CHEMISTRY 31 EXAM 1
Oct. 5, 2016

SOLUTIONS

Some Useful Equations and Constants:
Propagation of uncertainty:

Addition/subtraction:

$$y = a + b \text{ or } y = a - b$$

$$S_y = \sqrt{S_a^2 + S_b^2}$$

multiplication/division:

$$y = a \cdot b \text{ or } y = a/b$$

$$\frac{S_y}{y} = \sqrt{\left(\frac{S_a}{a}\right)^2 + \left(\frac{S_b}{b}\right)^2}$$

Exponents:

$$y = a^n$$

$$\frac{S_y}{y} = n\frac{S_a}{a}$$

Note: n = constant with no uncertainty

Statistics:
Standard deviation:

$$S = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n-1}}$$

Grubbs Test: $G_{calculated} = \frac{|x_{suspect} - \bar{x}|}{S}$

F-Test: $F_{calc} = S_1^2/S_2^2$ (where $S_1 > S_2$)

Thermodynamics:
$\Delta G = \Delta G° + RT\ln Q$ $\Delta G° = -RT\ln K$ (at equilibrium) $R = 8.314\ J\ mol^{-1}\ K^{-1}$, $0°C = 273.15\ K$

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

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

1. The SI base units for length, mass, time and amount are:

a) meter, kilogram, second, and mole
b) centimeter, gram, second, and mole
c) meter, pound, minute and dozen
d) meter, gram, minute, and mole.

2. A concentration is given in parts per million by mass. An equivalent way of expressing this which is true for any solvent is:

a) (g solute/g solvent)*10^6
b) (g solute)/(10^6 g solution)
c) (μg solute/kg solution)
d) (μg solute)/(L solution)

Note: It was meant that an equivalent way to express the ***units*** *(ppm by mass) is (g solute)/(10^6 g solution). Since the "this" in the second sentence also could refer to a concentration* ***value*** *(in which case it would be equal to (g solute/g* ***solution****)*10^6) – no listed answer is correct), this problem is ambiguous.*

3. A student calibrating a buret in a 0 to 40 mL interval finds that the true volume delivered is 0.07 ± 0.02 mL (mean $\pm$ uncertainty) greater than measured volume. When performing a titration with a measured volume of about 40 mL, the student should:
a) ignore the difference – the measured volume is the true volume
b) ignore the difference – it is insignificant
c) subtract 0.07 mL from the measured volume d) add 0.07 mL to the measured volume
mathematical statement: $V_{true} = 0.07\ mL + V_{meas}$ *So we want to add 0.07 to correct the vol.*

4. In the calculation 98.32 - 7.1, how many significant figures should be used to express the answer?
a) 2 b) 3 c) 4 d) 5
answer = 91.22 (first 2 is place of last significant digit)

5. A researcher has invented a cheaper method to measure glucose in blood. She is interested in comparing the precision of her method compared to a standard method. She measures one blood sample 6 times by her method and the standard method to compare the standard deviations from the two methods. Which test is best to use to compare precision?
a) case 1 t-test b) case 2 t-test c) F-test d) Grubb's test

6. A new method is tested and found to have small standard deviations, under the 1% relative standard deviation desired. A case 1 t-test indicates significant systematic errors of over 5%. We can conclude this method is:
a) accurate and precise b) precise but not accurate
c) accurate but not precise d) neither accurate nor precise

7. A scientist is using an instrument where response is proportional to concentration. The main purpose of analyzing standards for use with a linear least squares calibration in this case is to:
a) determine m and b in the equation of a line to be used in the analysis of unknowns
b) determine if response is related to concentration
c) determine if the analysis is accurate for unknown compounds
d) determine if the uncertainty is from the response or the concentration of standards

8. Given that for $Hg^{2+} + 2CH_3CO_2^- \leftrightarrow Hg(CH_3CO_2)_2(aq)$, $K = 2.8 \times 10^8$ and for $CH_3CO_2H(aq) \leftrightarrow H^+ + CH_3CO_2^-$, $K = 1.8 \times 10^{-5}$, K for $Hg^{2+} + 2CH_3CO_2H(aq) \leftrightarrow Hg(CH_3CO_2)_2(aq) + 2H^+$, is:
a) 9.1×10^{-2} b) 1.0×10^4 c) 2.8×10^8 d) 8.6×10^{17}
If reactions (in order given) are 1, 2 and 3, rxn 3 = rxn1 + 2rxn2
or $K_3 = K_1 K_3^2 = (2.8 \times 10^8)(1.8 \times 10^{-5})^{0.5} =$

9. A reaction requires heat (the reaction container cools) and leads to an increase in disorder. This reaction is:
a) spontaneous at all T b) spontaneous at low T c) spontaneous at high T
d) never spontaneous
$\Delta G = \Delta H - T\Delta S$ *where* $\Delta H > 0$ *and* $\Delta S > 0$. $\Delta G < 0$ *only if the second term is larger (large T)*

10. For the exothermic reaction $NH_3(aq) + H^+ \leftrightarrow NH_4^+$, which of the following will shift the reaction to the product?

a) adding water (dilution) b) increasing the temperature

c) adding a strong acid (e.g. HCl) d) bubble N_2 gas through to remove NH_3 as a gas

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. $AgNO_3$ (aq) is being added to precipitate out Cl^-. Calculate the volume of 0.40 M $AgNO_3$ (in mL) that should be added to 0.61 g of NaCl (formula weight = 58.44 g/mol) so that there is a 10. % excess. (8 pts)

Our reaction is $AgNO_3$ (aq) + NaCl ↔ AgCl(s)
The 10% excess requirement means that n($AgNO_3$ - needed) = n(stoichiometric) + n(excess)
where n(excess) = 0.1n(stoichiometric) or n($AgNO_3$ - needed) = 1.10·n(stoichiometric)
n($AgNO_3$ - needed) = 1.10·n(NaCl) = 1.10(0.61 g NaCl)(1 mol NaCl/58.44 g NaCl)
= 0.01148 mol
$[AgNO_3]V_{AgNO3}$ = 0.01148 mol or V_{AgNO3} = (0.01148 mol)(1 L/0.40 mol)(1000 mL/L)
V_{AgNO3} = 29 mL

2. A metal object is chrome plated by electrical deposition. It is desired to determine the thickness of the chrome plating. The metal object weighs 142.11 ± 0.02 g before plating and 151.98 ± 0.02 g after plating. Given that chrome plating volume = (object surface area)(plating thickness), chrome density = 7.83 ± 0.04 g/cm^3, and the object surface area = 61.1 ± 0.5 cm^2, determine the thickness and uncertainty in thickness (in cm). Give to the correct number of significant figures. (14 pts)

We want to find the chrome plating thickness = t
We know chrome volume = (SA)t (where SA = surface area)
We also can calculate chrome volume from mass and density:
Vol (cm^3) = [mass (g)][1 cm^3/density g] = Δm/density where Δm = m_{final} - $m_{initial}$ (mass gain)
Now we can set this up as one equation: (m_{final} - $m_{initial}$)/density = (SA)t or
t = (m_{final} - $m_{initial}$)/[(density)(SA)]
t = (151.98 ± 0.02 g – 142.11 ± 0.02 g)/[(7.83 ± 0.04 g/cm^3)(61.1 ± 0.5 cm^2)] = 0.02063 cm
Now for propagation of uncertainty: first $S_{\Delta m} = [S^2_{mfinal} + S^2_{minitial}]^{0.5}$ = 0.0283
*Second, we can combine the * and / $S_t/t = [(S_{\Delta m}/\Delta m)^2 + (S_d/d)^2 + (S_{SA}/SA)^2]^{0.5}$*
$S_t/t = [(0.00287)^2 + (0.00511)^2 + (0.00818)^2]^{0.5}$ = 0.010 or S_t = (0.010)(0.0206 cm) = 0.0002 cm
t ± S_t = 0.0206 ± 0.0002 cm

Bonus – 3 pts) Which uncertainty contributed the most to the overall uncertainty?
In *$S_t/t = [(0.00287)^2 + (0.00511)^2 + (0.00818)^2]^{0.5}$ the 3rd term is the largest so **the uncertainty in the surface area** contributed the most*

3. A standard of MTBE (methyl tertiary butyl ether) in gasoline, was analyzed 4 times to test a method. The measured values were: 0.81 wt %, 0.68 wt %, 0.73 wt %, and 0.79 %.
a) Using the table below, give the 95% confidence value about the mean using the correct number of significant figures. (8 pts)

Degrees of freedom	3	4	5
t-value (at 95% level)	3.18	2.776	2.571

Mean = 0.7525 wt % Standard Deviation = 0.0591 wt % n = 4, degrees of freedom = n-1 = 3
95% CI = mean $\pm$ *tS/(n)*$^{0.5}$ *= 0.7525* $\pm$ *3.18(0.0591)/(4)*$^{0.5}$ *= 0.7525* $\pm$ *0.0940 wt %*
With correct sig fig: 95% CI = ***0.75*** $\pm$ ***0.09 wt %***

b) If the true MTBE standard concentration was 0.67 wt %, determine if there was a significant bias in the method at the 95% confidence level. Fully explain your answer. (6 pts)
We need to see if 0.67 wt % is within the confidence interval.
= 0.75 $\pm$ *0.09 wt % = 0.066 wt % to 0.84 wt % which encompasses 0.67 wt % so*
No Significant Bias *is observed*

4. It is desired to measure the concentration of CO emitted from cars. Standards ranging from 25 to 500 ppmv are prepared and analyzed by a CO analyzer giving the following equation for the calibration line:
response = m*concentration + b
where m = 0.950 mV/ppmv and b = -12.1 mV
A 16 year-old car gives a response of 214 mV.
a) Calculate the concentration of CO emitted from this car.
b) Is this value reliable (based on where the value falls relative to standards)?
(9 pts)
a) y = response = mx + b (x = conc.) or x = (y – b)/m = [214 mV – (-12.1 mV)]/(0.950 mV/ppmv)
x = conc. = ***238 ppmv***
b) ***Yes*** *it is reliable – it is near the middle of the calibration range ~260 ppmv*

5. The equilibrium constant for the reaction: $MnCO_3(s) \leftrightarrow Mn^{2+} + CO_3^{2-}$ is 5.3×10^{-10} at 25°C. Determine the value of ΔG° in kJ/mol for the reaction. (7 pts)

$\Delta G° = - RT\ln K = - (8.314\ J/(mol\ K))(273.15 + 25K)\ln(5.3 \times 10^{-10})$
$\Delta G° = (-2478.8\ J/mol)(-21.36)(1\ kJ/1000\ J) = \mathbf{53\ kJ/mol}$

6. Given that the K_{sp} for MgF_2 is 3.9×10^{-11}, determine the solubility of MgF_2 in water in mol/L. (8 pts)

Reaction + ICE Tabel:	$MgF_2(s)$	$\leftrightarrow Mg^{2+}$	+	$2F^-$
Init		0		0
Change		+x		+2x
Equil		x		2x

$K_{sp} = 3.9 \times 10^{-11} = [Mg^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3$
or $x = (3.9 \times 10^{-11}/4)^{1/3} = \mathbf{2.1 \times 10^{-4}\ M = solubility}$