WRITE YOUR NAME ON EACH EXAM PAGE NOW. THERE ARE 11 QUESTIONS AND
220 POINTS TOTAL IN THIS EXAM. EXAM % = POINTS/2

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, as long as the answer is expressed in its final form
and all algebraic manipulations and numerical substitutions have been made. Little will be
subtracted for routine arithmetic errors. A calculator may be used, but not shared with anyone
else.

A sheet of scrap paper is at the back of the exam booklet. Tear it off now. The two previous
pages contain (a) $z$, $t$, and $Q$-tables and (b) a listing of constants, units, conversion factors, and
some useful equations.

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 x 10^-14.

QUESTION 1 ___________ /21          Question 7 ___________ /24

QUESTION 2 ___________ /30          Question 8 ___________ /10

QUESTION 3 ___________ /10          Question 9 ___________ /22

QUESTION 4 ___________ /16          Question 10 ___________ /28

QUESTION 5 ___________ /15          Question 11 ___________ /30

QUESTION 6 ___________ /14          TOTAL ___________ /220
1. (21 points) The level of a gasoline additive was measured five times with the following results: 0.13, 0.11, 0.12, 0.20, and 0.14 % by mass.

   a. (8 points) Calculate the arithmetic mean and the (absolute) standard deviation of the data.

   b. (7 points) Calculate the 95% confidence limits.

   c. (6 points) Can any of the values be rejected by the Q test at the 90% confidence level.
2. (30 points) Very briefly define, explain, or illustrate the following terms.

   a. Precision

   b. Standard deviation of the mean

   c. Amphiprotic salt

   d. Colloid

   e. Base hydrolysis

   f. Galvanic cell
3. (10 points) Potassium dichromate is a powerful oxidizing agent that can be used to titrate the ethanol in beer, wine, and liquor. The reaction is slow and must be conducted in hot, acidic solutions. Balance the reaction shown below.

\[
\text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Cr}^{3+} + \text{CH}_3\text{COOH}
\]

4. (16 points) A titrimetric method for the determination of calcium in limestone was tested by analysis of an NIST (National Institute of Standards and Technology) standard sample containing 30.15% CaO. The mean and standard deviation of four analyses was 30.26%.

a. Do the data indicate the presence of a systematic error in the method if the standard deviation of the four measurements was \( s = \pm 0.085\% \)?

b. What if was known from many other measurements that \( \sigma = \pm 0.094\% \)?
5. (15 points) Lanthanum hydroxide, La(OH)$_3$, is relatively insoluble, $K_{sp} = 2.0 \times 10^{-19}$. Calculate the equilibrium solubility, $S$, and the resultant pH of a saturated solution.

6. (14 points) Calculate both the resultant absolute and the relative standard deviations for the Nernst factor at 298 K using the currently accepted best values and uncertainties for the gas and Faraday constants as shown below; $n = 1$, and is an integer with no uncertainty; and the best you can control the temperature in a typical experimental situation is to within $\pm 0.02$ K. [+/- is the same thing as $\pm$.]

$$y = \frac{RT}{nF} = \frac{(8.314 \, 472 \, +/- \, 0.000 \, 015 \, J/K\text{-}\text{mol})(298.00 \, +/- \, 0.02 \, K)}{(96 \, 485.3415 \, +/- \, 0.0039 \, \text{C/mol})} = 0.0256796807 \, +/- \, V$$

[Hint: Think carefully for a minute before you start. You can save yourself a lot of arithmetic with a simple simplification.]
7. (24 points) You wish to ascertain whether the mercuric ion will disproportionate in the presence of elemental mercury to form the mercurous ion. That is, will the reaction below proceed spontaneously left to right? Some $E^\circ$ values are provided.

\[
\text{Hg}^{2+}(aq) + \text{Hg}(l) \rightarrow \text{Hg}_2^{2+}(aq)
\]

\[
\begin{align*}
2 \text{Hg}^{2+}(aq) + 2 \text{e}^- &\rightleftharpoons \text{Hg}_2^{2+}(aq) & E^\circ &= +0.920 \text{ V} \\
\text{Hg}^{2+}(aq) + 2 \text{e}^- &\rightleftharpoons \text{Hg}(l) & E^\circ &= +0.854 \\
\text{Hg}_2^{2+}(aq) + 2 \text{e}^- &\rightleftharpoons 2 \text{Hg}(l) & E^\circ &= +0.789
\end{align*}
\]

(a) (10 points) Calculate the $E^\circ$ for the disproportionation reaction above.

(b) (6 points) Will the reaction proceed spontaneously left to right at 25 °C? Why or why not?

(c) (8 points) Calculate the $K_{eq}$ for the reaction.
8. (10 points) Commercial concentrated hydrochloric acid (36.46 g/mol) is approximately 36% by weight HCl and has a density of 1.18 g/mL. How many milliters of the commercial acid would you need in order to prepare 1.0 L of 1.0 M HCl?

9. (22 points) Calcium fluoride, CaF$_2$, is not particularly soluble; it has a relatively large $K_{sp}$. The fluoride ion is the conjugate base of the weak acid HF that has an acid dissociation constant $K_a$. Thus, when CaF$_2$ dissolves the fluoride ion would tend to hydrolyze. In addition, this system is further complicated because the fluoride ion will bind to a calcium ion to form the soluble complex CaF$^+$ with a reasonably large formational constant $K_{f1}$. You wish to calculate exactly the equilibrium solubility, $S$, of CaF$_2$, and the pH of the resultant solution.

(a) (10 points) Write all the pertinent equilibrium reactions and their associated equilibrium constants that are necessary to solve this problem exactly.

(b) (7 points) Write the mass-balance expressions for this system.

(c) (5 points) Write the charge-balance expression.
10. (28 points) Calculate the pH of the following solutions.

a. (9 points) 0.075 M formic acid, HCOOH. $K_a = 1.80 \times 10^{-4}$.

b. (7 points) 0.040 M sodium hydrogen phthalate (KHP), NaHC$_8$H$_4$O$_4$, which is commonly used to make a standard pH solution. $o$-Phthalic acid, H$_2$C$_8$H$_4$O$_4$, is a diprotic acid with $K_{a1} = 1.12 \times 10^{-3}$, $K_{a2} = 3.91 \times 10^{-6}$.

c. (12 points) A 0.40 M solution of pyridine, C$_6$H$_5$N. The acid dissociation constant for the pyridinium ion, C$_6$H$_5$NH$^+$, is $K_a = 5.90 \times 10^{-6}$. 

11. (30 points) Calculate the pH of the following aqueous solutions.

a. (10 points) 20.0 mL of 0.200 M nitrous acid, HNO₂, titrated with 25.0 mL of 0.200 M NaOH. \( K_a \) of nitrous acid = 7.1 x 10⁻⁴.

b. (10 points) 60.0 mL of 0.100 M citric acid \([H_3\text{Cit}]\) titrated with 13.50 mL of 1.000 M NaOH. The \( K_a \)'s for citric acid = 7.45 x 10⁻⁴, 1.73 x 10⁻⁵, 4.02 x 10⁻⁷.

c. (10 points) The second equivalence point in the titration of 20.0 mL of 0.100 M ethylenediamine, \( \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \), [EDA], with 0.100 M HCl. \( K_{b1} = 8.54 \times 10^{-5} \), \( K_{b2} = 7.10 \times 10^{-8} \).
Confidence Levels for Various Values of \( z \)

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Values of \( t \) for Various Levels of Probability

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

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<th>95% C.L.</th>
<th>99% C.L.</th>
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<td>10</td>
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<td>0.568</td>
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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):** \( c = 2.999 \, 792 \, 458 \, (exact) \times 10^8 \, \text{m/s} \)

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

**Length:** \( 1 \, \text{km} = 1000 \, \text{m} = 0.62137 \, \text{mi} \quad 1 \, \text{in} = 2.54 \, \text{cm} \, (\text{exactly}) \)

**Mass:** \( 1 \, \text{kg} = 1000 \, \text{g} \quad 1 \, \text{pound} = 453.59237 \, \text{g} \)

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

**Volume:** \( 1 \, \text{L} = 10^{-3} \, \text{m}^3 = 1000 \, \text{mL} = 1000 \, \text{cm}^3 = 1.056710 \, \text{quarts} \)

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

\[
\begin{align*}
\Delta G^o &= -nFE^o = -RT(\ln K_{eq}) \\
\mu &= \frac{x \pm z \sigma/n^{1/2}}{n} \\
\Delta G &= -nFE = -RT(\ln Q) \\
\mu &= \frac{x \pm ts/n^{1/2}}{n}
\end{align*}
\]

**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.]

Name ________________________________

CHE 226  Final Exam  11  Fall 2003