}_3) = 2.42 \times 10^{-2}, K_{a2} = 2.89 \times 10^{-7}, K_{a3} = 1.96 \times 10^{-11}\} \quad (18\text{pts})$$

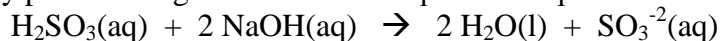
Set it up like a stoichiometry problem to get to the *second* equivalence point...



$$(0.02500\text{L H}_3\text{PO}_3(\text{aq})) \left(\frac{0.773\text{mols H}_3\text{PO}_3}{1\text{mol H}_3\text{PO}_3(\text{aq})} \right) \left(\frac{2\text{mol NaOH}}{1\text{mol H}_3\text{PO}_3} \right) \left(\frac{1}{0.04417\text{L NaOH}(\text{aq})} \right) = 0.875\text{M NaOH}(\text{aq})$$

9. You have titrated 25.00mL of an unknown sulfurous acid { $\text{H}_2\text{SO}_3(\text{aq})$, $\text{pK}_{a1}=1.770$, $\text{pK}_{a2}=7.201$ } solution to the second equivalence point with 41.64mL of 0.637M potassium hydroxide. Sketch the titration curve and label all equivalence points and all sulfurous acid-based species in solution in all portions of the curve. What is the concentration of the unknown sulfurous acid solution? How many milliliters were required to reach the *first* equivalence point in this titration? (18pts)

Set it up like a stoichiometry problem to get to the *second* equivalence point...



$$(0.04164\text{L KOH}(\text{aq})) \left(\frac{0.637\text{mols KOH}}{1\text{mol KOH}(\text{aq})} \right) \left(\frac{1\text{mol H}_2\text{SO}_3}{2\text{mol KOH}} \right) \left(\frac{1}{0.02500\text{L H}_2\text{SO}_3(\text{aq})} \right) = 0.530\text{M H}_2\text{SO}_3(\text{aq})$$

The first equivalence point required *half* as much as the second equivalence point, 20.82mL.