WRITE YOUR NAME ON EACH EXAM PAGE NOW. THERE ARE 7 QUESTIONS AND 104 PERCENT TOTAL IN THIS EXAM.

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, \( T = 298 \text{ K} \); \( K_w = 1.008 \times 10^{-14} \).

QUESTION 1 ___________ / 24  

QUESTION 2 ___________ / 10  

QUESTION 3 ___________ / 12  

QUESTION 4 ___________ / 5  

QUESTION 5 ___________ / 12  

QUESTION 6 ___________ / 29  

TOTAL ___________ / 104
1. (24 Points) You wish to calculate the solubility \( S \) of silver phosphate, \( \text{Ag}_3\text{PO}_4 \), taking into account all possible reactions. Silver phosphate is relatively insoluble, it has a \( K_{sp} \). The hydrogen phosphate ion is one of the acid-base forms originating from phosphoric acid, \( \text{H}_3\text{PO}_4 \), which has three acid dissociation constants. Designate them as \( K_{a1} \), \( K_{a2} \), and \( K_{a3} \).

(a) (10 Points) Write out all the relevant chemical equilibrium reactions for this system, along with the appropriate equilibrium constant for each equation.

(b) (9 Points) Write the mass-balance equation(s) for this system

(c) (5 Points) Write the charge-balance equation for this system.
2. (10 points) The experimental molar solubility, $S$, of Ag$_3$PO$_4$ in water is $4.8 \times 10^{-5}$ M. Calculate the numerical value for the $K_{sp}$ of silver phosphate. *Assume that no hydrolysis or complexation of the dissolved ions occurs.*

3. (12 Points) Calculate the solubility, $S$, of PbI$_2$ in 0.10 M NaI if the $K_{sp}$ for lead iodide is $7.1 \times 10^{-9}$.

4. (5 points) The ferric ion, Fe$^{3+}$, can be complexed by up to three chloride ions to form soluble complexes. The three *stepwise* formational constants have been measured to be $K_{f1} = 30$, $K_{f2} = 135$, and $K_{f3} = 98$. Calculate the value for the *overall* formational constant, $\beta_3$, for the reaction:

$$\text{Fe}^{3+} + 3 \text{Cl}^- \rightleftharpoons \text{FeCl}_3 (aq)$$
5. (12 Points) Calculate the ionic strength of a solution that is 0.030 M in Rb₂SO₄.

6. (29 Points) Calculate the pH of the following aqueous solutions.

   (a) (5 Points) 0.0010 M HCl

   (b) (12 Points) Saturated Pb(OH)₂. \( K_{sp} = 1.2 \times 10^{-15} \).

   (c) (12 Points) 0.075 M sodium hypochlorite, NaOCl. The \( K_a \) for hypochlorous acid is \( 3.0 \times 10^{-8} \).
7. (12 Points) In order to evaluate a spectrophotometric method for the determination of titanium, the method was applied to a certified alloy sample that contained 0.496 % Ti by mass. The average and standard deviation for 8 replicate analyses were 0.482 ± 0.0257 % by mass. Does the mean differ significantly from the certified value at the 95% confidence level?
### Confidence Levels for Various Values of \( z \)

<table>
<thead>
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<th>Confidence Level, %</th>
<th>( z )</th>
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<tr>
<td>68.3</td>
<td>1.000</td>
</tr>
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<tr>
<td>90</td>
<td>1.645</td>
</tr>
<tr>
<td>95</td>
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<td>3.000</td>
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<tr>
<td>99.9</td>
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</table>

\[ z = \frac{(x - \mu)}{\sigma} \]

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

<table>
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<th>Degrees of Freedom, ( \nu )</th>
<th>Factors for the Confidence Interval</th>
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</table>

### Number of Observations, \( n \) (Reject if \( Q_{\text{calc}} > Q_{\text{crit}} \))

<table>
<thead>
<tr>
<th>Observations, ( n )</th>
<th>90% C.L.</th>
<th>95% C.L.</th>
<th>99% C.L.</th>
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<tr>
<td>10</td>
<td>0.412</td>
<td>0.466</td>
<td>0.568</td>
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</table>
SELECTED CONSTANTS, UNITS, AND CONVERSION FACTORS

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

Atomic mass constant:  \( m_u = 1.660 \, 538 \, 73 \times 10^{-27} \, kg \)
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:  \( R = 8.314 \, 472 (15) \, \text{J/K-mol} = 1.9872 \, \text{cal/K-mol} \)
\[ = 0.082 \, 057 \, \text{L-atm/K-mol} = 0.022 \, 414 \, \text{m}^3/\text{mol at STP} \]
\( \pi = 3.141 \, 592 \, 653 \, 6 \)
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:  \( g_n = 9.806 \, 65 \, \text{(exact)} \, \text{m/s}^2 \)
Wein constant:  \( k = 2.897 \, 7686 (57) \times 10^{-3} \, \text{m-K} \)

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

Length:  \( 1 \, \text{km} = 1000 \, \text{m} = 0.62137 \, \text{mi} \)  \( 1 \, \text{in} = 2.54 \, \text{cm (exactly)} \)
Mass:  \( 1 \, \text{kg} = 1000 \, \text{g} \)  \( 1 \, \text{pound} = 453.59237 \, \text{g} \)
Pressure:  \( 101 \, 325 \, \text{(exact)} \, \text{Pa} = 1 \, \text{atm} = 760 \, \text{mm Hg} = 17.70 \, \text{lb/in}^2 \)
\( 133.322 \, \text{Pa} = 1 \, \text{torr} = 1 \, \text{mm Hg} \)  \( 10^5 \, \text{Pa} = 1 \, \text{bar} \)  \( 1 \, \text{Pa} = 1 \, \text{N/m}^2 \)
Volume:  \( 1 \, \text{L} = 10^{-3} \, \text{m}^3 = 1000 \, \text{mL} = 1000 \, \text{cm}^3 = 1.056710 \, \text{quarts} \)

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

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

[See http://physics.nist.gov/cuu/index.html for additional information.]
Ion Product for Water

\[ pK_w = 14.3463 \text{ at } 15 \, ^\circ \text{C}, \quad 13.9965 \text{ at } 25 \, ^\circ \text{C}, \quad 13.5348 \text{ at } 40 \, ^\circ \text{C} \]

Debye-Huckel Theory

Debye-Huckel Limiting Law (DHLL):

\[ - \log \gamma_i = A \frac{z_i^2 \mu^{1/2}}{\mu} = 0.5 \frac{z_i^2 \mu^{1/2}}{\mu} \]

Debye-Huckel Equation (DHE):

\[ - \log \gamma_i = \left( \frac{A z_i^2 \mu^{1/2}}{1 + B a^o \mu^{1/2}} \right) = \left( \frac{0.51 z_i^2 \mu^{1/2}}{1 + 0.33 a^o \mu^{1/2}} \right) \]

\[ A = 0.5115, \quad B = 0.3291 \text{ on a volume (molar) basis at } 298 \, \text{K} \]

\[ A = 0.5108, \quad B = 0.3286 \text{ on a mass (molal) basis at } 298 \, \text{K} \]

Ion-size parameters, \( a^o \), 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\(^+\)