Chem 210 – Exam 3 Summer 2010 **Chemistry 210**

Name:

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 = $6.022 \times 10^{23} \text{ units}/_{mol}$ $32.00^{\circ}\text{F} = 0.000^{\circ}\text{C} = 273.15\text{K}$ Density of Water = $1.000^{\text{g}}/_{\text{mL}}$ $R = 0.08206^{\text{L*atm}}/_{\text{mol*K}} = 8.314^{\text{J}}/_{\text{mol*K}}$ PV=nRT $\Delta T_{\text{fp/bp}} = k_{\text{fp/bp}} \cdot \text{m} \cdot \text{i}$ For water, $k_{\text{fp}} = -1.86^{\circ}\text{C}/_{\text{m}}$; $k_{\text{bp}} = 0.52^{\circ}\text{C}/_{\text{m}}$ $P_1 = X_1P_1^{\circ}$ P = cRTi $C_1V_1 = C_2V_2$ Quadratic formula: $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Integrated Rate Laws: $\begin{array}{ll}
0^{th} \text{ order } & [A]_t = -kt + [A]_o \\
1^{st} \text{ order } & \ln[A]_t = -kt + \ln[A]_o \\
2^{nd} \text{ order } & 1/[A]_t = kt + 1/[A]_o \\
k = Ae^{-Ea/RT} \\
\ln(k) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A) \\
\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\
pH = pK_a + \log\left(\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}\right)$

$$\begin{split} E_{cell} &= E_{cell}^{\circ} - {}^{RT}/{}_{nF} lnQ \\ E_{cell}^{\circ} &= {}^{RT}/{}_{nF} lnK^{\circ} \\ K^{\circ} &= e^{\wedge}({}^{nF}/{}_{RT} E_{cell}^{\circ}) \\ F &= 96485 {}^{J}/{}_{V \cdot mol of electrons} \\ \Delta G^{\circ} &= \Delta H^{\circ}{}_{system} - T\Delta S^{\circ}{}_{system} \\ \Delta G^{\circ} &= -nFE_{cell}^{\circ} &= -RT lnK^{\circ} \\ \Delta G &= \Delta G^{\circ} + RT lnQ \\ F &= 96485 {}^{C}/{}_{mol electrons} \\ 1A &= 1 C / sec \end{split}$$

	_																
1																	2
Η																	He
1.0079																	4.0026
3	4											5	6	7	8	9	10
Li	Be											В	С	Ν	0	F	Ne
6.941	9.0122											10.811	12.011	14.007	15.999	18.998	20.180
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	Р	S	Cl	Ar
22.990	24.305											26.982	28.086	30.974	32.066	35.453	39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Κ	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.098	40.078	44.956	47.88	50.942	51.996	54.938	55.847	58.933	58.69	63.546	65.39	69.723	72.61	74.922	78.96	79.904	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Ι	Xe
85.468	87.62	88.906	91.224	92.906	95.94	(98)	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60	126.90	131.29
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
132.91	137.33	138.91	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)
87	88	89	104	105	106	107	108	109	110	111	112		114		116		
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt									
(223)	226.03	227.03	(261)	(262)	(263)	(262)	(265)	(266)	(269)	(272)	(277)						

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

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

$[H_3O^+]$	[OH [.]]	рН	рОН	Acidic, Basic or Neutral?
5.37x10 ⁻⁶	1.86x10⁻⁹	5.270	8.730	Acidic
1.52x10 ⁻¹⁰	6.56x10 ⁻⁵	9.817	4.183	Basic

Conjugate Acid	K _a @25°C	Conjugate Base	К _b @25°С
$H_2PO_3^-$	1.95 x10 ⁻⁷	HPO ₃ ²⁻	5.13x10 ⁻⁸
HTe	1.58×10^{-11}	Te ²⁻	6.33x10 ⁻⁴

2. Explain why each of the following *does not* result in an effective buffer? (15pts) 0.38mol HClO₄(aq) + 0.38mol NaClO₄(aq)

This is a combination of a strong acid with its conjugate base. Strong acid/conjugate base and strong base/conjugate acid mixtures do not make effective pH buffers.

 $1.28mol\ K_2HPO_3(aq) + 1.28mol\ HClO_4(aq)$

The result of mixing these will be a solution of $H_2PO_3^{-}(aq)$, not an effective buffer on its own. This *could* be an effective buffer if only 0.64mols of perchloric acid were used; the result in that case would be 0.64mols HPO_3^{-2} (aq) and 0.64mols $H_2PO_3^{-}(aq)$, an equimolar mixture of a weak conjugate base and its weak conjugate acid.

 $1.24mol\ Na_2SO_3(aq) + 0.03mol\ NaHSO_3(aq)$

The ratio of conjugate acid to conjugate base is not between 0.1 and 10, so this would not make an effective buffer. If more HSO_3^- were used, this would make an effective buffer.

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3. How much 1.183M KOH(aq) must be added to 25.00mL of 1.262M HCl(aq) to reach the equivalence point? (14pts)

$$\frac{\text{KOH}(\text{aq}) + \text{HCl}(\text{aq})}{(12.262 \text{mols HCl})} \approx \frac{12}{1000 \text{mL}} \frac{11}{1000 \text{mL}} \frac{11}{1000 \text{mL}} \frac{11}{1000 \text{mL}} \frac{11}{1.183 \text{mol KOH}} \frac{11}{1.183 \text{mol KOH}} \frac{1000 \text{mL}}{11} = 26.67 \text{mL KOH}(\text{aq})$$

This could also have been reported as 0.02667L KOH(aq)

4. You have dissolved 11.338g of sodium fluoride in enough water to make 300.0mL of solution. What is the expected pH of this solution? { $K_b(F) = 1.52 \times 10^{-11}$ } (15pts)

	F(aq) +	$H_2O(l) \Leftrightarrow$	OH (aq) +	HF(aq)					
Initial $\left(\frac{11.338g}{41.988\frac{g}{mol}}\right) = 0.900M$ 10^{-7} 0 0.3000L									
Δ	-X		+x	+x					
@Equilibrium $(0.900-x)M$ $(10^{-7}+x)M$ x M									
Plugging in and solving $K_{b} = \frac{\left[OH^{-}\right]_{eq}\left[HF\right]_{eq}}{\left[F^{-}\right]_{eq}} = \frac{\left(10^{-7} + x\right)(x)}{(0.900 - x)} \approx \frac{(x)(x)}{(0.900)} \approx 1.52x10^{-11}$ $x = 3.70x10^{-6} = [OH^{-}]_{eq}$ NOTE: 10 ⁻⁷ is less than 3% of 3.70x10 ⁻⁶ , so our assumption is OK									
 $pOH = -log(3.70x10^{-6}) = 5.432$ pH = 14 - pOH = 14 - 5.432 = 8.568									

5. What is the expected pH of a buffer prepared by dissolving 13.537g of selenous acid and 14.661g of sodium hydrogen selenite in enough water to make 150.00mL of solution? $\{K_a(H_2SeO_3) = 2.43x10^{-8}\}$ (18pts)

$$pK_{a}(H_{2}SeO_{3}) = -\log(K_{a}(H_{2}SeO_{3})) = -\log(2.43x10^{-8}) = 7.614$$

$$pH = pK_{a} + \log\frac{\left[HSeO_{3}^{-}\right]}{\left[H_{2}SeO_{3}\right]} = 7.614 + \log\frac{\left(\frac{\left(\frac{14.661g \text{ NaHSeO}_{3}}{150.955\frac{\text{g}}{\text{mol}}}\right)}{0.15000L}\right)}{\left(\frac{\left(\frac{13.537g \text{ H}_{2}SeO_{3}}{128.973\frac{\text{g}}{\text{mol}}}\right)}{0.15000L}\right)} = 7.580$$

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6. What is the K_a of an acid if 250.0mL of a solution containing 0.318 mol of the acid and 0.393 mol of its conjugate base has a pH of 9.357? Over what pH range would this conjugate acid/ conjugate base pair make an effective buffer? (20pts)

$$pK_{a}(H_{2}SeO_{3}) = -log(K_{a}(H_{2}SeO_{3})) = -log(2.43x10^{-8}) = 7.614$$

$$pH = pK_{a} + log \frac{\left[A^{-}\right]}{\left[HA\right]}$$
9.357 = pK_{a} + log $\frac{\left(\frac{0.393mols A}{0.25000L}\right)}{\left(\frac{0.318mols HA}{0.25000L}\right)}$

$$pK_{a} = 9.265$$

$$K_{a} = 10^{-9.265} = 5.43x10^{-10}$$
conjugate base pair will make an effective buffer over the pH range (pK_{a}-1) to (pK_{a}+1), so

This conjugate acid/conjugate base pair will make an effective buffer over the pH range (pK_a -1) to (pK_a +1), so 8.265 to 10.265

7. You have titrated 25.00mL of 0.773M sulfurous 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? What is the expected pH of the sulfurous acid solution before the titration begins? $\{K_{a1}(H_2SO_3) = 1.68 \times 10^{-2}, K_{a2}(H_2SO_3) = 6.42 \times 10^{-8}\}$ (20pts)

$$\begin{aligned} &H_2 SO_3(aq) + 2 NaOH(aq) \rightarrow 2 H_2 O(l) + Na_2 SO_3(aq) \\ &\left(\frac{0.773 \text{mols } H_2 SO_3}{1L H_2 SO_3(aq)}\right) &\left(0.02500L H_2 SO_3(aq)\right) \\ &\left(\frac{2 \text{mol } NaOH}{1 \text{mol } H_2 SO_3}\right) &\left(\frac{1}{0.04417L NaOH(aq)}\right) = 0.875M NaOH(aq) \end{aligned}$$

	$H_2SO_3(aq) +$	$H_2O(l) \Leftrightarrow$	$H_3O^+(aq) +$	HSO ₃ (aq)
Initial	0.773		10-7	0
Δ	-X		+x	+x
@Equilibrium	(0.773-x)M		$(10^{-7}+x)M$	x M

Plugging in and solving...

$$K_{a} = \frac{\left[H_{3}O^{+}\right]_{eq}\left[HSO_{3}^{-}\right]_{eq}}{\left[H_{2}SO_{3}\right]_{eq}} = \frac{\left(10^{-7} + x\right)(x)}{(0.773 - x)} \approx \frac{(x)(x)}{(0.773)} \approx 1.68 \times 10^{-2}$$

x = 0.114 This is NOT small compared to 0.773 (almost 15%), so we cannot make that assumption. 0.114 is much larger than 10^{-7} , so that assumption is OK. Re-solving to a quadratic...

$$K_{a} = \frac{[H_{3}O^{+}]_{eq}[HSO_{3}^{-}]_{eq}}{[H_{2}SO_{3}]_{eq}} = \frac{(10^{-7} + x)(x)}{(0.773 - x)} \approx \frac{(x)(x)}{(0.773 - x)} \approx 1.68 \times 10^{-2}$$

$$x^{2} + (1.68 \times 10^{-2})x + (-0.0129864) = 0$$
Plugging in to the quadratic formula, $x = 0.106 = [H_{3}O^{+}]$

$$pH = -\log(0.106) = 0.975$$

NOTE: 0.106 isn't too far away from 0.114, so the assumption would probably be fine for an approximate pH, but it's far enough off to alter the results just a little bit.