

# 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 =  $6.022 \times 10^{23}$  units/mol

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

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

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

$1\text{atm} = 760\text{torr} = 760\text{mmHg} = 101.325\text{kPa}$

$PV = nRT$

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

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

$P_1 = X_1 P_1^\circ$

$\Pi = MRTi$

$C_1 V_1 = C_2 V_2$

Integrated Rate Laws:

0<sup>th</sup>  $[A]_t = -kt + [A]_o$

1<sup>st</sup>  $\ln[A]_t = -kt + \ln[A]_o$

2<sup>nd</sup>  $1/[A]_t = kt + 1/[A]_o$

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

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

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

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

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

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

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

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

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

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

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

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

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

Quadratic formula:

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

1 <b>H</b> 1.0079																	2 <b>He</b> 4.0026				
3 <b>Li</b> 6.941	4 <b>Be</b> 9.0122															5 <b>B</b> 10.811	6 <b>C</b> 12.011	7 <b>N</b> 14.007	8 <b>O</b> 15.999	9 <b>F</b> 18.998	10 <b>Ne</b> 20.180
11 <b>Na</b> 22.990	12 <b>Mg</b> 24.305															13 <b>Al</b> 26.982	14 <b>Si</b> 28.086	15 <b>P</b> 30.974	16 <b>S</b> 32.066	17 <b>Cl</b> 35.453	18 <b>Ar</b> 39.948
19 <b>K</b> 39.098	20 <b>Ca</b> 40.078	21 <b>Sc</b> 44.956	22 <b>Ti</b> 47.88	23 <b>V</b> 50.942	24 <b>Cr</b> 51.996	25 <b>Mn</b> 54.938	26 <b>Fe</b> 55.847	27 <b>Co</b> 58.933	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.546	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.723	32 <b>Ge</b> 72.61	33 <b>As</b> 74.922	34 <b>Se</b> 78.96	35 <b>Br</b> 79.904	36 <b>Kr</b> 83.80				
37 <b>Rb</b> 85.468	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.906	40 <b>Zr</b> 91.224	41 <b>Nb</b> 92.906	42 <b>Mo</b> 95.94	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.07	45 <b>Rh</b> 102.91	46 <b>Pd</b> 106.42	47 <b>Ag</b> 107.87	48 <b>Cd</b> 112.41	49 <b>In</b> 114.82	50 <b>Sn</b> 118.71	51 <b>Sb</b> 121.76	52 <b>Te</b> 127.60	53 <b>I</b> 126.90	54 <b>Xe</b> 131.29				
55 <b>Cs</b> 132.91	56 <b>Ba</b> 137.33	71 <b>Lu</b> 174.97	72 <b>Hf</b> 178.49	73 <b>Ta</b> 180.95	74 <b>W</b> 183.84	75 <b>Re</b> 186.21	76 <b>Os</b> 190.23	77 <b>Ir</b> 192.22	78 <b>Pt</b> 195.08	79 <b>Au</b> 196.97	80 <b>Hg</b> 200.59	81 <b>Tl</b> 204.38	82 <b>Pb</b> 207.2	83 <b>Bi</b> 208.98	84 <b>Po</b> (209)	85 <b>At</b> (210)	86 <b>Rn</b> (222)				
87 <b>Fr</b> (223)	88 <b>Ra</b> 226.03	103 <b>Lr</b> (260)	104 <b>Rf</b> (261)	105 <b>Db</b> (262)	106 <b>Sg</b> (263)	107 <b>Bh</b> (262)	108 <b>Hs</b> (265)	109 <b>Mt</b> (266)	110 <b>(269)</b>	111 <b>(272)</b>	112 <b>(277)</b>			114			116				

57 <b>La</b> 138.91	58 <b>Ce</b> 140.12	59 <b>Pr</b> 140.91	60 <b>Nd</b> 144.24	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.36	63 <b>Eu</b> 151.97	64 <b>Gd</b> 157.25	65 <b>Tb</b> 158.93	66 <b>Dy</b> 162.50	67 <b>Ho</b> 164.93	68 <b>Er</b> 167.26	69 <b>Tm</b> 168.94	70 <b>Yb</b> 173.04
89 <b>Ac</b> 227.03	90 <b>Th</b> 232.04	91 <b>Pa</b> 231.04	92 <b>U</b> 238.03	93 <b>Np</b> 237.05	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (258)	101 <b>Md</b> (258)	102 <b>No</b> (259)

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?
$1.39 \times 10^{-9}$	$7.19 \times 10^{-6}$	8.857	5.143	Basic
$2.41 \times 10^{-3}$	$4.15 \times 10^{-12}$	2.618	11.382	Acidic

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

Conjugate Acid	$K_a$ @25°C	Conjugate Base	$K_b$ @25°C
$\text{HNO}_2$	$4.011 \times 10^{-4}$	$\text{NO}_2^-$	$2.493 \times 10^{-11}$
$\text{H}_2\text{PO}_4^-$	$1.586 \times 10^{-7}$	$\text{HPO}_4^{2-}$	$6.305 \times 10^{-8}$

3. A labmate has prepared a lactate/lactic acid buffer solution
- $\{\text{C}_3\text{H}_5\text{O}_3^- (\text{aq}) / \text{HC}_3\text{H}_5\text{O}_3 (\text{aq})\}$
- at pH=4.05, but does not write much information down in a lab notebook. You know that the concentration of the buffer is 0.995M and
- $\text{p}K_b=10.140$
- for
- $\text{C}_3\text{H}_5\text{O}_3^- (\text{aq})$
- . 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 lactate/lactic acid make an effective buffer? Explain your answers. (10pts)

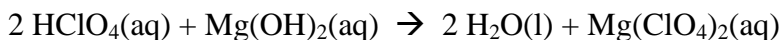
$$\text{p}K_a \text{ for lactic acid must be: } 14 - 10.140 = 3.860$$

The pH of the prepared buffer is higher (more basic) than the  $\text{p}K_a$  of the conjugate acid of the buffer system, so there must be more of the conjugate base in the buffer.

{If [conjugate acid] = [conjugate base], the pH of the buffer is equal to the  $\text{p}K_a$  of the conjugate acid.}

A given system will be an effective buffer within 1 pH unit of the  $\text{p}K_a$  of the weak acid component of the buffer, so this system would be an effective buffer over the range 2.860 to 4.860

4. How many milliliters of 0.439M
- $\text{HClO}_4 (\text{aq})$
- must be added to 25.00mL of 0.396M
- $\text{Mg}(\text{OH})_2 (\text{aq})$
- to reach the equivalence point? What is the pH of this solution at the equivalence point? Explain any assumptions. (10pts)



This is a strong acid/strong base titration.

$$(0.02500 \text{L Mg}(\text{OH})_2 (\text{aq})) \left( \frac{0.396 \text{mol Mg}(\text{OH})_2}{1 \text{L Mg}(\text{OH})_2 (\text{aq})} \right) \left( \frac{2 \text{mol HClO}_4}{1 \text{mol Mg}(\text{OH})_2} \right) \left( \frac{1 \text{L HClO}_4 (\text{aq})}{0.439 \text{mol HClO}_4} \right) \left( \frac{1000 \text{mL}}{1 \text{L}} \right) = 45.10 \text{mL HClO}_4 (\text{aq})$$

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

5. What is the expected pH of a 0.834M aqueous solution of hypochlorous acid?  $\{K_a(\text{HClO}) = 3.462 \times 10^{-8}\}$  (10pts)

	$\text{HClO}(\text{aq}) +$	$\text{H}_2\text{O}(\text{l}) \rightleftharpoons$	$\text{H}_3\text{O}^+(\text{aq}) +$	$\text{ClO}^-(\text{aq})$
[ ] <sub>initial</sub>	0.834M	XXXXX	0 M	0 M
$\Delta[ ]$	- x M	XXXXX	+ x M	+ x M
[ ] <sub>equilibrium</sub>	(0.834 - x) M	XXXXX	x M	x M

$$K_a = (x)(x) / (0.834 - x) \approx (x)(x) / (0.834) = 3.462 \times 10^{-8} \quad (\text{assume } x \ll 0.834)$$

$$x = 1.699 \times 10^{-4} = [\text{H}_3\text{O}^+] \quad (\text{assumption is OK})$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.699 \times 10^{-4}) = 3.770$$

6. What is the expected pH of a 0.337M aqueous solution of potassium cyanide?  $\{K_b(\text{CN}^-) = 3.0 \times 10^{-5}\}$  (10pts)

	$\text{CN}^-(\text{aq}) +$	$\text{H}_2\text{O}(\text{l}) \rightleftharpoons$	$\text{OH}^-(\text{aq}) +$	$\text{HCN}(\text{aq})$
[ ] <sub>initial</sub>	0.337M	XXXXX	0 M	0 M
$\Delta[ ]$	- x M	XXXXX	+ x M	+ x M
[ ] <sub>equilibrium</sub>	(0.337 - x) M	XXXXX	x M	x M

$$K_b = (x)(x) / (0.337 - x) \approx (x)(x) / (0.337) = 3.0 \times 10^{-5} \quad (\text{assume } x \ll 0.337)$$

$$x = 3.1796 \times 10^{-3} = [\text{OH}^-] \quad (\text{assumption is OK})$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(3.1796 \times 10^{-3}) = 2.4976$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.4976 = 11.502$$

7. You have prepared a buffer solution by combining 0.537mols of benzoic acid ( $\text{HC}_7\text{H}_5\text{O}_2$ ,  $K_a = 6.4 \times 10^{-5}$ ) and 0.394mols of sodium benzoate in enough water to make 600.0mL of solution. What is the pH of this buffer solution? (10pts)

Plugging in to the Henderson-Hasselbalch equation...

$$\text{pH} = (-\log(6.4 \times 10^{-5})) + \log\left(\frac{0.394}{0.537}\right) = 4.059$$

8. What is the  $K_b$  of a weak base if 500.0mL of a solution containing 0.218mol of the base and 0.243mol of its conjugate acid has a pH of 6.837? Over what pH range would this conjugate acid/ conjugate base pair make an effective buffer? (12pts)

Plugging in to the Henderson-Hasselbalch equation...

$$6.837 = \text{p}K_a + \log\left(\frac{0.218}{0.243}\right)$$

$$\text{p}K_a = 6.884$$

$$\text{p}K_b = 14 - 6.884 = 7.116$$

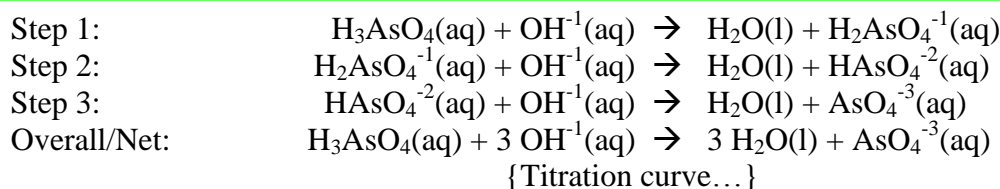
$$K_b = 10^{-7.116} = 7.659 \times 10^{-8}$$

Effective buffers are within 1 pH unit of the  $\text{p}K_a$  of the weak conjugate acid component of the buffer, so this system would be an effective buffer from 5.884 to 7.884.

9. You have titrated 25.00mL of 0.413M sulfurous acid solution with an unknown sodium hydroxide solution. You reach the second equivalence point when 39.62mL of base is added. What is the concentration of the original stock sodium hydroxide solution?  $\{K_{a1}(\text{H}_2\text{SO}_3) = 1.54 \times 10^{-2}, K_{a2} = 1.02 \times 10^{-7}\}$  (12pts)

$$(0.02500\text{LH}_2\text{SO}_4(\text{aq})) \left( \frac{0.413\text{molH}_2\text{SO}_4}{1\text{LH}_2\text{SO}_4(\text{aq})} \right) \left( \frac{2\text{molNaOH}}{1\text{molH}_2\text{SO}_4} \right) \left( \frac{1}{0.03962\text{LNaOH}(\text{aq})} \right) = 0.521\text{MNaOH}(\text{aq})$$

10. You have titrated 20.00mL of an unknown arsenic acid  $\{\text{H}_3\text{AsO}_4(\text{aq}), \text{pK}_{a1}=2.30, \text{pK}_{a2}=7.10, \text{pK}_{a3}=11.53\}$  solution to the second equivalence point with 41.63mL of 0.387M potassium hydroxide. Write out balanced chemical equations for the step-wise deprotonation of arsenic acid. Sketch the titration curve and label all equivalence points and all arsenic acid-based species in solution in all portions of the curve. What is the concentration of the unknown arsenic acid solution? How many milliliters were required to reach the *first* equivalence point in this titration? (18pts)



$$(0.04163\text{LKOH}(\text{aq})) \left( \frac{0.387\text{molKOH}}{1\text{LKOH}(\text{aq})} \right) \left( \frac{1\text{molH}_3\text{AsO}_4}{2\text{molKOH}} \right) \left( \frac{1}{0.02000\text{LH}_3\text{AsO}_4(\text{aq})} \right) = 0.4028\text{MH}_3\text{AsO}_4(\text{aq})$$

Each step in the rxn requires the same number of moles of base, so to get to the first equivalence point we'd need half the volume that was required to reach the second equivalence point, 20.815mL

11. You need to determine the exact concentration of a freshly prepared solution of propanoic acid ( $\text{C}_2\text{H}_5\text{COOH}(\text{aq}), K_a = 1.34 \times 10^{-5}$ ) that is approximately 0.5M, but your pH probe is not working. You have found the following visual pH indicators in your lab: Methyl Red (MR, endpoint = 4.4-6.2), Phenol Red (PR, endpoint = 6.4-7.7), Cresol Red (CR, endpoint = 7.2-8.8). If you are titrating with a 0.429M NaOH(aq) solution, which indicator(s) would you choose for this titration? Explain your answer. (10pts)

Propanoic acid is a weak acid (based upon the given  $K_a$  value) and NaOH is a strong base, so the equivalence point for this titration should be on the basic side of neutral. Of the 3 indicators, Cresol Red is the only one with a clearly basic endpoint, so of the options available it would probably be the best indicator for this titration.