

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 = 1.000g/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: $k_{\text{fp}} = -1.86^\circ\text{C}/m$

$k_{\text{bp}} = 0.512^\circ\text{C}/m$

$P_1 = X_1 P_1^\circ$

$\Pi = MRTi$

$C_1 V_1 = C_2 V_2$

Quadratic formula:

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

Integrated Rate Laws:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

If you use $C_1 V_1 = C_2 V_2$ to calculate a titration, you will receive zero points for that problem.

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	71 Lu 174.97	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	103 Lr (260)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (269)	111 Rg (272)	112 Cn (277)	113	114 Fl	115	116 Lv	117	118				

57 La 138.91	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
89 Ac 227.03	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)

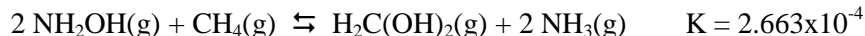
1. Complete each **row** of the following tables for aqueous solutions at 25°C (5pts per box):

$[\text{H}_3\text{O}^+]$	$[\text{OH}^-]$	pH	pOH	Acidic, Basic or Neutral?
4.61×10^{-12}	2.17×10^{-3}	11.336	2.664	Basic
6.348×10^{-11}	1.575×10^{-4}	10.1974	3.8026	Basic

Conjugate Acid	K_a @ 25°C	Conjugate Base	K_b @ 25°C
H_2SeO_3	3.51×10^{-3}	HSeO_3^-	2.85×10^{-12}
HBrO	2.1×10^{-9}	BrO^-	4.8×10^{-6}

Problems: Show your work.

2. You are studying the reaction:



At some point the following concentrations are observed:

$$[\text{NH}_2\text{OH}] = 0.228\text{M}, [\text{CH}_4] = 0.304\text{M}, [\text{H}_2\text{C}(\text{OH})_2] = 3.18 \times 10^{-2}\text{M}, [\text{NH}_3] = 0.184\text{M}$$

Is the reaction at equilibrium at this point? If not, does the reaction have to shift to the left toward reactants to reach equilibrium or does it have to shift to the right toward products to reach equilibrium? (10pts)

Plugging the given values into the reaction quotient expression:

$$Q = \frac{[\text{H}_2\text{C}(\text{OH})_2]_t [\text{NH}_3]_t^2}{[\text{NH}_2\text{OH}]_t^2 [\text{CH}_4]_t} = \frac{(3.18 \times 10^{-2})(0.184)^2}{(0.228)^2 (0.304)} = 6.81 \times 10^{-2}$$

Since Q is **not** equal to K, the system is **not** at equilibrium at this point. The value of Q is larger than K, so the reaction is too product-rich at this point, it has to shift to the left toward reactants to reach equilibrium.

3. What is the expected pH of a 0.372M aqueous solution of sodium nitrite? $\{K_b(\text{NO}_2^-) = 1.41 \times 10^{-11}\}$ (10pts)

Write a K_b -type equation and organize with a table:

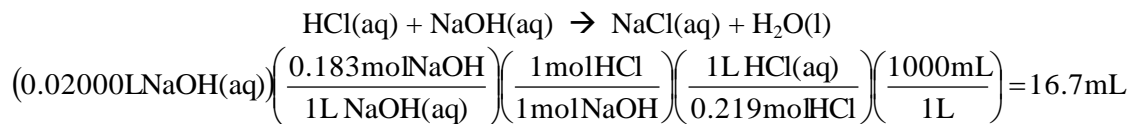
	$\text{NO}_2^-(\text{aq}) +$	$\text{H}_2\text{O}(\text{l}) \rightleftharpoons$	$\text{OH}^-(\text{aq}) +$	$\text{HNO}_2(\text{aq})$
$[\]_{\text{initial}}$	0.372 M		10^{-7} M	0 M
$\Delta[\]$	- x M		+ x M	+ x M
$[\]_{\text{equilibrium}}$	$(0.372 - x)$ M		$(10^{-7} + x)$ M	x M

$$K_b = \frac{[\text{OH}^-]_{\text{eq}} [\text{HNO}_2]_{\text{eq}}}{[\text{NO}_2^-]_{\text{eq}}} = \frac{(10^{-7} + x)(x)}{(0.372 - x)} \approx \frac{(x)(x)}{(0.372)} = 1.41 \times 10^{-11}$$

$$x = 2.290 \times 10^{-6} \rightarrow [\text{OH}^-]_{\text{eq}} = 2.290 \times 10^{-6} \text{ M} \rightarrow [\text{H}_3\text{O}^+]_{\text{eq}} = 4.3668 \times 10^{-9} \text{ M} \rightarrow \text{pH} = -\log(4.3668 \times 10^{-9}) = 8.360$$

If you checked your assumptions on this one, you'll find that 10^{-7} is *almost* 5% of the value of "x", so the assumption we made to simplify this problem is OK, but it's getting a little suspicious.

4. How much 0.219M HCl(aq) must be added to 20.00mL of 0.183M NaOH(aq) to reach the equivalence point? What is the expected pH of this solution at the equivalence point? Explain. (10pts)



This is the titration of a strong monoprotic acid with a strong monoprotic (or monobasic) base, so the equivalence point should be at pH = 7.

5. You have prepared a buffer solution by combining 0.391mols of benzoic acid ($\text{C}_6\text{H}_5\text{CO}_2\text{H}$, $K_a = 6.28 \times 10^{-4}$) and 0.228mols of potassium benzoate ($\text{C}_6\text{H}_5\text{CO}_2\text{K}$) in enough water to make 750.0mL of solution. What is the expected pH of this buffer solution? (10pts)

Use a K_a expression directly, or use the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{C}_6\text{H}_5\text{CO}_2^-]}{[\text{C}_6\text{H}_5\text{CO}_2\text{H}]} \right) = 3.202 + \log \left(\frac{\left(\frac{0.228\text{mol C}_6\text{H}_5\text{CO}_2^-}{0.7500\text{L}} \right)}{\left(\frac{0.391\text{mol C}_6\text{H}_5\text{CO}_2\text{H}}{0.7500\text{L}} \right)} \right) = 2.968$$

6. What is the K_a of a weak acid if 500.0mL of a solution containing 0.149mol of its conjugate base and 0.128mol of the acid has a pH of 4.992? Over what pH range would this conjugate acid/ conjugate base pair make an effective buffer? (10pts)

Use a K_a expression directly, or use the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)$$

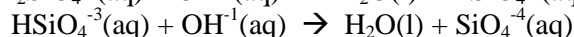
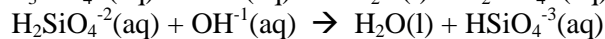
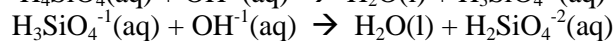
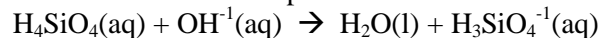
$$4.992 = \text{p}K_a + \log \left(\frac{\left(\frac{0.149\text{mol A}^-}{0.5000\text{L}} \right)}{\left(\frac{0.128\text{mol HA}}{0.5000\text{L}} \right)} \right)$$

$$\text{p}K_a = 4.926 \rightarrow K_a = 10^{-4.926} = 1.19 \times 10^{-5}$$

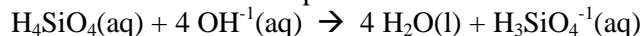
This system will be an effective buffer within 1 pH unit of the $\text{p}K_a$, so 3.926-5.926

7. You would like to titrate an unknown solution of silicic acid (H_4SiO_4 , $\text{pK}_{\text{a}1} = 4.92$, $\text{pK}_{\text{a}2} = 7.02$, $\text{pK}_{\text{a}3} = 9.84$, $\text{pK}_{\text{a}4} = 13.28$) with a 0.264M NaOH(aq) .
- a. Write out the chemical equations for the step-wise deprotonation/neutralization of silicic acid and the overall/net chemical reaction. (8pts)

Stepwise:

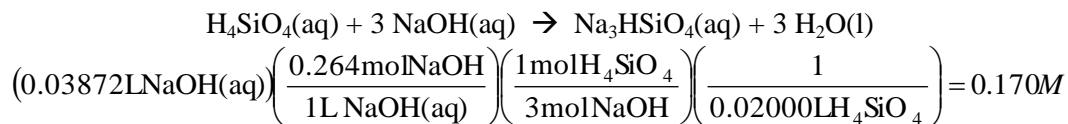


Net process:



- b. Sketch the titration curve you would expect for this titration, labeling all equivalence points and silicic acid-based species present in each portion of the curve. Wherever reasonable, include pH values. (10pts)

- c. You titrate 20.00mL of the unknown silicic acid solution to the third equivalence point with 38.72mL of 0.264M NaOH(aq) . What is the concentration of the unknown silicic acid solution? (10pts)



8. You will be performing a series of titration described below and have the following acid-base visual indicators available:

Indicator Name:	Endpoint pH Range:
Cresol Red	1.0-2.0
Congo Red	3.1-4.9
Phenol Red	6.4-8.0
Thymol Blue	8-9.6
Orange G	11.5-14.0

For each titration, choose an appropriate acid-base visual indicator and explain (briefly) your choice. You may use any of the indicators more than once, and some indicators might not be used at all. (12pts)

Titration:	Indicator Choice:	Explain:
A titration with a known equivalence point at pH = 4.	Congo Red	pH=4 falls within the endpoint range Congo Red
A 0.925M NaOH(aq) solution being titrated with 1.031M HCl(aq)	Phenol Red	This is strong monoprotic acid/strong monoprotic (or monobasic) base titration so the equivalence point should at or very near pH=7.
A weak monoprotic acid ($K_a = 7 \times 10^{-6}$) being titrated with 0.293M NaOH(aq)	Thymol Blue	This is a weak acid/strong base titration so the equivalence point should be basic. {phenol red might also work for this one, but thymol blue is probably the better choice.}
A diprotic acid ($K_{a1} = 4 \times 10^{-3}$, $K_{a2} = 2 \times 10^{-7}$) being titrated with NaOH(aq).	Congo Red	The 2 given pK_as are 2.4 and 6.7, the equivalence point should be pretty close to right between them at pH = 4.5, Congo Red again. The <i>second</i> equivalence point is probably around pH = 8, so Thymol Blue might be a good indicator for the 2nd equivalence point, but since we have more information about the 1st equivalence point, that's probably more reliable.