

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?
2.77×10^{-6}	3.61×10^{-9}	5.558	8.442	Acidic
2.56×10^{-9}	3.899×10^{-6}	8.591	5.409	Basic

Conjugate Acid	K_a @ 25°C	Conjugate Base	K_b @ 25°C
HCN	3.3×10^{-10}	CN^-	3.0×10^{-5}
H_2PO_3^-	2.9×10^{-7}	HPO_3^{2-}	3.45×10^{-8}

2. A labmate has prepared a sulfite/hydrogen sulfite buffer solution at pH=7.09, but does not write much information down in a lab notebook. You know that the concentration of the buffer is 0.63M and $\text{p}K_b=6.80$ for $\text{SO}_3^{2-}(\text{aq})$. 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 sulfite/hydrogen sulfite make an effective buffer? Explain your answers. (8pts)

If $\text{p}K_b$ for sulfite is 6.80, $\text{p}K_a$ for HSO_3^- must be $14 - 6.80 = 7.20$

Since the pH of the buffer is lower than the $\text{p}K_a$ of the conjugate acid, the concentration of conjugate acid must be higher than the concentration of the conjugate base.

This system would be an effective buffer within 1 pH unit of the $\text{p}K_a$ of the conjugate acid, 6.20-8.20

3. What is the expected pH of a 0.464M aqueous solution of potassium nitrite? $\{K_b(\text{NO}_2^-)=2.2 \times 10^{-11}\}$ (10pts)

Since we know K_b , let's set this up as a K_b equilibrium problem.

	$\text{NO}_2^-(\text{aq}) +$	$\text{H}_2\text{O}(\text{l}) \rightleftharpoons$	$\text{OH}^-(\text{aq}) +$	$\text{HNO}_2(\text{aq})$
[] _{initial}	0.464M	XXXX	10^{-7} M	0 M
Δ []	-x	XXXX	+x	+x
[] _{equilibrium}	$(0.464 - x)$ M	XXXX	$(10^{-7} + x)$ M	x M

$$K_b = [\text{OH}^-]_{\text{eq}}[\text{HNO}_2]_{\text{eq}} / [\text{NO}_2^-]_{\text{eq}} = (10^{-7} + x)(x) / (0.464 - x) = 2.2 \times 10^{-11}$$

Assuming "x" is much larger than 10^{-7} and much smaller than 0.464, the K_b expression simplifies to:

$$K_b = (x)(x) / 0.464 = 2.2 \times 10^{-11} \rightarrow x = 3.195 \times 10^{-6} \text{ \{assumptions OK\}}$$

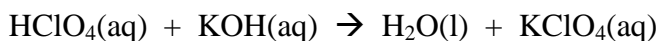
$$\text{pOH} = 5.496 \rightarrow \text{pH} = 14 - 5.496 = 8.504$$

4. You have prepared a buffer solution by combining 0.472mols of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$, $K_a = 1.8 \times 10^{-5}$) and 0.394mols of sodium acetate in enough water to make 400.0mL of solution. What is the pH of this buffer solution? (10pts)

Plugging in to the Henderson-Hasselbalch equation...

$$\text{pH} = \text{p}K_a + \log \left\{ \frac{[\text{conjugate base}]}{[\text{conjugate acid}]} \right\} = 4.745 + \log(0.394 / 0.472) = 4.667$$

5. How much 0.237M $\text{HClO}_4(\text{aq})$ must be added to 25.00mL of 0.144M $\text{KOH}(\text{aq})$ to reach the equivalence point? What is the pH of this solution at the equivalence point? Explain. (10pts)



$$(0.02500\text{L KOH}(\text{aq}))(0.144\text{mols KOH/L KOH}(\text{aq}))(1\text{mol HClO}_4/1\text{mol KOH})(1\text{L HClO}_4(\text{aq}) / 0.237\text{mol HClO}_4) = 0.0152\text{L HClO}_4(\text{aq}) = 15.2\text{mL HClO}_4(\text{aq})$$

Because this is the titration of a strong monoprotic acid with a strong monobasic base, the equivalence point should be at $\text{pH} = 7.0$

6. What is the K_b of a weak base if 500.0mL of a solution containing 0.181mol of the base and 0.216mol of its conjugate acid has a pH of 6.815? Over what pH range would this conjugate acid/ conjugate base pair make an effective buffer? (10pts)

Plugging in to the Henderson-Hasselbalch equation...

$$\text{pH} = \text{p}K_a + \log \left\{ \frac{[\text{conjugate base}]}{[\text{conjugate acid}]} \right\}$$

$$6.815 = \text{p}K_a + \log(0.181/0.216)$$

$$\text{p}K_a = 6.892$$

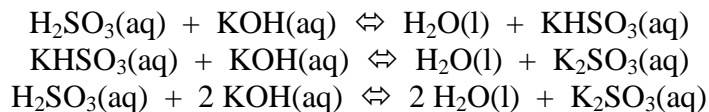
$$\text{p}K_b \text{ of the conjugate base is } 14 - \text{p}K_a = 14 - 6.892 = 7.108$$

$$K_b = 10^{-\text{p}K_b} = 10^{-7.108} = 7.79 \times 10^{-8}$$

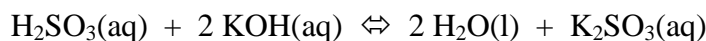
Effective buffer within 1 pH unit of the $\text{p}K_a$ of the conjugate acid, 5.892-7.892

For questions 7-12: You are going to use a titration to determine the concentration of an unknown sulfurous acid solution (H_2SO_3 , $\text{pK}_a = 1.77$). The base you have chosen to use is 0.715M potassium hydroxide.

7. Write out the chemical equations for the step-wise deprotonation/neutralization of sulfurous and the overall/net chemical reaction. (8pts)



8. You titrate 20.00mL of the unknown sulfurous acid solution to the second equivalence point with 32.62mL of potassium hydroxide solution. What is the concentration of the unknown sulfurous acid solution? (10pts)



$$(0.03262\text{L KOH}(\text{aq}))(0.715\text{mols KOH/L KOH}(\text{aq}))(1\text{mol H}_2\text{SO}_3/2\text{mol KOH})(1 / 0.02000\text{L H}_2\text{SO}_3) = 0.583\text{M H}_2\text{SO}_3(\text{aq})$$

9. What is the pH of the sulfurous acid solution before the titration begins? (10pts)

Let's set this up as a K_a equilibrium problem.

	$\text{H}_2\text{SO}_3(\text{aq}) +$	$\text{H}_2\text{O}(\text{l}) \rightleftharpoons$	$\text{H}_3\text{O}^+(\text{aq}) +$	$\text{HSO}_3^{-1}(\text{aq})$
[] _{initial}	0.583M	XXXX	10^{-7} M	0 M
Δ []	-x	XXXX	+x	+x
[] _{equilibrium}	$(0.583 - x)\text{M}$	XXXX	$(10^{-7} + x)\text{M}$	x M

Assuming "x" is much smaller than 0.583 and much larger than 10^{-7} :

$$\text{K}_a = (x)(x) / 0.583 = 0.01698 \rightarrow x = 0.0903 \rightarrow \text{not "much smaller" than } 0.583!!$$

$$\text{K}_a = (x)(x) / (0.583 - x) = 0.01698 \rightarrow \text{solving with quadratic formula} \rightarrow x = 0.1083 = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.1083) = 0.965$$

10. What is the expected pH when the titration in #8 reaches the *first* equivalence point? (10pts)

This could be explicitly calculated, or explained qualitatively. Since the sulfurous acid solution starts out quite acidic (see #9), and it's a di-protic acid, it's probably safe to assume that the first equivalence point will be a bit on the acidic side. If we want to think about it in terms of the buffers that will form during the titration, we can nail down the number a little better... The first 1:1 buffer $\{\text{H}_2\text{SO}_3(\text{aq}):\text{HSO}_3^{-1}(\text{aq})\}$ should have a pH of 1.77 $\{\text{pH}=\text{pK}_a \text{ of the acid for a 1:1 buffer}\}$. Looking back at question #2, the pK_b for $\text{SO}_3^{-2}(\text{aq})$ is given $\{6.80\}$, so the pK_a for $\text{HSO}_3^{-1}(\text{aq})$ must be $14-6.80=7.20$. This means the *second* 1:1 buffer $\{\text{HSO}_3^{-1}(\text{aq}):\text{SO}_3^{-2}(\text{aq})\}$ should have a pH of 7.20. The pH of the first *equivalence point* should be right between those two buffers, around 4.5

11. Sketch the titration curve you would expect for this titration, labeling all equivalence points and sulfurous acid-based species present in each portion of the curve. (10pts)

Some day I'll draw (or calculate) a nice electronic version of a titration curve. Not today...

12. You will have to repeat this titration regularly as part of your job and would like to use a visual indicator in the future. You have the following indicators available: Bromocresol Green (BCG, endpoint range = 3.8-5.4), Brilliant Yellow (BY, endpoint range = 6.6-7.8), Thymol Blue (TB, endpoint range = 8.0-9.6). Which of these visual indicators would be useful in your titration? Explain your choice(s). (8pts)

This answer will be based upon the answers to #10 and #11. From #10, if the pH of the 1st equivalence point is around 4.5, the BCG would be a spectacularly good indicator for the first equivalence point. The second 1:1 buffer should have a pH around 7.2, so BY will be changing color when the solution is buffered, making it a horrible indicator for this titration. The second equivalence point should be a bit more basic than 7.2, so TB might be a good indicator for the second equivalence point.

Just because BY is a horrible indicator *for this specific titration*, that doesn't mean it's always a bad indicator. In fact, for the titration in #5 it would probably be great.