CHEMISTRY 31 EXAM 1
Mar. 2, 2015
KEY

Some Useful Equations and Constants:
Propagation of uncertainty:

Addition/subtraction:

$y = a + b$ or $y = a - b$

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

multiplication/division:

$y = a \cdot b$ 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: $G_{calculated} = \frac{|x_{suspect} - \bar{x}|}{S}$

Thermodynamics:
$\Delta G = \Delta G° + RT\ln Q$ $\quad \Delta G° = -RT\ln K$ (at equilibrium) R = 8.314 J mol^{-1} K^{-1}, 0°C = 273.13 K

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

1. Which of the following units is an SI base unit?
a) centimeter b) minute c) atmosphere **d) mole**

2. The point in a titration in which an indicator changes color (in response to a change in reactant concentration) is called:
a) the end point b) the equivalence point c) the half way point
d) the equilibrium point

3. How many significant figures are there in the value 0.00302?
a) 2 **b) 3** c) 4 d) 5

4. A scientist is analyzing water samples for iron concentration. She wants to see if adding nitric acid will help preserve samples. She has collected 20 samples from different lakes and streams. Half of each sample is treated with nitric acid, and then both (with and without nitric acid) are analyzed for iron. What statistical test should be performed to see if there is a significant difference in iron concentration by adding nitric acid?
a) case 1 t-test **b) case 3 t-test** c) F-test d) Grubbs test

5. When would you want to use a Z-based-, as opposed to a t-based-, confidence interval?
condition: __**when σ (the population standard deviation) is well known**_________

6. Calibration standards are prepared of known concentration and analyzed by an instrument giving a measure response. When using linear least squares properly to fit the data, response is plotted on the __**y-** axis and the uncertainty in response should be _**constant**______.

7. Given that the following reaction: $MgCO_3(s) \Leftrightarrow Mg^{2+} + CO_3^{2-}$ is exothermic, which of the following changes would lead to a shift to the products? Assume the reaction is initially at equilibrium with $MgCO_3(s)$ present.
a) add $MgCO_3(s)$ b) add $MgCl_2(aq)$ **c) add water (dilute reaction)**
d) increase the temperature

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. The actinide thorium (Th) reacts with fluoride as: $Th^{4+} + 4F^{-} \Rightarrow ThF_4$. If 25.0 mL of 0.0246 M Th^{4+} are added to an HF solution,

a) calculate the moles of F^- reacted if the reaction goes to completion. (6 pts)
$n(F^-)/n(Th^{4+}) = 4/1$ or $n(F^-) = 4n(Th^{4+}) = 4(25.0\ mL)(0.0246\ mol/L)(10^{-3}\ L/1\ mL)$
$n(F^-) = 2.46 \times 10^{-3}$ mol

b) calculate the mass (in g) of a 0.521 wt % aqueous HF solution needed to provide the moles of F^- in a). The formula weight of HF is 20.01 g/mol. (6 pts)
mass(HF) = (2.46×10^{-3} mol)(20.01 g/mol) = 0.04922 g HF
0.521 wt % aqueous HF solution means 0.521 g HF/100 g sol'n
mass sol'n = (0.04922 g HF)(100 g sol'n/0.521 g HF) = ***9.45 g***

2. 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 6 year-old car gives a response of 194 mV.
a) Calculate the concentration of CO emitted from this car. (6 pts)
C = (response – b)/m = [194 – (-12.1)]/(0.950 mV/ppmv) = ***217 ppmV***

b) Is this value reliable (based on where the value falls relative to standards)? (4 pts)
This is reliable, because it is in the upper two thirds region (183 to 500 ppmV) of the calibration line.

3. A student has a solution of sulfuric acid, H_2SO_4, of unknown concentration. She pipets 15.0+0.2 mL of the solution into an Ehrlenmeyer flask and titrates it with 0.100$\pm$0.001 M NaOH which reacts as: $H_2SO_4 + 2OH^- \rightarrow Na_2SO_4 + 2H_2O(l)$. The buret delivering the OH^- goes from 0.22$\pm$0.04 to 13.91$\pm$0.04 mL (initial volume to equivalence point). Calculate the concentration of the sulfuric acid in the unknown solution and its absolute uncertainty (with the correct number of significant figures). (20 pts)

$[H_2SO_4] = n(H_2SO_4)/V_{H2SO4} = n(OH^-)(1\ mol\ H_2SO_4/2\ mol\ OH^-)/V_{H2SO4}$

$[H_2SO_4] = 0.5[OH^-]V_{OH-}/V_{H2SO4}$

Since V_{OH-} is determined by buret delivery, it is equal to: 13.91 – 0.22 mL = 13.69 mL

The propagation of uncertainty for this step is the one for addition/subtration:

$S(V_{OH-}) = [S_{V1}^2 + S_{V2}^2]^{0.5} = [0.0032]^{0.5} = 0.0566$

$[H_2SO_4] = 0.5[OH^-]V_{OH-}/V_{H2SO4} = 0.5(0.100\ M)(13.69\ mL)/(15.0\ mL) = 0.04563\ M$

*The remaining steps for calculation of $[H_2SO_4]$ are * and /, so we use those rules:*

$S([H_2SO_4])/[H_2SO_4] = [(S_{[OH-]}/[OH^-])^2 + (S_{(VOH-)}/V_{OH-})^2 + (S_{V(H2SO4)}/V_{H2SO4})^2]^{0.5}$

$S([H_2SO_4])/[H_2SO_4] = [(0.001/0.100)^2 + (0.0566/13.69)^2 + (0.2/15.0)^2]^{0.5} = 0.0172$

$S([H_2SO_4]) = (0.0172)(0.04563\ M) = 0.00078\ M$

$[H_2SO_4] \pm S([H_2SO_4]) = 0.04563 \pm 0.00078\ M =$ ***0.0456 ± 0.0008 M***

4. A research scientist is investigating a new method to determine the concentrations of carbohydrates in food samples which is faster and has potential to be more precise than the old method. A food sample is analyzed 4 times by the new method. The individual values are listed in the table below:

Sample % carbohydrate

Analysis 1	Analysis 2	Analysis 3	Analysis 4
18.5	19.1	19.4	18.8

a) Using the table below, determine the 95% confidence level for the food sample % carbohydrate giving the correct number of significant figures. (10 pts)

t Table for 95% confidence

Degrees of freedom	1	2	**3**	4	5
t value	12.71	4.30	**3.18**	2.78	2.57

mean = 18.95%; standard deviation = 0.387% (absolute sd), n = 4, so n – 1 = 3

95% CI = mean $\pm$ $t(S)/(n)^{0.5}$ = 18.95% $\pm$ $(3.18)(0.387\%)/(4)^{0.5}$

95% CI = 18.95% ± 0.62% or = **19.0 ± 0.6%**

b) If the same food sample was analyzed using the old method, which type of test should be used for the above data to **determine if the new method is more precise**? (4 points)

The F test should be used as that will tell if there is a significant difference in standard deviations for the two methods.

Bonus question (part of #4 on p.3) The scientist needs a 95% confidence of under $\pm$ 1% (absolute uncertainty in % carbohydrate). What is the minimum number of replicate sample analyses needed to meet this using the new method (assuming the standard deviation for other samples will be roughly the same as calculated above)? (3 pts)

We can set $t(S)/(n)^{0.5} < 1$ to meet the desired criterion. We also know that n = 4 (above), gave a 0.6% (below the criterion), so it is likely that 2 or 3 trials are needed and we can calculate the +/- for those numbers: n = 2, $t(S)/(n)^{0.5}$ = 3.5% and n = 3, $t(S)/(n)^{0.5}$ = 0.96%, so ***n = 3 trials is needed***

5. Given the equilibrium constants for reactions 1 to 4 (below), ~~determine the K for reaction 5 (8 pts)~~,

(1) $Cu(OH)_2$ (*s*) ↔ $Cu^{2+} + 2OH^-$ K = 4.8×10^{-20}
(2) $HC_2H_3O_2$ (*aq*) ↔ $H^+ + C_2H_3O_2^-$ K = 1.75×10^{-5}
(3) H_2O (*l*) ↔ $H^+ + OH^-$ K = 1.00×10^{-14}
(4) $Cu^{2+} + 2C_2H_3O_2^-$ ↔ $Cu(C_2H_3O_2)_2$ (*aq*) K = 4.27×10^3
(5) $Cu(OH)_2$ (*s*) + $2HC_2H_3O_2$ (*aq*) ↔ $Cu(C_2H_3O_2)_2$ (*aq*) + $2H_2O$ (*l*)

a) determine **K for reaction 5** (9 pts)

K_5 can be determined by figuring out how reactions 1 through 4 are combined to make reaction 5.

rxn 5 = rxn 1 + 2(rxn 2) -2(rxn 3) + rxn 4 (see below for confirmation)

so $K_5 = K_1K_2^2K_4/K_3^2$ = $\mathbf{6.3 \times 10^3}$

(1)	$Cu(OH)_2$ (s) ↔ ~~Cu^{2+}~~ + ~~$2OH^-$~~
2(2)	$2HC_2H_3O_2$ (aq) ↔ ~~$2H^+$~~ + ~~$2C_2H_3O_2^-$~~
-2(3)	~~$2H^+$~~ + ~~$2OH^-$~~ ↔ $2H_2O$ (l)
(4)	~~Cu^{2+}~~ + ~~$2C_2H_3O_2^-$~~ ↔ $Cu(C_2H_3O_2)_2$ (aq)
sum:	$Cu(OH)_2$ (s) + $2HC_2H_3O_2$ (aq) ↔ $Cu(C_2H_3O_2)_2$ (aq) + $2H_2O$ (l)

b) calculate **ΔG° for reaction 1** at 25°C. [See p. 1 for constants] (7 pts)

ΔG° = -RTlnK = -[8.314 J/(mol K)](273 + 25K)ln(4.8×10^{-20})

ΔG° = -[8.314 J/(mol K)](298 K)(-44.48) = $\mathbf{1.1 \times 10^5}$ ***J/mol***