

# 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 =  $1.000^{\text{g}}/\text{mL}$

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

$PV = nRT$

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

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:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

1 <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	57 <b>La</b> 138.91	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	89 <b>Ac</b> 227.03	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							

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	71 <b>Lu</b> 174.97
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)	103 <b>Lr</b> (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?
	$3.82 \times 10^{-11}$			
		11.158		

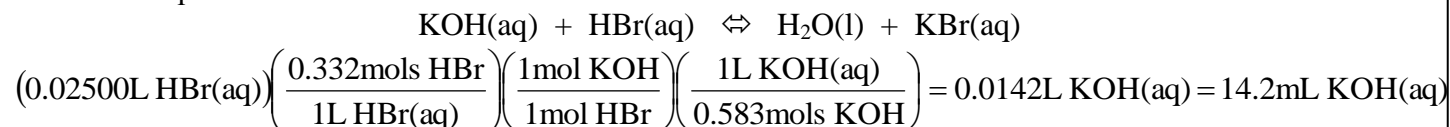
Conjugate Acid	$K_a$ @ 25°C	Conjugate Base	$K_b$ @ 25°C
$\text{H}_2\text{SeO}_3$	$2.33 \times 10^{-3}$	$\text{HSeO}_3^-$	$4.3 \times 10^{-12}$
$\text{H}_2\text{AsO}_4^-$	$1.0 \times 10^{-7}$	$\text{HAsO}_4^{2-}$	$1.0 \times 10^{-7}$

2. Does the combination listed result in an effective buffer solution? (4pts each)

- Yes **No** 0.64mol  $\text{HClO}_4(\text{aq})$  + 0.68mol  $\text{KOH}(\text{aq})$   
**Yes** No 0.90mol  $\text{Na}_2\text{HPO}_4(\text{aq})$  + 0.45mol  $\text{HNO}_3(\text{aq})$   
**Yes** No 1.28mol  $\text{Na}_2\text{CO}_3(\text{aq})$  + 1.92mol  $\text{HCl}(\text{aq})$   
**Yes** No 0.93mol  $\text{CH}_3\text{COOH}(\text{aq})$  + 1.06mol  $\text{CH}_3\text{COOK}(\text{aq})$   
 Yes **No** 0.06mol  $\text{HNO}_2(\text{aq})$  + 1.18mol  $\text{LiNO}_2(\text{aq})$

3. How much 0.583M  $\text{KOH}(\text{aq})$  must be added to 25.00mL of 0.332M  $\text{HBr}(\text{aq})$  to reach the equivalence point? What is the pH of this solution at the equivalence point? Explain. (10pts)

This is a titration problem, so we should treat it the same way we treat *every* stoichiometry problem. Start with a balanced equation...



Since this is the titration of a strong monoprotic acid with a strong monoprotic base, the equivalence point should be very close to pH = 7.

4. You have prepared a buffer solution by combining 0.482mols of chlorous acid ( $\text{HClO}_2$ ,  $K_a = 1.2 \times 10^{-2}$ ) and 0.513mols of potassium chlorite in enough water to make 500.0mL of solution. What is the pH of this buffer solution? (15pts)

If it's a buffer, we can probably use the Henderson-Hasselbalch equation...

$$\text{pH} = (-\log(1.2 \times 10^{-2})) + \log \left( \frac{\left( \frac{0.513 \text{ mols ClO}_2^-}{0.5000 \text{ L}} \right)}{\left( \frac{0.482 \text{ mols HClO}_2}{0.5000 \text{ L}} \right)} \right) = 1.95$$

5. What is the  $K_a$  of a weak acid if 500.0mL of a solution containing 0.278mol of the acid and 0.327 mol of its conjugate base has a pH of 8.243? Over what pH range would this conjugate acid/ conjugate base pair make an effective buffer? (15pts)

Since the word "buffer" is in there, let's try the Henderson-Hasselbalch equation again...

$$8.243 = (-\log(K_a)) + \log \left( \frac{\left( \frac{0.327 \text{ mols conj. base}}{0.5000 \text{ L}} \right)}{\left( \frac{0.278 \text{ mols conj. acid}}{0.5000 \text{ L}} \right)} \right)$$

Solving,  $\text{p}K_a = 8.172$  and  $K_a = 6.73 \times 10^{-9}$ . Combinations of a weak acid and its conjugate base usually make effective buffers within 1 pH unit of the  $\text{p}K_a$  of the conjugate acid, so this system would make effective buffers in the pH range of 7.172 and 9.172.

6. You are going to use a titration to determine the concentration of an unknown potassium sulfite solution ( $\text{K}_2\text{SO}_3$ ,  $\text{p}K_b = 6.806$ ). The acid you have chosen to use is 0.927M perchloric acid.
- Write out the chemical equations for the step-wise protonation/neutralization of sulfite and the overall/net chemical reaction. (6pts)

First step:  $\text{SO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{HSO}_3^-(\text{aq})$

Second step:  $\text{HSO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{H}_2\text{SO}_3(\text{aq})$

Overall/net equation:  $\text{SO}_3^{2-}(\text{aq}) + 2 \text{H}^+(\text{aq}) \rightleftharpoons \text{H}_2\text{SO}_3(\text{aq})$

If you prefer to write out the full molecular equation, that's fine, you'll have  $\text{KClO}_4(\text{aq})$  as a product of each step and 2  $\text{KClO}_4(\text{aq})$ 's in the net reaction.

- Someone left your pH probe laying on the bench and it has dried out. After a short search, you have found the following three visual indicators: Thymolphthalein (TP, endpoint pH range = 9.5-10.5); Phenol red (PR, endpoint pH range = 6.8-8.3); Bromophenol Blue (BPB, endpoint pH range = 3.1-4.6). Which of these visual indicators would be useful in your titration? Explain your choice(s). (12pts)

You could answer this one qualitatively: Since sulfite is a weak base and perchloric acid is a strong acid, we'd expect the first equivalence point to be acidic, so the acidic indicator (BPB) is probably best.

To be a little more quantitative, we could use the  $\text{p}K_b$  given in the problem... if the  $\text{p}K_b$  of sulfite is 6.806, then the  $\text{p}K_a$  of  $\text{HSO}_3^-(\text{aq})$  should be  $14 - 6.806 = 7.194$ . At the first equivalence point, we can think of the mixture as a solution of *only*  $\text{HSO}_3^-(\text{aq})$  in water. Using the  $K_a$  of  $\text{HSO}_3^-(\text{aq})$   $\{K_a = 10^{-\text{p}K_a} = 10^{-7.194} = 6.40 \times 10^{-8}\}$ , we can calculate that a 1M solution of  $\text{HSO}_3^-(\text{aq})$  should have a pH of around 3.6. This unknown solution probably doesn't have a concentration of 1M, but the pH at the equivalence point should be somewhere in that neighborhood, so BPB should be an OK indicator for the first equivalence point.

(#6 continued)

- c. Sketch the titration curve you would expect for this titration, labeling all equivalence points and sulfite-based species present in each portion of the curve. (6pts)

- d. As you are about to start your titration, a package arrives with a new pH probe, so you decide to use the pH probe to monitor your titration. You find that 25.00mL of potassium sulfite requires 34.62mL of perchloric acid to reach the first equivalence point. What is the concentration of the potassium sulfite solution? (12pts)

Titration is stoichiometry problems, we'll use the equation for the first equivalence point from the first part of this problem

$$(0.03462\text{L HClO}_4(\text{aq})) \left( \frac{0.927\text{mols HClO}_4(\text{aq})}{1\text{L HClO}_4(\text{aq})} \right) \left( \frac{1\text{mol SO}_3^{2-}(\text{aq})}{1\text{mol HClO}_4(\text{aq})} \right) \left( \frac{1}{0.02500\text{L SO}_3^{2-}(\text{aq})} \right) = 1.28\text{M SO}_3^{2-}(\text{aq})$$

- e. How much perchloric acid solution would be required to reach the second equivalence point in part “d”? Explain your answer. (6pts)

It should take twice as much perchloric acid titrant to reach the second equivalence point, 69.24mL.