

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

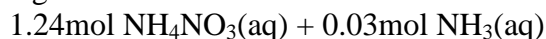
|                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                   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

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

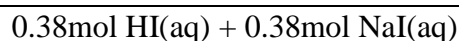
| $[\text{H}_3\text{O}^+]$ | $[\text{OH}^-]$       | pH    | pOH   | Acidic, Basic or Neutral? |
|--------------------------|-----------------------|-------|-------|---------------------------|
| $6.81 \times 10^{-8}$    | $1.47 \times 10^{-7}$ | 7.167 | 6.833 | basic or neutral          |
| $9.84 \times 10^{-10}$   | $1.02 \times 10^{-5}$ | 9.007 | 4.993 | basic                     |

| Conjugate Acid         | $K_a$ @ 25°C         | Conjugate Base       | $K_b$ @ 25°C          |
|------------------------|----------------------|----------------------|-----------------------|
| $\text{H}_3\text{O}^+$ | 1                    | $\text{H}_2\text{O}$ | $1.0 \times 10^{-14}$ |
| $\text{HSO}_3^-$       | $6.2 \times 10^{-8}$ | $\text{SO}_3^{2-}$   | $1.6 \times 10^{-7}$  |

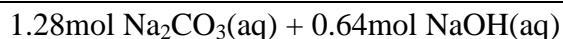
2. Explain why each of the following *does not* result in an effective buffer? (15pts)



The amounts of conjugate acid ( $\text{NH}_4^+$ ) and conjugate base ( $\text{NH}_3$ ) are too far apart to make an effective buffer. The concentrations should be within a factor of 10 of each other.



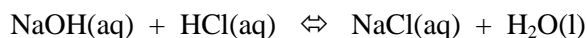
HI/I<sup>-</sup> are a conjugate acid/conjugate base pair, but HI is a strong acid so it will not make an effective buffer when combined with its conjugate base.



Carbonate ions *can* be made into an effective buffer by addition of some strong acid to protonate some of the carbonate ions, but in this case a strong *base* is being added, so this will not make an effective buffer.

3. How much 0.461M NaOH(aq) must be added to 25.00mL of 0.399M HCl(aq) to reach the equivalence point? What is the pH of this solution at the equivalence point? (10pts)

Balanced chemical equation:



$$(0.02500 \text{ L HCl}(\text{aq})) \left( \frac{0.399 \text{ mols HCl}(\text{aq})}{1 \text{ L HCl sol'n}} \right) \left( \frac{1 \text{ mol NaOH}(\text{aq})}{1 \text{ mol HCl}(\text{aq})} \right) \left( \frac{1 \text{ L NaOH sol'n}}{0.461 \text{ mols NaOH}(\text{aq})} \right) = 0.0216 \text{ L NaOH}(\text{aq})$$

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

4. Describe how you would prepare 1.00L of a 1.00M buffer at pH 6.70. You have the following reagents available: Nitrous acid ( $\text{HNO}_2$ ,  $K_a = 7.2 \times 10^{-4}$ ), Hydrosulfuric acid ( $\text{H}_2\text{S}$ ,  $K_a = 1.1 \times 10^{-7}$ ), Boric acid ( $\text{H}_3\text{BO}_3$ ,  $K_a = 5.8 \times 10^{-10}$ ),  $\text{NaOH}(s)$ , distilled/deionized water. (15pts)

Looking at the  $\text{p}K_a$ 's of all the available acids,  $\text{H}_2\text{S}$  has  $\text{p}K_a = 6.96$ , so it will be the only one that will make an effective buffer at  $\text{pH} = 6.70$ . To make 1.00L of a 1.00M solution, we'll need...1mol of  $\text{H}_2\text{S}$ , so 34.082g of  $\text{H}_2\text{S}$ . To figure out how much base to add, we need to plug in to the H-H equation:

$$6.70 = 6.96 + \log\left(\frac{[\text{HS}^-]}{[\text{H}_2\text{S}]}\right)$$

$$\text{(mols HS}^-) / \text{(mols H}_2\text{S)} = 0.5495 = x / (1-x)$$

$$x = 0.355 \text{ mols HS}^- \rightarrow \text{formed by adding 0.355 mols of NaOH} \rightarrow 15.186\text{g NaOH}$$

So add 15.186g NaOH to the 34.082g  $\text{H}_2\text{S}$  and dilute to 1.00L.

5. What is the  $K_b$  of a base if 500.0mL of a solution containing 0.261 mol of the base and 0.216 mol of its conjugate acid has a pH of 5.761? Over what pH range would this conjugate acid/ conjugate base pair make an effective buffer? (12pts)

This is an approximately equal mixture of a weak conjugate acid and its conjugate base, so it should be a buffer and we can use the Henderson-Hasselbalch equation to figure out the answer...

$$5.761 = \text{p}K_a + \log\left(\frac{0.261}{0.216}\right)$$

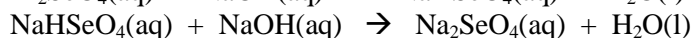
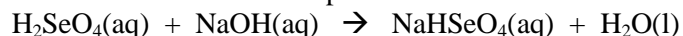
$$\text{p}K_a = 5.679 \rightarrow \text{p}K_b = 14 - 5.679 = 8.321 \rightarrow K_b = 4.77 \times 10^{-9}$$

A weak conjugate acid/base mixture is a good buffer within 1 pH unit of the  $\text{p}K_a$ , so this is a good buffer 4.679  $\rightarrow$  6.679

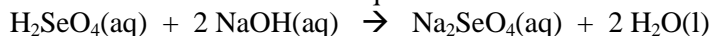
6. You are going to use a titration to determine the concentration of an unknown selenic acid solution ( $\text{H}_2\text{SeO}_4$ ,  $\text{p}K_a = -7$ ). The base you have chosen to use is 1.031M sodium hydroxide.

- a. Write out the chemical equations for the step-wise deprotonation/neutralization of selenic acid and the overall/net chemical reaction. (6pts)

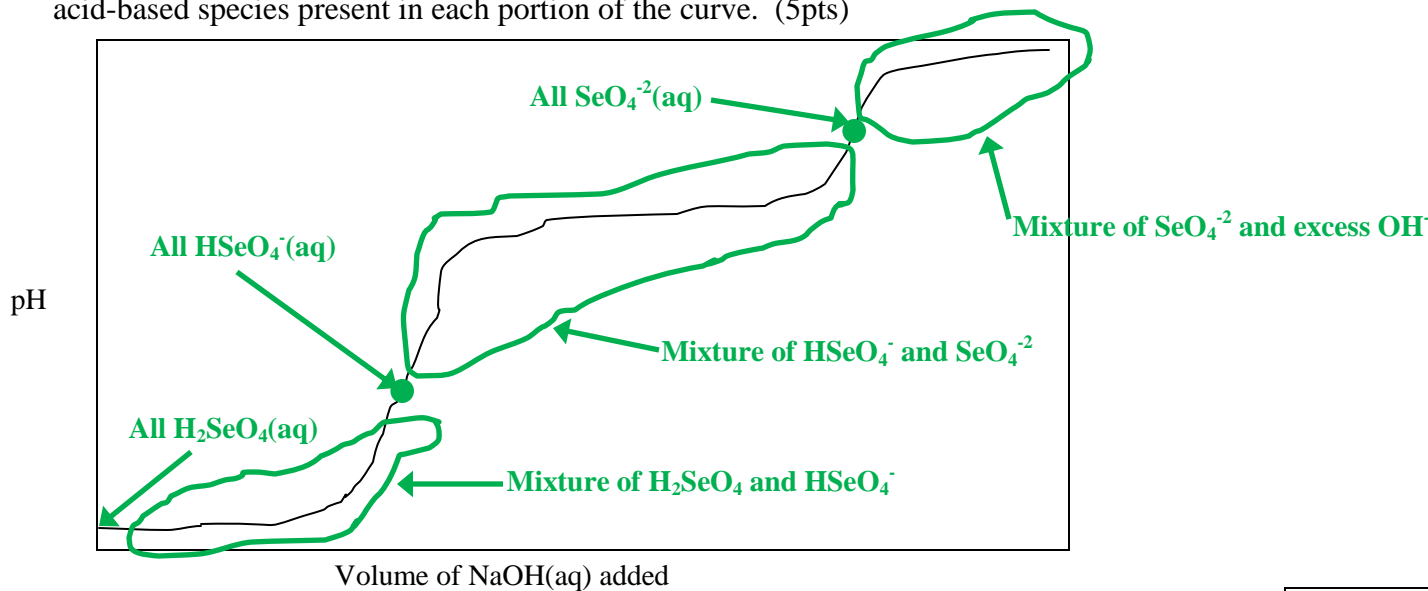
Stepwise:



Overall equation:



- b. Sketch the titration curve you would expect for this titration, labeling all equivalence points and selenic acid-based species present in each portion of the curve. (5pts)



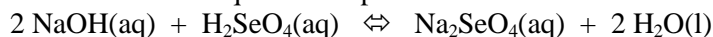
(#6 continued...)

- c. 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); Bromothymol Blue (BTB, endpoint pH range = 6.0-7.5); 2,4-dinitrophenol (DNP, endpoint pH range = 2.8-4.0). Which of these visual indicators would be useful in your titration? Explain your choices. (10pts)

Since selenic acid is a strong acid (first  $pK_a = -7$ ) being titrated with a strong base, the first equivalence point should be somewhere around neutral, maybe a little on the acidic side, so BTB should be a good indicator for the first equivalence point because its endpoint is slightly acidic to neutral. Selenic acid is diprotic, so there is a second step in the deprotonation, meaning that there will be a second equivalence point. This equivalence point should be on the basic side of neutral, so TP would probably be a good indicator for the second equivalence point because the endpoint of TP is fairly basic.

- 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 50.00mL of selenic acid requires 46.93mL of sodium hydroxide to reach the second equivalence point. What is the concentration of the selenic acid solution? (10pts)

Balanced chemical equation to reach the second equivalence point:



$$(0.04693\text{L NaOH(aq)}) \left( \frac{1.031\text{mols NaOH}}{1\text{L NaOH sol'n}} \right) \left( \frac{1\text{ mol H}_2\text{SeO}_4}{2\text{ mol NaOH}} \right) \left( \frac{1}{0.05000\text{L H}_2\text{SeO}_4} \right) = 0.4838\text{M H}_2\text{SeO}_4\text{(aq)}$$

- e. How much sodium hydroxide solution was required to reach the first equivalence point in part “d”? Explain your answer. (4pts)

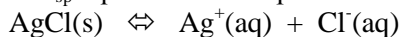
It should take exactly half as much titrant to get to the first equivalence point as it took to get to the second equivalence point, so it should take 23.47mL of sodium hydroxide solution to reach the first equivalence point.

7. Which solution has a higher concentration of silver(I) ions? Explain your answer. (15pts)

Saturated silver(I) chloride,  $K_{sp}(\text{AgCl}) = 1.77 \times 10^{-10}$

Saturated silver(I) phosphate,  $K_{sp}(\text{Ag}_3\text{PO}_4) = 8.89 \times 10^{-17}$

Writing out  $K_{sp}$  equations and expressions for each...



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (x)(x) = 1.77 \times 10^{-10}$$

$$x = 1.33 \times 10^{-5} = [\text{Ag}^+]$$



$$K_{sp} = [\text{Ag}^+]^3[\text{PO}_4^{3-}] = (3x)^3(x) = 27x^4 = 8.89 \times 10^{-17}$$

$$x = 4.26 \times 10^{-5}$$

$$[\text{Ag}^+] = 1.28 \times 10^{-4} \text{M}$$

Silver phosphate has a higher concentration of silver(I) ions.