WRITE YOUR NAME ON EACH EXAM PAGE NOW. THERE ARE 8 QUESTIONS AND 103 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 will be ignored unless you add an explanatory note on the front of the page.

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 __________ /6        QUESTION 7 __________ /14

QUESTION 2 __________ /8        QUESTION 8 __________ /34

QUESTION 3 __________ /6        QUESTION 9 __________ /

QUESTION 4 __________ /10       QUESTION 10 __________ /

QUESTION 5 __________ /10       QUESTION 11 __________ /

QUESTION 6 __________ /15       TOTAL __________ /103
Phosphoric acid, \( \text{H}_3\text{PO}_4 \), is very important in biological systems, even though it is a relatively simple inorganic acid. Often referred to as “inorganic phosphate” or “monophosphate”, \( \text{P}_i \), it is involved in a myriad of enzymatic and other biological reactions. Phosphate is a vital constituent of nucleotides and nucleic acids and a major component of calcium hydroxyapatite, \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \), which forms teeth and bones. Although the carbonate buffer primarily controls physiological pH in most mammals, phosphate also contributes to the buffering action.

The \( pK_a \)’s for phosphoric acid, \( \text{H}_3\text{PO}_4 \), are 2.15, 7.20, and 12.15. Questions #1-6 following immediately below deal directly with phosphoric acid and its acid-base properties.

1. (6 Points) Calculate the values of the \( K_a \)’s for phosphoric acid.

2. (8 Points) The pH of blood is normally about 7.40 in healthy humans. Identify the two predominant chemical forms of phosphoric acid (or, “the phosphate system”) at this pH, and calculate the concentration ratio of the basic to the acidic form.
3. (6 Points) Calculate the theoretical pH of a 0.0500 M solution of Na$_2$HPO$_4$. Assume that all the simplifying assumptions that are typically used to reduce an acid-base system to one controlling equilibrium when calculating pHs are valid.

4. (10 Points) Now, calculate the theoretical pH of 0.0500 M Na$_2$HPO$_4$ using the full equation derived when none of the simplifying assumptions is made. [See the last page.]

5. (10 Points) Using the hydrogen ion concentrations obtained from Questions 3 and 4 above, calculate the relative error in the hydrogen ion concentration obtained in Question 3. [This assumes that the more extensive equation provides the “true value”, or at least a better estimate of it.] Does the simple approach provide an acceptable level of error?
6. (15 Points) Calculate the theoretical pH of a solution formed by mixing 50.0 mL of 0.200 M NaH$_2$PO$_4$ with 50.0 mL of 0.120 M HCl?

7. (14 Points) Calculate the pH of a solution that is 0.100 M in 2-(2-aminoethyl)pyridine -- H$_2$NCH$_2$CH$_2$C$_5$H$_5$N, AEP. This is a dibasic compound – the amino group and the ring nitrogen. A handbook table of $pK_a$ values for the protonated forms indicates that the $pK_{a1} = 4.24$ for the diprotonated (+2) form, H$_2$AEP$^{2+}$, and $pK_{a2} = 9.78$ for the monoprotonated (+1) form, H$_2$AEP$^{2+}$. 
8. (34 Points) Barium iodate, $\text{Ba(IO}_3\text{)}_2$, is relatively insoluble [$K_{sp} = 1.57 \times 10^{-9}$]. Iodic acid is a fairly strong “weak acid” [$K_a = 1.7 \times 10^{-1}$]. You wish to calculate the theoretical solubility $S$ of barium iodate in a solution that is also 0.10 M in iodic acid. Because of its acid strength you must use the full systematic approach to solving this problem.

(a) (12 Points) **Accurately** write all the equilibrium reactions for this system. Next to each equation write its associated equilibrium constant.

(b) (5 Points) List **all** the chemical species that exist in this solution whose concentrations are **not** known and must therefore be calculated.

(c) (10 Points) Write the **mass-balance equations** for this system. Let $S$ stand for the equilibrium solubility of barium iodate.

(d) (7 Points) Write the **charge-balance equation** for this solution.
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: \( k = 1.380 \, 650 \, (24) \times 10^{-23} \, \text{J/K} \)

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): \( c = 2.999 \, 792 \, 458 \, (exact) \times 10^8 \, \text{m/s} \)

Stefan-Boltzmann constant: \( \sigma = 5.670 \, 400 \, (40) \times 10^{-8} \, \text{W/m}^2\text{-K}^4 \)

Standard acceleration of gravity: \( g_n = 9.806 \, 65 \, (exact) \, \text{m/s}^2 \)

Wein constant: \( k = 2.897 \, 7686 \, (51) \times 10^{-3} \, \text{m-K} \)

Force: \( 1 \, \text{N} = 1 \, \text{kg-m/s}^2 \)

Joule: \( 1 \, \text{J} = 1 \, \text{N-m} = 1 \, \text{kg-m}^2/\text{s}^2 = 10^7 \, \text{ergs} = 1 \, \text{V} \times 1 \, \text{C} = 1 \, \text{V-C} = (\text{J/C})(\text{C}) \)

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): \( 1 \, \text{cal} = 4.184 \, \text{J} \) \[\text{[Food “calorie”} = 1 \, \text{Cal} = 1000 \, \text{cal} \]

Length: \( 1 \, \text{km} = 1000 \, \text{m} = 0.62137 \, \text{mi} \)

Mass: \( 1 \, \text{kg} = 1000 \, \text{g} \)

Pressure: \( 101 \, 325 \, (exact) \, \text{Pa} = 1 \, \text{atm} = 760 \, \text{mm Hg} = 17.70 \, \text{lb/in}^2 \)

Volume: \( 1 \, \text{L} = 10^{-3} \, \text{m}^3 = 1000 \, \text{mL} \)

Nernst factor: \( (RT/nF) \ln = (0.05916 \, \text{V/n}) \log_{10} \) \[\text{at 25} \, ^\circ \text{C} \]

\[ nF/RT = 38.920 \, n \, \text{V}^{-1} \, \text{K} \]

\[ RT/nF = 0.02569/n \, \text{V} \]

\[ \Delta G = -nFE = -RT(\ln Q) \]

\[ \mu = x \pm z\sigma/\sqrt{n} \]

Some Less Common Multiplicative Prefixes:

\[ \text{P = peta} = 10^{15} \]

\[ \text{T = tera} = 10^{12} \]

\[ \text{G = giga} = 10^9 \]

\[ \text{n = nano} = 10^{-9} \]

\[ \text{p = pico} = 10^{-12} \]

\[ \text{f = femto} = 10^{-15} \]

\[ \text{a = atto} = 10^{-18} \]

\[ \text{z = zepto} = 10^{-21} \]

\[ \text{y = yocto} = 10^{-24} \]

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

Debye-Hückel Theory

Debye-Hückel Limiting Law (DHLL): $-\log \gamma_i = A z_i^2 \mu^{1/2} = 0.5 z_i^2 \mu^{1/2}$

Debye-Hückel Equation (DHE): $-\log \gamma_i = (A z_i^2 \mu^{1/2})/(1 + B a^0 \mu^{1/2})$

$A = 0.5115, B = 0.3291$ 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$^{2+}$, Li$^+$, Mn$^{2+}$, Ni$^{2+}$, 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$^+$, Tl$^+$

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