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

$32.00^{\circ}F = 0.000^{\circ}C = 273.15K$

Density of Water = 1.000 g/mL

$R = 0.08206$ L·atm/mol·K = 8.314 J/mol·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

$P_1 = X_1 P_1^{\circ}$

$\Pi = MRTi$

$C_1 V_1 = C_2 V_2$

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

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

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

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

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

$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln Q$

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

$K^{\circ} = e^{\wedge}(\frac{nF}{RT} E^{\circ}_{cell})$

$F = 96485$ J/V·mol of electrons

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

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

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

$F = 96485$ C/mol electrons

$1A = 1$ C / sec

1																	2
H																	**He**
1.0079																	4.0026
3	4											5	6	7	8	9	10
Li	**Be**											**B**	**C**	**N**	**O**	**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**	**P**	**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
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**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**	**I**	**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**	**Ta**	**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**	**Ho**	**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)

Score

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

$[H_3O^+]$	$[OH^-]$	pH	pOH	Acidic, Basic or Neutral?
2.13×10^{-10}	4.69×10^{-5}	9.671	4.329	Basic
8.07×10^{-12}	1.24×10^{-3}	11.093	2.917	Basic

Conjugate Acid	K_a @25ºC	Conjugate Base	K_b @25ºC
HNO_2	4.0×10^{-4}	NO_2^{-1}	2.5×10^{-11}
HSO_4^{-1}	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}

2. A labmate has prepared an acetic acid/acetate buffer solution at pH=5.15, but does not write much information down in a lab notebook. You know that the concentration of the buffer is 0.85M and pK_b=9.25 for $C_2H_3O_2^{-1}$(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 acetic acid/acetate make an effective buffer? Explain your answers. (8pts)

From the given pK_b of acetate ions, the pK_a of acetic acid = 14 – 9.25 = 4.75
Since the pH of the buffer is higher than the pK_a of the conjugate acid, the buffer must contain more conjugate base.
A given conjugate acid/conjugate base pair is an effective buffer within 1 pH unit of the pK_a of the conjugate acid, so acetic acid/acetate would be an effective buffer from pH = 3.75 to pH = 5.75.

3. What is the expected pH of a 0.628M aqueous solution of sodium fluoride? $\{K_b(F^{-1})=1.47 \times 10^{-11}\}$ (10pts)

	F^{-1}(aq) +	H_2O(l) ⇔	OH^{-1}(aq) +	HF(aq)
[ ]$_{initial}$	0.628M	XXXX	10^{-7} M	0 M
Δ[ ]	- x	XXXX	+ x	+ x
[ ]$_{equilibrium}$	(0.628 – x)M	XXXX	$(10^{-7} + x)$ M	x M

$$K_b = [OH^{-1}][HF] / [F^{-1}] = \{(10^{-7} + x)(x)\} / (0.628 – x) = 1.47 \times 10^{-11}$$
$$\text{Assume } x \gg 10^{-7} \text{ and } x \ll 0.628 \rightarrow \{(x)(x)\} / (0.628) = 1.47 \times 10^{-11}$$
$$x = 3.038 \times 10^{-6} = [OH^{-1}]$$
CHECK ASSUMPTIONS: 10^{-7} is ~3% of 3×10^{-6} so that one's OK, 3×10^{-6} is definitely much smaller than 0.628
$$pOH = -\log[OH^{-1}] = -\log(3.038 \times 10^{-6}) = 5.517$$
$$pH = pK_w – pOH = 14 – 5.517 = 8.483$$
NOTE: This could also be done as a K_a-type problem.

Score

4. You have prepared a buffer solution by combining 0.492mols of formic acid (HCO_2H, $K_a = 1.77 \times 10^{-4}$) and 0.385mols of sodium formate in enough water to make 600.0mL of solution. What is the expected pH of this buffer solution? (10pts)

> This could be done as a regular K_a-type equilibrium problem, or it can use the Henderson-Hasselbalch equation. For H-H:
> $$pH = pK_a + \log \{[HCO_2^{-1}] / [HCO_2H]\}$$
> $$pK_a = -\log(K_a) = -\log(1.77 \times 10^{-4}) = 3.752$$
> $$pH = 3.752 + \log\{0.385/0.492\} = 3.645$$

5. How much 0.187M HBr(aq) must be added to 15.00mL of 0.207M NaOH(aq) to reach the equivalence point? What is the expected pH of this solution at the equivalence point? Explain. (10pts)

> Titration stoichiometry problem…
> (0.01500L NaOH(aq)) (0.207M NaOH(aq)) (1mol HBr / 1mol NaOH) / (0.187M HBr(aq)) = 0.0166L = 16.6mL
> Strong acid/strong base titration, the equivalence point should be neutral.

6. What is the K_a of a weak acid if 500.0mL of a solution containing 0.134mol of its conjugate base and 0.162mol 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)
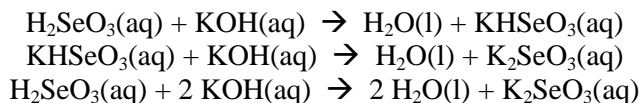
> Another probably Henderson-Hasselbalch plug in problem…
> $$pH = pK_a + \log \{[A^{-1}] / [HA]\}$$
> $$4.992 = pK_a + \log \{ 0.134 / 0.162 \}$$
> $$pK_a = 5.0744$$
> $$K_a = 10^{-pK_a} = 10^{-5.0744} = 8.43 \times 10^{-6}$$

Score
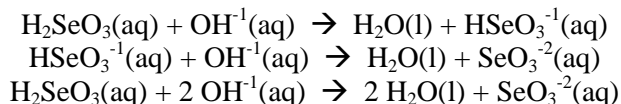
For questions 7-11: You are going to use a titration to determine the concentration of an unknown selenous acid solution (H_2SeO_3, pK_{a1} = 2.62, pK_{a2} = 8.32). The base you have chosen to use is 0.648M potassium hydroxide.

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

"Full formula" balanced equations:
$$H_2SeO_3(aq) + KOH(aq) \rightarrow H_2O(l) + KHSeO_3(aq)$$
$$KHSeO_3(aq) + KOH(aq) \rightarrow H_2O(l) + K_2SeO_3(aq)$$
$$H_2SeO_3(aq) + 2\ KOH(aq) \rightarrow 2\ H_2O(l) + K_2SeO_3(aq)$$

Net ionic equations:
$$H_2SeO_3(aq) + OH^{-1}(aq) \rightarrow H_2O(l) + HSeO_3^{-1}(aq)$$
$$HSeO_3^{-1}(aq) + OH^{-1}(aq) \rightarrow H_2O(l) + SeO_3^{-2}(aq)$$
$$H_2SeO_3(aq) + 2\ OH^{-1}(aq) \rightarrow 2\ H_2O(l) + SeO_3^{-2}(aq)$$

Either form is equally correct/

8. You titrate 20.00mL of the unknown selenous acid solution to the second equivalence point with 31.83mL of potassium hydroxide solution. What is the concentration of the unknown selenous acid solution? (10pts)

Titration stoichiometry problem…
(0.03183L KOH(aq)) (0.648M KOH(aq)) (1mol H_2SeO_3 / 2mol KOH) / (0.02000L H_2SeO_3(aq)) = 0.516M

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

	$H_2SeO_3(aq)$ +	$H_2O(l) \Leftrightarrow$	$H_3O^{+1}(aq)$ +	$HSeO_3^{-1}(aq)$
[ ]$_{initial}$	0.516M	XXXX	10^{-7} M	0 M
Δ[ ]	- x	XXXX	+ x	+ x
[ ]$_{equilibrium}$	(0.516 – x)M	XXXX	(10^{-7} + x) M	x M

$$K_a = [H_3O^{+1}][HSeO_3^{-1}] / [H_2SeO_3] = \{(10^{-7} + x)(x)\} / (0.516 - x) = 10^{-2.62} = 2.40 \times 10^{-3}$$
Assume x>>10^{-7} and x<<0.516 → $\{(x)(x)\} / (0.516) = 2.40 \times 10^{-3}$
$$x = 3.519 \times 10^{-2} = [H_3O^{+1}]$$
CHECK ASSUMPTIONS: 10^{-7} is much smaller than 3.5×10^{-5}; 3.5×10^{-2} is almost 7% of 0.516, so that one's probably not good. Arg, looks like quadratic formula time…
$$\{(x)(x)\} / (0.516 - x) = 2.40 \times 10^{-3}$$
$$x^2 + (2.40 \times 10^{-3}) + (-1.238 \times 10^{-3}) = 0$$
$$x = 0.034 = [H_3O^+]$$
$$pH = -\log[H_3O^+] = -\log(0.034) = 1.469$$
Using incorrect assumptions, pH = 1.454

Name: _____

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

11. 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: Methyl Red (MR, endpoint range = 4.4-6.2), 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) and any assumptions. (8pts)

Using the 2 pK_as, the pH of the first equivalence point can be estimated to be about pH = 5.5. This would make Methyl Red an excellent indicator of the first equivalence point.
Brilliant Yellow might be OK as well, although the higher pH side of its endpoint would probably be into the buffering region of the titration curve.
Thymol Blue would definitely be a bad indicator for this titration because its endpoint range is definitely in the buffering region of the titration curve.

Score