

CHEMISTRY 31 EXAM 2

April 13, 2015

SOLUTIONS

Some Useful Equations and Constants:

K_w (autoprotolysis constant for H_2O) = 1.0×10^{-14}

h = Planck's constant = 6.63×10^{-34} J·s; c = speed of light = 3.00×10^8 m s⁻¹

Debye-Hückel Equation:

$$\log \gamma = \frac{-0.51 \cdot z^2 \sqrt{\mu}}{1 + (\alpha \sqrt{\mu} / 305)}$$

Where: γ = activity coefficient, μ = ionic strength, α = hydrated ion radius, and z = ion charge

Quadratic Equation: for $ax^2 + bx + c = 0$, $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

A. Multiple Choice/Fill in the Blank Section. Only one correct answer for multiple choice questions. (4 points for each question)

1. In the reaction $Ca^{2+} + Y^{4-} \leftrightarrow CaY^{2-}$ ($Y = EDTA$), Ca^{2+} can be considered the:

- a) **Lewis acid** b) ligand c) Lewis base d) complex ion

2. In the reaction (forward direction): $HPO_4^{2-} + H_2O \leftrightarrow H_2PO_4^- + OH^-$, **H_2O** is the Bronsted-Lowry acid.

3. The following salts are dissolved in water. Predict which results in an acidic solution.

- a) NaBr b) $K_2C_2O_4$ c) **$Fe(NO_3)_3$** d) $Ca(OH)_2$

HBr and HNO_3 are strong acids, $H_2C_2O_4$ is a weak acid, and Na and K are group I metals.

4. A student first calculates the solubility of $MgCO_3$ assuming dissolution/dissociation ($MgCO_3(s) \leftrightarrow Mg^{2+} + CO_3^{2-}$) is the only reaction that occurs. Then he finds out that CO_3^{2-} can react significantly with water (forming HCO_3^- and OH^-). Addition of the second reaction will:

- a) decrease solubility b) **increase solubility** c) have no effect on solubility
over what is expected from just dissociation

5. If a photon is produced as an excited atom returns to its ground state, the process is called:

- a) **emission** b) absorption c) infrared light d) Beer's law

6. Benzyl amine is a weak base of moderate polarity. It is desired to transfer it from an octanol (weakly polar, water immiscible solvent) to water. To improve the transfer, one should:

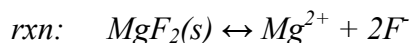
- a) **replace water with a low pH buffer** b) replace water with a high pH buffer
c) replace octanol with hexanol (more polar) d) use a smaller volume of water

7. List the component in a chromatograph that gets the sample into the fluid flow before the column. Component = **injector**

B. Problem Section. Show all needed calculations to receive full credit. The number of points are shown in parentheses. Use the back side of the page if needed.

1. MgF_2 is a sparingly soluble salt ($K_{sp} = 7.4 \times 10^{-9}$).

a) Without considering the effects of activity or secondary reactions, determine the concentration of Mg^{2+} and F^- in a saturated solution of MgF_2 ($K_{sp} = 7.4 \times 10^{-9}$). (8 pts)



initial 0 0

change +x +2x

equil x 2x

$$K_{sp} \text{ (from Appendix F)} = 7.4 \times 10^{-9} = [\text{Mg}^{2+}][\text{F}^-]^2 = (x)(2x)^2 = 4x^3$$

$$x = (7.4 \times 10^{-9}/4)^{0.333} = \mathbf{1.23 \times 10^{-3} \text{ M}} = [\text{Mg}^{2+}], [\text{F}^-] = 2x = \mathbf{2.46 \times 10^{-3} \text{ M}}$$

b) Now if one considers a non-zero ionic strength from dissolution of Mg^{2+} and F^- ions, **qualitatively** (no calculations needed), how does this affect solubility? (4 pts)

The presence of these ions (and increased ion strength) will stabilize the ions and increase their concentrations, increasing solubility. Alternatively, a non-zero ionic strength will decrease activity coefficients from one, requiring higher concentrations so that the activity product (K_{sp}) remains unchanged.

2. Using activities (but not needing to use the systematic method), calculate the pH for a solution containing 0.0050 M NaOH plus 0.0080 M Na_2SO_4 . The K_w (dissociation constant) of water is 1.0×10^{-14} . Assume that SO_4^{2-} does not react any further in water.

a) What is the ionic strength of the solution? (6 pts)

$$\text{concentrations of ions in solution: } [\text{OH}^-] = 0.0050 \text{ M}, [\text{SO}_4^{2-}] = 0.0080 \text{ M},$$

$$[\text{Na}^+] = 0.0050 + 2(0.008) = 0.021 \text{ M}$$

$$\mu = 0.5[(0.021 \text{ M})(+1)^2 + (0.0050)(-1)^2 + (0.0080)(-2)^2] = 0.5(0.058 \text{ M}) = \mathbf{0.029 \text{ M}}$$

b) Using the activity coefficient table (below) and the true definition of the pH, determine the pH (4 sig fig.s) of the solution. (9 pts)

	Activity		Coefficients	
Ionic Strength	0.013 M	0.025 M	0.029 M	0.037 M
H^+	0.904	0.881	0.875	0.866
OH^-	0.888	0.855	0.846	0.831

(Select the closest the ionic strength closest to your calculated value from a)). The systematic approach is not needed.

$$K_w = 1.0 \times 10^{-14} = \gamma(\text{H}^+)[\text{H}^+]\gamma(\text{OH}^-)[\text{OH}^-] \text{ and } \text{pH} = -\log\{\gamma(\text{H}^+)[\text{H}^+]\}$$

by solving the left equation for $\gamma(\text{H}^+)[\text{H}^+]$ and substituting, we get:

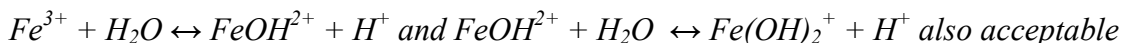
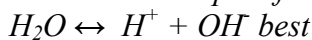
$$\text{pH} = -\log\{1.0 \times 10^{-14}/\gamma(\text{OH}^-)[\text{OH}^-]\} = -\log[1.0 \times 10^{-14}/(0.846 \cdot 0.005)] = -\log(2.36 \times 10^{-12}) = \mathbf{11.63}$$

3. A solution is prepared in which 0.0020 moles of FeCl_3 is dissolved completely in water making a 1.000 L solution. The following reactions are known to occur:

- 1) $\text{FeCl}_3 \rightarrow \text{Fe}^{3+} + 3\text{Cl}^-$ Note: FeCl_3 does not exist as a complex.
- 2) $\text{Fe}^{3+} + \text{OH}^- \leftrightarrow \text{FeOH}^{2+}$
- 3) $\text{FeOH}^{2+} + \text{OH}^- \leftrightarrow \text{Fe}(\text{OH})_2^+$

Assume no other complexation reactions occur. (19 pts)

a) Add one other reaction to the list above. Hint: This reaction would be needed if you wanted to calculate the pH of the solution.



b) Give a charge balance equation based on the listed reactions above (and in a).

$$3[\text{Fe}^{3+}] + 2[\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+] + [\text{H}^+] = [\text{OH}^-] + [\text{Cl}^-]$$

c) Give two mass balance equations based on the reactions and on the initial concentration of the dissolved ionic compound.

Mass balance equations come from the 0.0020 M FeCl_3 ($[\text{FeCl}_3]_o = 0.0020\text{M}$). Since it is an ionic compound, it will totally dissociate giving two mass balance equations: one related to Fe and one to Cl

$$[\text{Cl}^-] = 3[\text{FeCl}_3]_o \text{ or } [\text{Cl}^-] = \mathbf{0.0060\text{ M}}$$

$$[\text{F}]_{\text{Total}} = [\text{FeCl}_3]_o = \mathbf{0.0020\text{ M}} = [\text{Fe}^{3+}] + [\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+]$$

d) Give Equilibrium equations (not reactions), ignoring activity.

no equilibrium for rxn 1

$$K_2 = \frac{[\text{FeOH}^{2+}][\text{Fe}^{3+}][\text{OH}^-]}{[\text{Fe}^{3+}][\text{OH}^-]} \quad K_3 = \frac{[\text{Fe}(\text{OH})_2^+][\text{FeOH}^{2+}][\text{OH}^-]}{[\text{FeOH}^{2+}][\text{OH}^-]}$$

$$K_w = 1.0 \times 10^{-14} = [\text{H}^+][\text{OH}^-]$$

4. Mercury(II) ion (Hg^{2+}) reacts with CH_3CO_2^- in the reaction, $\text{Hg}^{2+} + 2\text{CH}_3\text{CO}_2^- \leftrightarrow \text{Hg}(\text{CH}_3\text{CO}_2)_2(\text{aq})$ forming a complex ion ($K = 2.82 \times 10^8$). Calculate the concentration of CH_3CO_2^- at equilibrium if equilibrium concentrations of Hg^{2+} and $\text{Hg}(\text{CH}_3\text{CO}_2)_2(\text{aq})$ are found to be $1.0 \times 10^{-5}\text{ M}$ and $4.2 \times 10^{-3}\text{ M}$, respectively. Ignore activity for this problem. (8 pts)

$$K = 2.82 \times 10^8 = \frac{[\text{Hg}(\text{CH}_3\text{CO}_2)_2(\text{aq})]}{[\text{Hg}^{2+}][\text{CH}_3\text{CO}_2^-]^2}$$

$$\text{or } [\text{CH}_3\text{CO}_2^-]^2 = \frac{[\text{Hg}(\text{CH}_3\text{CO}_2)_2(\text{aq})]}{K[\text{Hg}^{2+}]} = \frac{(4.2 \times 10^{-3})}{(1.0 \times 10^{-5})(2.82 \times 10^8)}$$

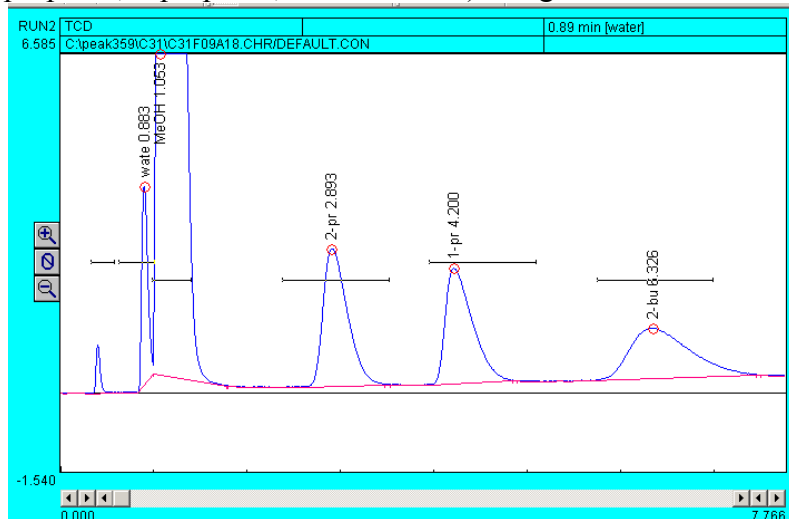
$$\text{or } [\text{CH}_3\text{CO}_2^-] = (1.489 \times 10^{-6})^{0.5} = \mathbf{1.2 \times 10^{-3}\text{ M}}$$

5. Calculate the energy (in J) of an X-ray photon with a wavelength of 8.0 nm. (8 pts)

1 nm = 10^{-9} m ; see p 1 for constants.

$$E = hc/\lambda = (6.63 \times 10^{-34}\text{ J}\cdot\text{s})(3.00 \times 10^8\text{ m/s})/(8.0 \times 10^{-9}\text{ m}) = \mathbf{2.5 \times 10^{-17}\text{ J}}$$

6. Looking at the following chromatogram and data table which show the separation of 3 alcohols (1-propanol, 2-propanol, and 2-butanol) using GC at 150°C.



Compound	Retention Time (min.)	Area	Wb (min.)	Boiling Point (C)
Air (unretained)	0.45	NA	NA	NA
water	0.88	15.6988	0.119149	100
Methanol (solvent)	1.05	754.6922	0.329078	65
2-propanol	2.89	46.9456	0.470922	82.5
1-propanol	4.20	43.8508	0.52766	97
2-butanol	6.33	43.7124	1.236879	99

a. Calculate the retention factor (k) of 1-propanol. (5 pts)

$$k = (4.20 - 0.45) / 0.45 = 8.3$$

b. Increasing the GC oven temperature would have what effect on retention times? Explain (5 pts)
Decrease retention times. Increasing T will increase vapor pressure and decrease time spent in condensed phase.

Bonus Given the retention time of water and 2-butanol and looking at their boiling point temperatures, explain whether you believe the stationary phase is polar or non-polar. (3 pts)

The column is non-polar because two compounds with nearly the same boiling point (volatility elute with very different retention times. In this case an early eluter must have polarity opposite to the stationary phase. Since water is more polar than 2-butanol and elutes early, the stationary phase must be non-polar (more like the 2-butanol).