

**CHEMISTRY 1B – Fall, 2015**  
**EXAM 2 – VERSION A Key**

Equations and constants that you could need:  $0^\circ\text{C} = 273\text{ K}$ ;  $K_w = 1.0 \times 10^{-14}$

The quadratic equation for  $ax^2 + bx + c = 0$  is  $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$R = \text{Universal Gas Constant} = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$

$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^\circ + RT \ln Q$        $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

A periodic table is provided on the last page along with a blank page to be used as scratch paper.

**Part I. Multiple Choice Section.** All Questions have only one correct answer. Each Question is worth 4 points.

Use the following information to answer questions 1 to 3. A buret is filled with 0.100 M HCl and it is used to titrate 35.0 mL of an unknown strong base. The titration requires 44.57 mL of HCl to reach the equivalence point.

1. The original concentration of  $\text{OH}^-$  in the unknown strong base is:

$$[\text{OH}^-]V_{\text{OH}} = [\text{HCl}]V_{\text{HCl}} \text{ or } [\text{OH}^-] = (0.100\text{ M})(44.57\text{ mL})/(35.0\text{ mL})$$

- a) 0.0785 M    **b) 0.127 M**    c) 0.156 M    d) 0.254 M    e) 1.56 M

2. The pH after adding 40.0 mL of HCl will be:

$$\text{excess OH}^- \text{ before equiv. pt. So } [\text{OH}^-] = [n(\text{OH}^-) - n(\text{H}^+) ] / (40\text{ mL} + 35\text{ mL})$$

$$= (4.457\text{ mmol} - 4.00\text{ mmol}) / 75\text{ mL} = 6.09 \times 10^{-3}\text{ M} \text{ or } \text{pOH} = 2.22 \text{ and } \text{pH} = 11.78$$

- a) 1.00    b) 1.25    c) 1.92    **d) 11.878**    e) 13.11

3. The pH at the equivalence point will be:

$$\text{equal moles of } \text{H}^+ \text{ and } \text{OH}^- \text{ so } \text{pH} = 7.0$$

- a) 2.8    b) 4.5    **c) 7.0**    d) 9.0    e) 11.5

4. Methyl amine ( $\text{CH}_3\text{NH}_2 - K_b = 4.35 \times 10^{-4}$ ) is a weak base and is being titrated with a strong acid. The pH at one half of the volume needed to reach the equivalence point will be:

$$\text{This is in the buffer region where half of } \text{CH}_3\text{NH}_2 \text{ is converted to } \text{CH}_3\text{NH}_3^+ \text{ and } \text{pH} = \text{p}K_a \text{ (for conj. acid)} + \log\left\{\frac{[\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]}\right\} = \text{p}K_a = 14 + \log K_b$$

- 3.36    b) 5.32    c) 7.00    **d) 10.64**    e) 10.94

5. A weak base is titrated by a strong acid. Which indicator (in general based on the indicator's  $\text{p}K_a$  value) would be the best for determining the endpoint?

$\text{pH} < 7$  as acid is stronger than base

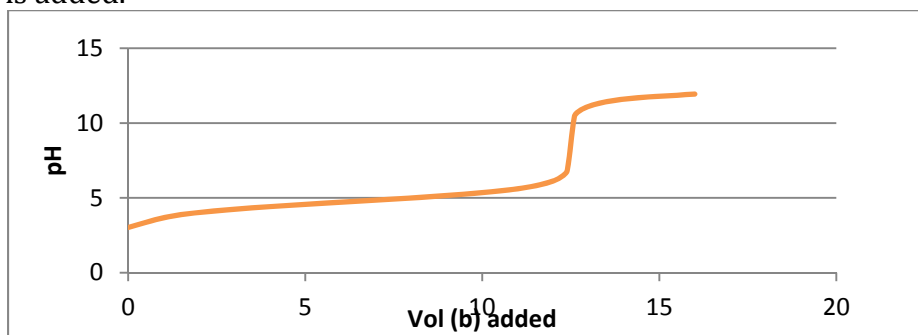
- a) Thymolphthalein ( $\text{p}K_a = 10.0$ )    b) Phenolphthalein ( $\text{p}K_a = 9.1$ )  
c) Bromocresol blue ( $\text{p}K_a = 6.8$ )    **d) Methyl red ( $\text{p}K_a = 5.00$ )**

6. Lead (II) chloride ( $\text{PbCl}_2$ ) has a  $K_{sp} = 1.17 \times 10^{-5}$ . Its molar solubility in water is:  
 Reaction:  $\text{PbCl}_2(s) \leftrightarrow \text{Pb}^{2+} + 2\text{Cl}^-$  Which gives equil. ICE table values of  $S$  and  $2S$ .

$$K_{sp} = 1.17 \times 10^{-5} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = S(2S)^2 = 4S^3 \text{ or } S = [1.17 \times 10^{-5}/4]^{1/3} =$$

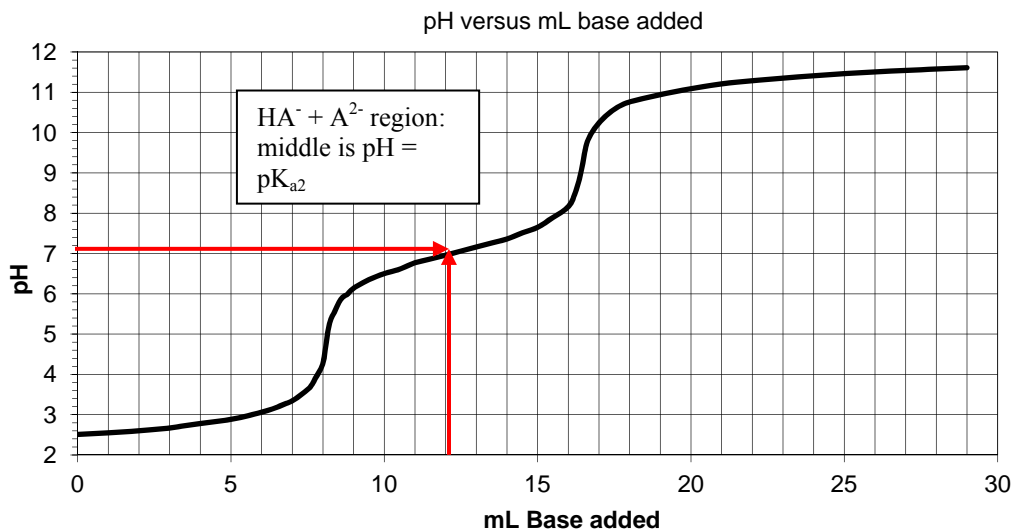
- a)  $3.42 \times 10^{-3} \text{ M}$     **b)  $1.43 \times 10^{-2} \text{ M}$**     c)  $1.80 \times 10^{-2} \text{ M}$     d)  $2.27 \times 10^{-2} \text{ M}$     e)  $4.67 \times 10^{-2} \text{ M}$

7. Looking at the following titration plot below, we can conclude that it is the titration of a \_\_\_\_\_ where (a) is in the container with the pH meter and (b) is added.



- a) Strong acid (a) by a strong base (b)    b) Strong base (a) by a strong acid (b)  
**c) Monprotic weak acid (a) by a strong base (b)** (eq. pt.  $\text{pH} > 7$ )  
 d) A Strong base (a) by a weak acid (b)  
 e) A diprotic weak base (a) by a strong acid (b)

8. The plot below shows the titration of a diprotic weak acid by a strong base, the  $\text{pK}_{a2}$  is approximately,



see lines on plot above

- a) 2.8    b) 4.5    **c) 7.0**    d) 9.0    e) 11.5

9. Solid silver phosphate ( $\text{Ag}_3\text{PO}_4$ ) is added to water to make a saturated solution. Which of the following additions will **decrease** the equilibrium concentration of  $\text{Ag}^+$ ?

- a)  $\text{Na}_3\text{PO}_4$       b)  $\text{HNO}_3$       c)  $\text{NH}_3$  (forms complex ion)      d) more  $\text{Ag}_3\text{PO}_4(\text{s})$   
a) decreases solubility through the common ion effect; b) and c) increase solubility and d) has no effect

10. Which of the following sparingly salts will see NO INCREASE in solubility with the addition of  $\text{HNO}_3$ ?

- a)  $\text{CaCO}_3$       b)  $\text{Mg}(\text{OH})_2$       c)  $\text{AgCl}$       d)  $\text{AlPO}_4$       e)  $\text{ZnCO}_3$

11. What is the concentration of  $\text{Mg}^{2+}$  when  $\text{Mg}(\text{OH})_2$  solid is placed in a  $\text{pH} = 10.00$  buffer? Assume the buffer  $\text{pH}$  is constant.  $K_{\text{sp}}(\text{Mg}(\text{OH})_2) = 2.06 \times 10^{-13}$ .

$\text{pOH} = 14 - \text{pH} = 4.0$  so  $[\text{OH}^-] = 10^{-4.00}$  and  $[\text{Mg}^{2+}] = K_{\text{sp}}/[\text{OH}^-]^2 =$

- a)  $4.5 \times 10^{-7} \text{ M}$       b)  $2.1 \times 10^{-5} \text{ M}$       c)  $4.7 \times 10^{-5} \text{ M}$       d)  $2.1 \times 10^{-1} \text{ M}$       e)  $2.1 \times 10^{14} \text{ M}$

12. Zinc oxalate,  $\text{ZnC}_2\text{O}_4$ , is a sparingly soluble salt ( $K_{\text{sp}} = 2.7 \times 10^{-8}$ ). However,  $\text{C}_2\text{O}_4^{2-}$  also acts as a ligand with  $\text{Zn}^{2+}$ , forming  $\text{Zn}(\text{C}_2\text{O}_4)_3^{4-}$  with a  $K_f = 1.4 \times 10^8$ . If oxalate anion is present at an **equilibrium concentration** of  $0.010 \text{ M}$  in a solution containing solid zinc oxalate and reaches an equilibrium with respect to all ions,  $[\text{Zn}(\text{C}_2\text{O}_4)_3^{4-}]$  will =

a) Solving by combining equilibria – sum of  $K_{\text{sp}}$  and  $K_f$  reactions:  $\text{ZnC}_2\text{O}_4(\text{s}) + 2\text{C}_2\text{O}_4^{2-}(\text{aq}) \leftrightarrow \text{Zn}(\text{C}_2\text{O}_4)_3^{4-}$  with  $K = K_{\text{sp}}K_f$  or  $K = 3.78$  and  $[\text{Zn}(\text{C}_2\text{O}_4)_3^{4-}] = 3.78[\text{C}_2\text{O}_4^{2-}]^2 =$

or b)  $[\text{Zn}^{2+}] = K/[\text{C}_2\text{O}_4^{2-}] = 2.7 \times 10^{-6} \text{ M}$  and  $[\text{Zn}(\text{C}_2\text{O}_4)_3^{4-}] = (1.4 \times 10^8)(2.7 \times 10^{-6})(0.01)^3 =$

- a)  $1.0 \times 10^{-7} \text{ M}$       b)  $2.8 \times 10^{-6} \text{ M}$       c)  $3.8 \times 10^{-4} \text{ M}$       d)  $2.3 \times 10^{-1} \text{ M}$       e)  $3.8 \text{ M}$

13. Silver chloride is an insoluble salt but can be dissolved by adding  $\text{NH}_3$  which forms the complex ion  $\text{Ag}(\text{NH}_3)_2^+$ . After dissolving  $\text{AgCl}$  by addition of  $\text{NH}_3$ , addition of  $\text{HNO}_3$  results in the re-precipitation of  $\text{Ag}^+$  because:

- a)  $\text{H}^+$  removes  $\text{Cl}^-$  to form  $\text{HCl}$  making  $\text{AgCl}$  less soluble  
b) all nitrate salts are insoluble, so  $\text{AgNO}_3$  precipitates  
c)  $\text{H}^+$  converts  $\text{NH}_3$  to  $\text{NH}_4^+$  so it is no longer a Lewis base to complex  $\text{Ag}^+$   
d) the  $K_{\text{sp}}$  for  $\text{AgCl}$  is lower in the presence of  $\text{NO}_3^-$   
e) all of the above

14. In which of the following reactions will the entropy increase?

only b) has an increase in moles of a higher entropy state – (aq) vs. (s)

- a)  $\text{I}_2(\text{aq}) \leftrightarrow \text{I}_2(\text{s})$       b)  $\text{I}_2(\text{s}) + \text{Br}_2(\text{aq}) \leftrightarrow 2\text{IBr}(\text{aq})$       c)  $\text{I}_2(\text{g}) \leftrightarrow \text{I}_2(\text{s})$   
d)  $2\text{I}(\text{g}) \leftrightarrow \text{I}_2(\text{g})$       e)  $\text{I}_2(\text{aq}) + \text{I}^-(\text{aq}) \leftrightarrow \text{I}_3^-(\text{aq})$

15. When any spontaneous reaction occurs,  $\Delta S_{\text{universe}}$  is

- a) positive      b) negative      c) opposite in sign of  $\Delta S_{\text{system}}$   
d) of the same sign as  $\Delta S_{\text{surroundings}}$

16. For the reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g})$ ,  $\Delta H^\circ = -91.8 \text{ kJ/mol}$ . This reaction is spontaneous for:

$\Delta S < 0$  due to fewer moles of product than reactant so  $\Delta G$  is  $< 0$  at low  $T$

- a) no temperatures  
 b) for low temperatures  
 c) for high temperatures  
 d) all temperatures

Use the table below to answer questions 17 and 18

Compound	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )
CO(g)	-110.5	197.7	-137.2
H <sub>2</sub> (g)	0	130.7	0
CH <sub>3</sub> OH(g)	-201.0	239.9	-162.3

17. Calculate  $K$  (equilibrium constant) at 298 K for the reaction  $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \leftrightarrow \text{CH}_3\text{OH}(\text{g})$

$\Delta G_{rxn}^\circ = -RT \ln K$  or  $K = e^{-\Delta G_{rxn}^\circ / RT}$  and  $\Delta G_{rxn}^\circ = [-162.3 - (-137.2) \text{ kJ mol}^{-1}](1000 \text{ J/kJ}) = -25,100 \text{ J/mol}$  or  $K = e^{-(-25100) / [(8.314)(298)]} =$

- a)  $4.0 \times 10^{-5}$     b) 0.97    c) 1.0    d)  $2.5 \times 10^4$     e)  $1.4 \times 10^{10}$

18. At what temperature will  $\Delta G^\circ$  for the reaction  $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \leftrightarrow \text{CH}_3\text{OH}(\text{g})$  be 0?

$\Delta H_{rxn}^\circ = [-201.0 - (-110.5 \text{ kJ mol}^{-1})] = -90.5 \text{ kJ mol}^{-1}$  and  $\Delta S_{rxn}^\circ = 239.9 - 2(130.7) - 197.7 = -219.2 \text{ J mol}^{-1} \text{ K}^{-1}$  and at  $\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$  or  $T = \Delta H^\circ / \Delta S^\circ = -90,500 / -219.2 =$

- a) 0.5 K    b) 120 K    c) 205 K    d) 413 K    e) 1111 K

19. The reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \leftrightarrow 2\text{HI}(\text{g})$  has a  $\Delta G^\circ = +3.4 \text{ kJ mol}^{-1}$ . If a system starts with  $P_{\text{H}_2} = 0.85 \text{ atm}$  and  $P_{\text{HI}} = 0.010 \text{ atm}$  and  $T = 298\text{K}$ ,  $\Delta G =$

$\Delta G_{rxn} = \Delta G_{rxn}^\circ + RT \ln \{P_{\text{HI}}^2 / P_{\text{H}_2}\}$   
 $= 3.4 \text{ kJ mol}^{-1} + (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(1 \text{ kJ}/1000 \text{ J})(298\text{K}) \ln [(0.010 \text{ atm})^2 / (0.85 \text{ atm})]$   
 $= 3.4 \text{ kJ mol}^{-1} - 22.4 \text{ kJ mol}^{-1} =$

- a)  $-19 \text{ kJ mol}^{-1}$     b)  $-9.5 \text{ kJ mol}^{-1}$     c)  $-7.6 \text{ kJ mol}^{-1}$     d)  $+3.4 \text{ kJ mol}^{-1}$     e)  $+19 \text{ kJ mol}^{-1}$

20. Which of the following cations will **not be precipitated** by the addition of  $\text{Cl}^-$  and of  $\text{SO}_4^{2-}$  (successively in a separation scheme)?

sodium is an always soluble cation

- a)  $\text{Na}^+$     b)  $\text{Pb}^{2+}$     c)  $\text{Ag}^+$     d)  $\text{Ba}^{2+}$

21. Hydrazine ( $\text{N}_2\text{H}_4$ ) is used to make rocket fuel and other products but it has positive  $\Delta G_f$  over all temperatures. A strategy to make it would be to:

- a) make from  $\text{N}_2$  and  $\text{H}_2$ , but using higher temperatures  
 b) make from  $\text{N}_2$  and  $\text{H}_2$ , but use catalysts  
 c) use a more stable reactant than  $\text{H}_2$  (such as  $\text{CH}_4$ )  
 d) use a less stable reactant than  $\text{N}_2$  (such as  $\text{N}_2\text{O}$ )  
 e) have the reaction also produce another unstable product (such as  $\text{N}_3$ )

22. Which of the following substances has the lowest entropy?

- a) Br<sub>2</sub>(g) at room temperature      b) Br<sub>2</sub>(l) at 0°C      c) Br<sub>2</sub>(s) at 0°C  
d) Br<sub>2</sub>(s) at 0 K      e) Br(g) at 1000 K

23 - Bonus. A mixture is expected to contain 0.010 M SO<sub>4</sub><sup>2-</sup> and 0.010 M C<sub>2</sub>O<sub>4</sub><sup>2-</sup>. If the K<sub>sp</sub> values for BaSO<sub>4</sub> and BaC<sub>2</sub>O<sub>4</sub> are 1.1 x 10<sup>-10</sup> and 1.0 x 10<sup>-6</sup>, respectively, the maximum percent of SO<sub>4</sub><sup>2-</sup> that can be precipitated without precipitating any C<sub>2</sub>O<sub>4</sub><sup>2-</sup> is:

We calculate [Ba<sup>2+</sup>] where the more soluble anion (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) starts to precipitate:

[Ba<sup>2+</sup>] = 1.0 x 10<sup>-6</sup>/0.010 = 1.0 x 10<sup>-4</sup> M. Next we calculate the concentration of SO<sub>4</sub><sup>2-</sup> left in equilibrium with that [Ba<sup>2+</sup>]: [SO<sub>4</sub><sup>2-</sup>] = 1.1 x 10<sup>-10</sup>/1.0 x 10<sup>-4</sup> = 1.1 x 10<sup>-6</sup>. The amount left is (1.1 x 10<sup>-6</sup>)(100)/(0.010) = 0.011%. Thus what precipitated was 100% - 0.011% =

- a) 0%      b) 0.01%      c) 91%      d) 99.99%      e) 99.999%

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**Work out Problem (12 pts) – Answer on the back of the Scantron and show work**

25.0 mL of a 0.0810 M acetic acid (K<sub>a</sub> = 1.8 x 10<sup>-5</sup>) is being titrated by 0.100 M NaOH. Determine: a) the volume of base needed to reach the equivalence point and b) the pH (to 3 sig figs) of the titration solution at the equivalence point. You must show your work for full credit. If you make any simplifying assumptions, show and validate them.

a) [HA]V<sub>HA</sub> = [NaOH]V<sub>NaOH</sub> or V<sub>NaOH</sub> = (25.0 mL)(0.0810 M)/0.100M = 20.25 mL (4 pts)

b) At the equivalence point, we use up acetic acid and NaOH and need to look at the back reaction: A<sup>-</sup>(aq) + H<sub>2</sub>O(l) ↔ HA(aq) + OH<sup>-</sup>(aq) using an ICE table

Initial	n/V	0	0
Change	-x	+x	+x
Equil	(n/V) - x	x	x

Where the "initial" concentration of acetate

$$= (25.0 \text{ mL})(0.0810 \text{ mol HA})(1 \text{ mol A}^-/1 \text{ mol HA})/(25 \text{ mL} + 20.25 \text{ mL}) = 0.0448 \text{ M}$$

$$K_b = K_w/K_a = 5.56 \times 10^{-10} = x^2/(0.0448 - x) \sim x^2/0.0448 \text{ (assuming } x \ll 0.0448)$$

$$\text{or } x = [(5.56 \times 10^{-10})(0.0448)]^{0.5} = 4.99 \times 10^{-6} \text{ M (validating assumption)}$$

$$\text{and } pOH = -\log(4.99 \times 10^{-6}) = 5.30 \text{ and } pH = 14 - pOH = 8.70$$