WRITE YOUR NAME ON EACH EXAM PAGE NOW. THERE ARE 8 QUESTIONS AND 185 TOTAL POINTS IN THIS EXAM. % Score = Points x 100% / 176.

Show clearly all work on these pages. Use the proper number of significant figures and the correct units in all final answers. You must show your calculations and/or reasoning, including equations, on a question to obtain any credit; no credit for answers appearing out of the blue. Your work must be understandable at the time it is being graded to obtain any partial credit.

You do not have to do the final arithmetic on a question unless you need to have a numerical value for the next part of a question, as long as the answer is expressed in its final form and all algebraic manipulations have been made. Very little will be subtracted for routine arithmetic errors, but all numerical answers must be shown to the proper number of significant figures. Programmable calculators must have all memory erased. A calculator may be used, but not shared with anyone else. Tables of data and other information that may be useful are appended to the back of the exam. Use the backs of the pages as scrap paper. Anything written on the backs of pages is totally irrelevant to the grading process.

Unless otherwise stated, assume all solutions are aqueous, density = 1.0000 g/mL; activity coefficients are unity (i.e., activity = concentration); temperature, $T = 298$ K; $K_w = 1.008 \times 10^{-14}$.

QUESTION 1 _________ /10  Question 7 _________ /30
QUESTION 2 _________ /24  Question 8 _________ /30
QUESTION 3 _________ /32  Question 9 _________ /
QUESTION 4 _________ /12  Question 10 _________ /
QUESTION 5 _________ /20  Question 11 _________ /
QUESTION 6 _________ /27  TOTAL _________ /185
1. (10 points) The atomic mass of fluorine is currently listed on periodic tables as 18.998403 g/mol, the most precisely known atomic mass for a naturally occurring element. The least well known is that of osmium at 190.2. Using the standard convention for the uncertainty of a measured number when one is not formally stated, calculate the relative uncertainty in the atomic mass of Os.

2. (24 points) Ferrous ammonium sulfate was used as a standard for iron in the absorbance experiment in lab. The stable solid weighing form has the formula Fe(NH₄)₂(SO₄)₂•6H₂O. Write all the charge- and mass-balance equations for a 0.050 M aqueous solution of “ferrous ammonium sulfate” as written above. Remember that the ammonium ion is the conjugate acid of a weak base. In addition, while the first proton on sulfuric acid ionizes completely, the second proton does not. Technically, the bisulfate ion, HSO₄⁻, is a “weak acid” and there is a measurable $K_{a2}$.
3. (32 points) The concentration of an additive in a standard sample of gasoline was measured 5 times with the following results: 0.13, 0.11, 0.12, 0.20, and 0.14 % by mass.

(a) Calculate the arithmetic average and standard deviation of the data

(b) Calculate the 95% confidence interval.

(c) If the accepted value for the standard sample is 0.11 % by mass, are the results for this set of measurements be significantly different at the 95% confidence level by the $t$ test.
(d) Can any of the data be rejected by the Q test?

4. (12 points) Calculate the change in pH that occurs when 0.050 mmol of a strong acid (such as HCl) is added to 100 mL of 0.0200 M lactic acid plus 0.0800 M sodium lactate. (CH$_3$CHOHCOOH, $K_a = 1.38 \times 10^{-4}$)
5. (20 points) Assuming there is no hydrolysis or complexation of the ions formed, calculate the concentration of the calcium ion in a solution that is saturated with

(a) Calcium fluoride, CaF$_2$, and also 0.050 M in KF. $K_{sp} = 5.3 \times 10^{-9}$

(b) Calcium phosphate, Ca$_3$(PO$_4$)$_2$. $K_{sp} = 2.0 \times 10^{-29}$
6. (27 Points) Fictitious acid (H$_3$Fi) is a triprotic acid with p$K_a$ values of precisely 4.00, 7.00, and 10.00. Calculate the theoretical pH of the following solutions.

(a) 0.15 M trisodium fictate, Na$_3$Fi.

(b) 0.15 M disodium fictate, Na$_2$HFi.

(c) 0.15 M fictitious acid, H$_3$Fi.
7. (30 Points) Very briefly define, explain, or illustrate the following terms.

(a) Electrolytic cell

(b) Peptization

(c) The (statistical) Population

(d) Mass-action effect

(e) Ligand

(f) Cathode
8. (30 Points) Consider the (unbalanced) electrochemical reaction involving the reaction of vanadium (IV) with vanadium (II) to produce vanadium (III).

\[ \text{VO}^{2+} + \text{V}^{2+} \rightleftharpoons \text{V}^{3+} \]

(a) Balance this full cell reaction. [If you wish, you can use the vanadium half-cell reactions on the last page of the exam to assist you.]

(b) Assuming the reaction proceeds spontaneously left to right as above, which species is the oxidizing agent and which is the reducing agent?

(c) Calculate the \( E^0 \) for the full cell reaction. [See half-cell data on last page.]

(d) Is the reaction spontaneous as written (assuming unit activities)? How do you conclude this?

(e) Calculate the equilibrium constant for the cell reaction.
### Confidence Levels for Various Values of $z$

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### Values of $t$ for Various Levels of Probability – Two-Tailed Test ($\pm$)

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### Number of Observations, $n$

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<th>99% C.L.</th>
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SELECTED CONSTANTS, UNITS, AND CONVERSION FACTORS

[The uncertainty in the last digit(s) is shown italicized in parentheses]

Atomic mass constant: \( m_u = 1.660\, 538\, 73 \times 10^{-27} \text{ kg} \)
Avogadro’s number: \( N = 6.022\, 141\, 99 (47) \times 10^{23} \text{ mol}^{-1} \)
Boltzmann constant: \( k = 1.380\, 650\, 3 (24) \times 10^{-23} \text{ J/K} \)
Elementary charge: \( e = 1.602\, 176\, 462 (63) \times 10^{-19} \text{ C} \)
Faraday constant: \( F = 96\, 485.3415 (39) \text{ C/mol} \)
Molar gas constant: \( R = 8.314\, 472 (15) \text{ J/K-mol} = 1.9872 \text{ cal/K-mol} \)
\[ = 0.082\, 057 \text{ L-atm/K-mol} = 0.022\, 414 \text{ m}^3/\text{mol at STP} \]
Pi: \( \pi = 3.141\, 592\, 653\, 6 \)
Planck’s constant: \( h = 6.626\, 068\, 76 (52) \times 10^{-34} \text{ J-s} \)
Speed of light (in a vacuum): \( c = 2.999\, 792\, 458 \text{ (exact)} \times 10^8 \text{ m/s} \)
Stefan-Boltzmann constant: \( \sigma = 5.670\, 400 (40) \times 10^{-8} \text{ W/m}^2\text{-K}^4 \)
Standard acceleration of gravity: \( g_n = 9.806\, 65 \text{ (exact) m/s}^2 \)
Wein constant: \( k = 2.897\, 768\, 6 (51) \times 10^{-3} \text{ m-K} \)

Force: \( 1 \text{ N} = 1 \text{ kg-m/s}^2 \)
Joule: \( 1 \text{ J} = 1 \text{ N-m} = 1 \text{ kg-m}^2/\text{s}^2 = 10^7 \text{ ergs} = 1 \text{ V x 1 C} = 1 \text{ V-C} = (\text{J/C})(\text{C}) \)
Power: \( 1 \text{ W} = 1 \text{ J/s} = 1 \text{ V x 1 A} = 1 \text{ V-A} = (\text{J/C})(\text{C/s}) \)
Electron Volt: \( 1 \text{ eV} = 1.602\, 176\, 462 (63) \times 10^{-19} \text{ J} = 3.827 \times 10^{-20} \text{ cal} \)
Calorie (thermochemical): \( 1 \text{ cal} = 4.184 \text{ J} \) [Food “calorie” = 1 Cal = 1000 cal]

Length: \( 1 \text{ km} = 1000 \text{ m} = 0.62137 \text{ mi} \)
Mass: \( 1 \text{ kg} = 1000 \text{ g} \)
Pressure: \( 101\, 325 \text{ (exact) Pa} = 1 \text{ atm} = 760 \text{ mm Hg} = 17.70 \text{ lb/in}^2 \)
\( 133.322 \text{ Pa} = 1 \text{ torr} = 1 \text{ mm Hg} \)
\( 10^5 \text{ Pa} = 1 \text{ bar} \)
Volume: \( 1 \text{ L} = 10^{-3} \text{ m}^3 = 1000 \text{ mL} = 1000 \text{ cm}^3 = 1.056710 \text{ quarts} \)

Nernst factor: \( (RT/nF) \ln = (0.05916 \text{ V/n}) \log_{10} \text{ at } 25 \text{ }^\circ \text{C} \)
\( nF/RT = 38.920 \text{ n V}^{-1} \)
\( RT/nF = 0.02569/n \text{ V} \)
\( \Delta G^o = -nFE^o = -RT(\ln K_{eq}) \)
\( \Delta G = -nFE = -RT(\ln Q) \)
\( \mu = x + z\sigma/n^{1/2} \)
\( \mu = x + ts/n^{1/2} \)

Some Less Common Multiplicative Prefixes:
\( P = \text{ peta} = 10^{15} \)
\( T = \text{ tera} = 10^{12} \)
\( G = \text{ giga} = 10^9 \)
\( n = \text{ nano} = 10^{-9} \)
\( p = \text{ pico} = 10^{-12} \)
\( f = \text{ femto} = 10^{-15} \)
\( a = \text{ atto} = 10^{-18} \)
\( z = \text{ zepto} = 10^{-21} \)
\( y = \text{ yocto} = 10^{-24} \)

[See http://physics.nist.gov/cuu/index.html for additional information.]
Ion Product for Water
\[ pK_w = 14.3463 \text{ at } 15 \degree C, 13.9965 \text{ at } 25 \degree C, 13.5348 \text{ at } 40 \degree C \]

Amphiprotic Salts (e.g., for NaHA):
\[ [H^+] = \left( \frac{(K_{a2}C_{NaHA} + K_w)}{(1 + C_{NaHA}/K_{a1})} \right)^{\frac{1}{2}} \]

Debye-Huckel Theory
Debye-Huckel Limiting Law (DHLL):
\[ -\log \gamma_i = A z_i^2 \mu^{\frac{1}{2}} = 0.5 z_i^2 \mu^{\frac{1}{2}} \]
Debye-Huckel Equation (DHE):
\[ -\log \gamma_i = \frac{(A z_i^2 \mu^{\frac{1}{2}})/(1 + B a^0 \mu^{\frac{1}{2}})}{\left(0.51 z_i^2 \mu^{\frac{1}{2}}/(1 + 0.33 a^0 \mu^{\frac{1}{2}})\right)} \]

where \( A = 0.5115, B = 0.3291 \) on a volume (molar) basis at 298 K
\( A = 0.5108, B = 0.3286 \) on a mass (molal) basis at 298 K

Ion-size parameters, \( a^0 \), in Angstroms
- 11: Ce\(^{4+}\), Sn\(^{4+}\), Th\(^{4+}\), Zr\(^{4+}\)
- 9: Al\(^{3+}\), Cr\(^{3+}\), Eu\(^{3+}\), Fe\(^{3+}\), H\(^+\), In\(^{3+}\), La\(^{3+}\), Sc\(^{3+}\), Y\(^{3+}\)
- 8: Be\(^{2+}\), Mg\(^{2+}\)
- 6: Ca\(^{2+}\), Co\(^{2+}\), Cu\(^{2+}\), Fe\(^{2+}\), Li\(^+\), Mn\(^{2+}\), Ni\(^{2+}\), Sn\(^{2+}\), Zn\(^{2+}\)
- 5: Ba\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\), Ra\(^{2+}\), Sr\(^{2+}\), S\(^{2-}\)
- 4.5: CH\(_3\)COO\(^-\), Pb\(^{2+}\), CO\(_3^{2-}\), SO\(_3^{2-}\), MoO\(_4^{2-}\), S\(_2\)O\(_3^{2-}\), HPO\(_4^{2-}\)
- 4: Na\(^{+}\), IO\(_3^{-}\), HSO\(_3^{-}\), SO\(_4^{2-}\), PO\(_4^{3-}\)
- 3.5: OH\(^-\), F\(^-\), SCN\(^-\), OCN\(^-\), SH\(^-\), ClO\(_3^{-}\), ClO\(_4^{-}\), BrO\(_3^{-}\), IO\(_4^{-}\)
- 3: CN\(^-\), K\(^+\), Cl\(^-\), Br\(^-\), I\(^-\), NO\(_2^{-}\), NO\(_3^{-}\)
- 2.5: Ag\(^+\), Cs\(^+\), NH\(_4^{+}\), Rb\(^+\), TI\(^+\)

\[ \begin{align*}
V^{2+} + 2 \text{ e}^- & \rightleftharpoons V(s) & E^o &= -1.18 \text{ V} \\
V^{3+} + \text{ e}^- & \rightleftharpoons V^{2+} & E^o &= -0.255 \\
\text{VO}^{2+} + 2 \text{ H}^+ + \text{ e}^- & \rightleftharpoons \text{V}^{3+} + \text{H}_2\text{O} & E^o &= +0.361 \\
\text{VO}_2^{+} + 2 \text{ H}^+ + \text{ e}^- & \rightleftharpoons \text{VO}^{2+} + \text{H}_2\text{O} & E^o &= +1.000
\end{align*} \]