Name: _____

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 $= 6.022 \times 10^{23}$ $^{units}/_{mol}$
$32.00°F = 0.000°C = 273.15K$
Density of Water $= 1.000^{g}/_{mL}$
$R = 0.08206$ $^{L \cdot atm}/_{mol \cdot K} = 8.314$ $^{J}/_{mol \cdot K}$
$PV = nRT$
$\Delta T_{fp/bp} = k_{fp/bp} \cdot m \cdot i$
For water: $k_{fp} = -1.86$ $^{°C}/_{m}$
               $k_{bp} = 0.512$ $^{°C}/_{m}$
$P_1 = X_1 P_1°$
$\Pi = MRTi$
$C_1 V_1 = C_2 V_2$
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 $1/[A]_t = kt + 1/[A]_o$
$k = Ae^{-Ea/RT}$

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

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

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

$E_{cell} = E°_{cell} - ^{RT}/_{nF} \, lnQ$
$E°_{cell} = ^{RT}/_{nF} \, lnK°$
$K° = e^{\wedge}(^{nF}/_{RT} E°_{cell})$
$F = 96485$ $^{J}/_{V \cdot mol \text{ of electrons}}$
$\Delta G° = \Delta H°_{system} - T\Delta S°_{system}$
$\Delta G° = -nFE°_{cell} = -RT ln K°$
$\Delta G = \Delta G° + RT ln Q$
$F = 96485$ $^{C}/_{mol \text{ electrons}}$
$1A = 1$ C / 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)

Score

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

$[H_3O^+]$	$[OH^-]$	pH	pOH	Acidic, Basic or Neutral?
1.97×10^{-8}	5.08×10^{-7}	7.706	6.294	Basic
3.72×10^{-6}	2.69×10^{-9}	5.429	8.571	Acidic

Conjugate Acid	K_a @25ºC	Conjugate Base	K_b @25ºC
H_2SO_3	1.7×10^{-2}	HSO_3^{-1}	5.9×10^{-13}
$HC_6H_6O_6^{-1}$	1.6×10^{-12}	$C_6H_6O_6^{2-}$ (ascorbate ion)	6.3×10^{-3}

2. A labmate has prepared a sulfate/hydrogen sulfate buffer solution at pH=2.15, but does not write much information down in a lab notebook. You know that the concentration of the buffer is 0.63M and pK_b=12.08 for SO_4^{-2}(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 sulfate/hydrogen sulfate make an effective buffer? Explain your answers. (12pts)

From the given pK_b for SO_4^{-2}, we can calculate the pK_a for HSO_4^{-1}
$$pK_a\{HSO_4^{-1}\} = 14 - 12.08 = 1.92$$
Since the pH of the buffer is higher (more basic) than the pK_a of the conjugate acid, there must be a higher concentration of the conjugate base in this buffer. This system will make an effective buffer for pH's within 1 unit of the pK_a, 0.92 to 2.92

3. How much 0.182M $HClO_4$(aq) must be added to 25.00mL of 0.153M $Ba(OH)_2$(aq) to reach the equivalence point? What is the pH of this solution at the equivalence point? Explain. (12pts) {Note: $Ba(OH)_2$ is a strong base.}

$$2\ HClO_4(aq)\ +\ Ba(OH)_2(aq)\ \rightarrow\ 2\ H_2O(l)\ +\ Ba(ClO_4)_2(aq)$$
$$\left(0.02500 \text{L Ba(OH)}_2 \text{(aq)}\right)\left(\frac{0.153 \text{mols Ba(OH)}_2}{\text{L Ba(OH)}_2 \text{(aq)}}\right)\left(\frac{2 \text{mol HClO}_4}{1 \text{mol Ba(OH)}_2}\right)\left(\frac{1 \text{L HClO}_4 \text{(aq)}}{0.182 \text{mol HClO}_4}\right) = 0.04203 \text{L HClO}_4 \text{(aq)}$$
$$42.03 \text{mL}$$
Since this is a strong acid/strong base titration, the equivalence point should be neutral, $pH = 7$

Score

4. You have prepared a buffer solution by combining 0.492mols of nitrous acid (HNO_2, $K_a = 4.6 \times 10^{-4}$) and 0.385mols of sodium nitrite in enough water to make 500.0mL of solution. What is the pH of this buffer solution? (12pts)

Plugging in to the Henderson-Hasselbalch equation…
$$pH = 3.337 + \log \{ 0.385\text{mols } NO_2^-(aq) \: / \: 0.492\text{mols } HNO_2(aq) \} = 3.23$$

5. What is the expected pH of a 0.923M aqueous solution of ammonium bromide? $\{K_b(NH_3) = 1.76 \times 10^{-5}\}$ (15pts)

Set up a table of initial/Δ/@Equilibrium concentrations, calculate K_a of $NH_4^+(aq)$ from the K_b of $NH_3(aq)$, make some simplifying assumptions, and we should get down to:
$$5.68 \times 10^{-10} = x^2 / 0.923$$
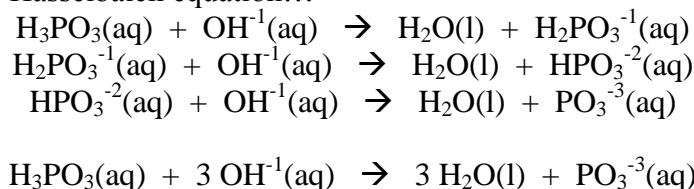$$x = 2.29 \times 10^{-5} = [H_3O^+]$$
$$pH = 4.640$$

6. What is the K_b of a weak base if 500.0mL of a solution containing 0.229mol of the base and 0.216mol of its conjugate acid has a pH of 9.286? Over what pH range would this conjugate acid/ conjugate base pair make an effective buffer? (15pts)

Plugging in to the Henderson-Hasselbalch equation…
$$9.286 = pK_a + \log \{ 0.229\text{mols conj. base } / \: 0.216\text{mols conj. acid} \}$$
$$pK_a = 9.2606 \rightarrow pK_b = 14 - 9.2606 = 4.739$$
Effective buffer within 1 unit of pK_a of the conjugate acid, 8.26 →10.26

7. You are going to use a titration to determine the concentration of an unknown phosphorous acid solution (H_3PO_3, $pK_a = 1.29$). The base you have chosen to use is 0.715M sodium hydroxide.
    a. Write out the chemical equations for the step-wise deprotonation/neutralization of phosphorous and the overall/net chemical reaction. (7pts)

Plugging in to the Henderson-Hasselbalch equation…
$$H_3PO_3(aq) + OH^{-1}(aq) \rightarrow H_2O(l) + H_2PO_3^{-1}(aq)$$
$$H_2PO_3^{-1}(aq) + OH^{-1}(aq) \rightarrow H_2O(l) + HPO_3^{-2}(aq)$$
$$HPO_3^{-2}(aq) + OH^{-1}(aq) \rightarrow H_2O(l) + PO_3^{-3}(aq)$$

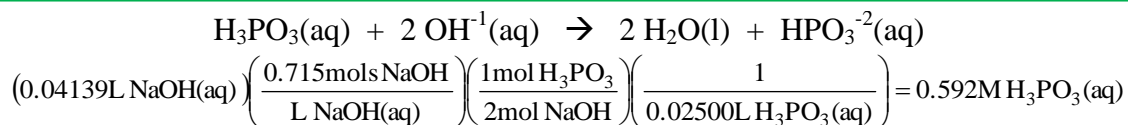$$H_3PO_3(aq) + 3\,OH^{-1}(aq) \rightarrow 3\,H_2O(l) + PO_3^{-3}(aq)$$

    b. 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). (6pts)

Strong base/weak acid, the equivalence point should be basic, but *which* equivalence point? {There are 3 of them…} Given the very low pK_a, the pH of the first equivalence point should be fairly acidic, so BPB is probably a good indicator for the 1st equivalence point. The second equivalence point should be somewhere around neutral (about 4-5 units higher than the first…), so PR is probably an OK indicator for the 2nd equivalence point. The third equivalence point should be another 4-5 units higher than the second, so TP might be an OK indicator for the 3rd equivalence point.

(#7 continued)

c. Sketch the titration curve you would expect for this titration, labeling all equivalence points and phosphorous acid-based species present in each portion of the curve. (7pts)

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 phosphorous acid requires 41.39mL of sodium hydroxide to reach the second equivalence point. What is the concentration of the phosphorous acid solution? (10pts)

$$H_3PO_3(aq) + 2\,OH^{-1}(aq) \;\rightarrow\; 2\,H_2O(l) + HPO_3^{-2}(aq)$$

$$\left(0.04139L\,NaOH(aq)\right)\left(\frac{0.715\,mols\,NaOH}{L\,NaOH(aq)}\right)\left(\frac{1\,mol\,H_3PO_3}{2\,mol\,NaOH}\right)\left(\frac{1}{0.02500L\,H_3PO_3(aq)}\right) = 0.592M\,H_3PO_3(aq)$$

e. How much sodium hydroxide solution would be required to reach the first equivalence point in part "d"? How much sodium hydroxide solution would be required to reach the third equivalence point in part "d"? Explain your answer. (6pts)

Each equivalence point is an equal step, so the volume of NaOH(aq) req   uired to reach each equivalence point is the same. If it took 41.39mL to reach the *2ⁿᵈ* equivalence point, then it would have taken {41.39/2}=21.70mL to reach the first. To reach the *3ʳᵈ* equivalence point, we need 3 times as much NaOH(aq) as it took to reach the 1ˢᵗ, {21.70 x 3} = 62.09mL

Score