1. [24 pts] Conceptual Tests – Check the right answer:

A(1) A quantitative transfer is
- (a) a complete transfer of material.
- (b) a liquid transfer using a pipette.
- (c) a powder transfer using a spatula.

A(2) A sample is said to be homogeneous if
- (a) the sample is the same throughout.
- (b) the sample has a different composition in different parts of the sample.
- (c) the sample can be separated into the individual components by filtering the sample.

A(3) Which of these statements concerning the solubility is correct?
- (a) A salt is less soluble if one of its ions is already present in solution.
- (b) A salt is no more soluble if one of its ions is already present in solution.
- (c) A salt is more soluble if one of its ions is already present in solution.

C(4) In the following reaction, identify the conjugate acid-base pair: $H_2PO_4^- + H_2O \leftrightarrow HPO_4^{2-} + H_3O^+$.
- (a) HPO_4^{2-}, H_2O
- (b) $H_2PO_4^-$, H_3O^+
- (c) $H_2PO_4^-$, HPO_4^{2-}

C(5) Which is the strongest base?
- (a) NH3
- (b) CH_3NH_2
- (c) KOH

C(6) In gravimetric analysis, the ideal product should be
- (a) very pure, soluble, and should possess a known composition.
- (b) very pure, insoluble, easily filterable, and should possess an unknown composition.
- (c) very pure, insoluble, easily filterable, and should possess a known composition.

A(7) An activity coefficient
- (a) measures the deviation of behavior of ions from ideality.
- (b) is obtained by multiplying the concentration of a solution times the ionic strength.
- (c) replaces the concentration term in chemical calculations. It corrects for the ionic strength of the solution.

C(8) The Debye-Hückel equation is $\log \gamma = (-0.51z^2\sqrt{\mu})/[1 + (\alpha\sqrt{\mu}/305)]$. Which of the following statements is true?
- (a) As the ionic strength increases, the activity coefficient increases.
- (b) As the charge of the ion increases, the departure of its activity coefficient from unity decreases.
- (c) The smaller the hydrated radius of the ion, the more important activity effects become.

C(9) Define the term precision.
- (a) Precision refers to how close a measured value is to the “true” value.
- (b) Precision refers to how accurately a given measurement is made.

(c) Precision is a measure of the reproducibility of a result.

A(10) A systematic error

(a) can be discovered and corrected.
(b) arises from the limitations on the ability to make a physical measurement.
(c) is also known as an indeterminate error.

A(11) Which of the following in untrue regarding a blank solution?

(a) Solutions containing known concentrations of analyte are called blank solutions.
(b) A solution containing all of the reagents and solvents used in the analysis and no deliberately added analyte is called a blank solution.
(c) A blank solution measures the response of the analytical procedure to impurities or interfering species in the reagents.

C(12) Often the analyst will compare known quantities of analyte to unknown quantities of the material to be analyzed. This may be done in one of three ways: use calibration curves; use standard additions; or use internal standards. The method of standard additions would be used when

(a) the standard solutions and the unknown solution all have similar characteristics are unaffected by the other material in the sample.
(b) the quantity of sample analyzed or the instrument response varies from run to run.
(c) the sample composition is unknown or complex and affects the analytical signal.

2. [14 pts] Unit conversion

(a) [6 pts] A solution was prepared by diluting 10.0 mL of 1.00 x 10^{-3} molar solution of potassium dichromate ($K_2Cr_2O_7$) to 100.0 mL. What is the concentration of potassium in the new solution in ppm?

Fw of $K_2Cr_2O_7$: 294.20

M1V1=M2V2 → So after dilution [$K_2Cr_2O_7$]: 1.00×10^{-4} M

[K] in ppm = $[2\times(1.00\times10^{-4})\times39.10\times10^{3}]$ mg / 1L = 7.82 ppm

(b) [Total 8 pts]

[6 pts] When concentrated hydrochloric acid is sold to the chemist, the label normally lists the concentration of hydrochloric acid as a wt/wt percent and the density of the hydrochloric acid solution. If the solution is 36.0 % (wt/wt %) hydrochloric acid and has a density of 1.18 g/mL, calculate the molarity of concentrated hydrochloric acid (FW: 36.5).

$$\frac{\frac{36\ g}{36.5\ g/mol}}{\frac{100\ g}{1.18\ g/mL} \times \frac{10^{-3} L}{mL}} = \frac{0.9863\ mol}{0.084746\ L} = 11.64\ M$$

[2 pts] How many milliliters of this concentrated hydrochloric acid are needed to make 1 liter 1M of HCl?

$$1\ mol/L \times 1\ L = 11.64\ mol/L \times x\ L$$

$$x = 0.09\ L = 90\ mL$$

+1pt

3. [26 pts] Gravimetric analysis

(a) [12 pts] How many milliliters of 2.15 wt% alcoholic dimthylglycoxime (DMG) should be used to provide a 50% excess for reacting 0.998 4 g of steel containing 2.07 wt% Ni? (The density of the DMG solution is 0.790 g/mL. $Ni^{2+} + 2DMG \rightarrow Ni(DMG)_2 + 2H^+$)

Ni 58.69

DMG 116.12

Ni:

$$0.9984 g \times 2.07\% = 0.020667\ g$$

$$\frac{0.020667 g}{58.69\ g/mol} = 3.521 \times 10^{-4}\ mol$$

DMG:

$$2 \times 3.521 \times 10^{-4}\ mol \times (1 + 0.5) = 1.0563 \times 10^{-3}\ mol$$

$$1.0563 \times 10^{-3}\ mol \times 116.12\ g/mol = 0.1227\ g$$

$$\frac{0.1227\ g}{0.0215} = 5.705003 g = 5.70_5\ g = 5.70\ g\ ✓$$

5.71 g ✓

$$\frac{5.71 g}{0.790\ g/mL} = 7.23\ mL$$

(b) [14 pts] A mixture of mercurous chloride (Hg_2Cl_2 FW 472.09) and mercurous bromide (Hg_2Br_2 FW 560.99) weighs 2.00 g. The mixture is quantitatively reduced to mercury metal (Hg AW 200.59) which weighs 1.50 g. Calculate the % mercurous chloride (Hg_2Cl_2) and mercurous bromide (Hg_2Br_2) in the original mixture.

mol of Hg = 2× mol of Hg_2Cl_2 + 2× mol of Hg_2Br_2

$$\frac{1.50\text{ g}}{200.59\text{ g/mol}} = \frac{2\times(2g\times x)}{472.09} + \frac{2\times[2g(1-x)]}{560.99}$$

$x = 25.9\%$ (Hg_2Cl_2) 74.1% (Hg_2Br_2)

$$1.50 = \frac{2\times 200.59\times x}{472.09} + \frac{2\times 200.59\,(2-x)}{560.99}$$

$x = 0.5182\text{ g}$

4. [36 pts] Chemical equilibrium and ionic strength

(a) [Total 12 pts]

[6 pts] What concentration of oxalate ($C_2O_4^{2-}$) must be added to 0.010 M Ce^{3+} to precipitate 99.9% of Ce^{3+}? ($Ce_2(C_2O_4)_3$ Ksp = 3.0 x 10^{-29})

$Ce_2(C_2O_4)_3 \rightleftharpoons 2Ce^{3+} + 3C_2O_4^{2-}$ $K_{sp} = 3.0\times10^{-29}$

$K_{sp} = [Ce^{3+}]^2[C_2O_4^{2-}]^3 = (0.010\times 0.1\%)^2\times[C_2O_4^{2-}]^3 = 3.0\times10^{-29}$

$[C_2O_4^{2-}] = 6.7\times10^{-7}$ M.

$[C_2O_4^{2-}]^3 = \frac{3.0\times10^{-29}}{1\times10^{-10}} = 3.0\times10^{-19}$

[6 pts] If 0.010 M Ca^{2+} is also in the solution, will Ca^{2+} be precipitated at this point? (CaC_2O_4 Ksp = 1.3 x 10^{-8}; $Ce_2(C_2O_4)_3$ Ksp = 3.0 x 10^{-29})

$CaC_2O_4 \rightleftharpoons Ca^{2+} + C_2O_4^{2-}$ $K_{sp} = 1.3\times10^{-8}$

$Q = [Ca^{2+}][C_2O_4^{2-}] = 0.010\times 6.7\times10^{-7}$

$= 6.7\times10^{-9} < K_{sp}$ for CaC_2O_4

Ca^{2+} will not precipitate.

(b) [12 pts]

[4 pts] Calculate the pH and pOH of a 1.00×10^{-8} M sodium hydroxide solution.

ok no substract ✓

① $pH = -\log[H^+]$ $(pOH = 8.00 \quad pH = 6.00)$

② $pOH = pH = 7.00$ usually pH use 3 sig. figure. 7.000 ✓ +2 pts.

[8 pts] What is the solubility of ferric hydroxide ($Fe(OH)_3$ $K_{sp} = 4.0 \times 10^{-38}$) in this solution?

ok.

$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$
$\quad x \quad 3x$

① $K_{sp} = [Fe^{3+}][OH^-]^3 = 4.0 \times 10^{-38} = x \cdot (3x)^3 = 27x^4$

$x = \sqrt[4]{\frac{4.0 \times 10^{-38}}{27}} = \sqrt[4]{1.4815 \times 10^{-39}} = \sqrt[4]{14.815 \times 10^{-40}}$

$= 1.96 \times 10^{-10}$ M $= 2.0 \times 10^{-10}$ M.

② $K_{sp} = [Fe^{3+}](1.00 \times 10^{-8})^3 = 4.0 \times 10^{-38}$ $\quad [Fe^{3+}] = \frac{4.0 \times 10^{-38}}{1.00 \times 10^{-24}} = 4.0 \times 10^{-14}$ M

(c) [12 pts]

[4 pts] Calculate the ionic strength of a solution that is 0.050 M in K_2SO_4 and 0.010 M in ~~Ba~~ Mg $(NO_3)_2$?

ok ① $\mu = \frac{1}{2}[(0.050 \times 2) \times 1^2 + 0.050 \times 2^2] + \frac{1}{2}[0.010 \times 2^2 + (0.010 \times 2) \times 1^2]$

$= \frac{1}{2}(0.100 + 0.200) + \frac{1}{2} \times (0.040 + 0.020) = 0.150 + 0.030 = 0.180$ M

② +2 pts

$K_2SO_4 + Ba(NO_3)_2 \rightarrow BaSO_4(s) + 2KNO_3$

	0.050	0.010	0.010	0.010 × 2
After.	0.040	0	0	0.020

$\frac{1}{2} \times [(0.040 \times 2) \times 1^2 + 0.040 \times 2^2]$
$+ \frac{1}{2} \times [0.020 \times 1^2 + 0.020 \times 1^2]$
$= \frac{1}{2}(0.080 + 0.160) + \frac{1}{2}(0.020 + 0.020) = 0.120 + 0.020$
$= 0.140$ M

[8 pts] Calculate the pH of water in the above solution at 25°C if the activity coefficients (γ) of H^+ and OH^- are 0.78 and 0.72, respectively.

$H_2O \rightleftharpoons H^+ + OH^-$
$\quad x \quad x \quad x$

$pH = -\log a_{H^+} = -\log \gamma_{H^+}[H^+]$

$K_w = a_{H^+} a_{OH^-} = [H^+]\gamma_{H^+}[OH^-]\gamma_{OH^-} = x \cdot 0.78 \cdot x \cdot 0.72 = 0.5616x^2$

$= 1.00 \times 10^{-14}$

$x = \sqrt{\frac{1}{0.5616} \times 10^{-14}} = 1.3344 \times 10^{-7}$ M

$pH = -\log \gamma_{H^+}[H^+] = -\log(0.78 \times 1.3344 \times 10^{-7}) = -\log(1.040836 \times 10^{-7})$

$= 6.98$