Chemistry 1A  Fall 2000

Final Exam, Version A  
December 13, 2000

(Closed book, 180 minutes, 350 points)

Name: ______________________    Section Number: ____________________
SID: _______________________    T.A. Name: ________________________

Exam information, extra directions, and useful hints to maximize your score:

- Write your name on all fourteen pages.
- There are two parts to the exam: 1) multiple choice and 2) short answer problems.
- **For the multiple choice problems, fill in the Scantron™ form AND circle the answer on your exam.**
- Answer the questions you know how to do first, then work on the questions you skipped.
- Show all work on the short answer problems for which you want credit and do not forget to include units!
- You may use the back side of the exam pages for scratch paper.
- Some possibly useful equations and diagrams are given on Page 2.

(Do not write in this box; it is for official use only.)

<table>
<thead>
<tr>
<th>Page</th>
<th>Points</th>
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<tbody>
<tr>
<td>3-10</td>
<td>/ 175</td>
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<tr>
<td>11</td>
<td>/ 52</td>
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<td>12-13</td>
<td>/ 75</td>
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<td>14</td>
<td>/ 48</td>
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<tr>
<td>Total</td>
<td>/ 350</td>
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Useful information:

<table>
<thead>
<tr>
<th>Unit Prefixes</th>
</tr>
</thead>
<tbody>
<tr>
<td>milli, m (x 10⁻³)</td>
</tr>
<tr>
<td>kilo, k (x 10³)</td>
</tr>
</tbody>
</table>

- \( E_{\text{photon}} = h = \frac{hc}{\lambda} \)
- \( \lambda_{\text{de Broglie}} = \frac{h}{p} = \frac{h}{mv} \)
- \( E_{\text{Kin}} = \frac{3}{2} nRT \)
- \( v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \)
- \( \Delta G = \Delta H - T\Delta S \)
- \( \Delta E = q + w \)
- \( \Delta G = \Delta G^o + RT\ln Q \)
- \( pX = -\log [X] \)
- \( pH = pK_a + \log \left[ A^- \right]/[HA] \)

\[
\Delta H^o = \sum \Delta H_f^o (\text{products}) - \sum \Delta H_f^o (\text{reactants})
\]

\[
\Delta S^o = \sum S^o (\text{products}) - \sum S^o (\text{reactants})
\]

\[
\Delta G^o = \sum \Delta G_f^o (\text{products}) - \sum \Delta G_f^o (\text{reactants})
\]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Average Bond Enthalpy (kJ/mol)</th>
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<tr>
<td>H-H</td>
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</tr>
<tr>
<td>C-Cl</td>
<td>389</td>
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<tr>
<td>Cl-Cl</td>
<td>242</td>
</tr>
<tr>
<td>H-Cl</td>
<td>431</td>
</tr>
<tr>
<td>Cl-O</td>
<td>270</td>
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<tr>
<td>O=O</td>
<td>497</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H_f^o ) (kJ/mol) at 25°C</th>
<th>( S^o ) (J/mol-K) at 25°C</th>
<th>( \Delta G_f^o ) (kJ/mol) at 25°C</th>
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<tbody>
<tr>
<td>NH₄NO₃ (s)</td>
<td>-365.6</td>
<td>151.1</td>
<td>-183.9</td>
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<tr>
<td>NH₄⁺ (aq)</td>
<td>-132.5</td>
<td>113.4</td>
<td>-79.3</td>
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<tr>
<td>NO₃⁻ (aq)</td>
<td>-205.0</td>
<td>146.4</td>
<td>-108.7</td>
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</table>

\( K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10} \)
Part 1: Multiple Choice.
(5 pts each, 175 pts total)

Instructions: Bubble in the correct answer on your Scantron sheet AND circle the answer on your exam. Each question has one correct answer.

1.) The answer to question 1 is A. Bubble in A on your Scantron™ form.

2.) Which of the following has the highest NO bond order?

A.) NO⁻ B.) NO⁺ C.) NO₂⁻ D.) NO₂⁺ E.) NO₃⁻

3.) In order that the diagram below correctly depict the structure of ICl₂⁻, at what positions should the Cl atoms be drawn?

A.) 1,2 B.) 1,4 C.) 2,3 D.) 2,5 E.) 4,5

4.) A compound contains carbon, hydrogen, and oxygen in the mass percentages given below. What is its empirical formula?

C: 40.0% H: 6.7% O: 53.3%

5.) Two moles of an element are added to a vessel of volume approximately 20 L containing oxygen gas at a pressure of 2 atm at 0°C. All of the element reacts, yielding 1 mole of an oxide and ½ atm of oxygen gas. Which of the following could be the oxide?

A.) Na₂O     B.) CaO          C.) CO₂    D.) Al₂O₃  E.) P₄O₁₀

6.) Blue light (450 nm) ejects photoelectrons from potassium (K) atoms. Light of which color could eject photoelectrons with the same kinetic energy from magnesium (Mg) atoms?

A.) Red       B.) Orange       C.) Yellow     D.) Green  E.) Violet

7.) Which of the following compounds from among ethylene (H₂C=CH₂) and its chlorinated derivatives has the greatest number of structural isomers?

A.) C₂H₄     B.) C₂H₃Cl     C.) C₂H₂Cl₂     D.) C₂HCl₃     E.) C₂Cl₄

8.) Which transition in He⁺ has the same energy difference as the n = 1 → n = 2 transition in a hydrogen atom?

A.) 1 → 2     B.) 1 → 3    C.) 2 → 3     D.) 2 → 4     E.) 3 → 4

9.) Which of the following species has the highest ionization energy?

A.) H (1s)     B.) H (2s)     C.) He⁺ (2s)    D.) He (1s²⁻)     E.) He (1s2p)
10.) Which of the following does **not** correspond to an allowed orbital (set of quantum numbers)?

A.) 1s  B.) 2d  C.) 3d  D.) 4f  E.) 5f

11.) Identify X from the electronic configuration of the ion $X^{-}$ ($1s^22s^22p^63s^2$).


12.) Which of the following atoms or ions is paramagnetic in its ground state?

A.) Be  B.) Cl$^{-}$  C.) Ar  D.) O  E.) Zn

13.) Which has the smallest atomic radius?

A) Ca  B) K  C) Ar  D) Cl  E) S
14.) Select the figure with the correct molecular orbital diagram and bond order.

A.) H₂ (ground state)
   σ*  
   σ  
   Bond Order = 1

B.) He₂ (ground state)
   σ*  
   σ  
   Bond Order = 2

C.) Li₂ (ground state)
   σ*  
   σ  
   Bond Order = 1

D.) O₂ (ground state)
   σ*  
   π*  
   π  
   σ  
   Bond Order = 2

E.) F₂ (ground state)
   σ*  
   π*  
   π  
   σ  
   Bond Order = 1

15.) At a constant pressure of 3.00 atm, 2.00 L of air is cooled from 10.0 °C to –75.0 °C. What is the new volume?

A.) 0.27 L  B.) 1.40 L  C.) 2.96 L  D.) 6.14 L  E.) 13.0 L

16.) The root-mean-square speed of $^{16}O^{16}$ is 482 ms⁻¹ at STP. What is the rms speed of $^{17}O^{18}$ at STP? *(both answers were accepted)*

A.) 441 ms⁻¹  B.) 461 ms⁻¹  C.) 482 ms⁻¹  D.) 501 ms⁻¹  E.) 527 ms⁻¹
17.) The equilibrium constant for the endothermic reaction

\[ \text{N}_2\text{O}_4 (g) \rightleftharpoons 2\text{NO}_2 (g) \]

at 25° C is \( K = 8.8 \). Which could be the magnitude of the equilibrium constant \( K \) at 34° C?

A) 1.1  B) 2.2  C) 4.4  D) 8.8  E) 17.6

18.) For the following reaction at 25° C,

\[ \text{CH}_2\text{ClOOH} (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{CH}_2\text{ClCOO}^- (aq) + \text{H}_3\text{O}^+ (aq) \]

the equilibrium concentrations are \([\text{CH}_2\text{ClCOOH}] = 0.0888 \text{ M}, [\text{CH}_2\text{ClCOO}^-] = [\text{H}_3\text{O}^+] = 0.0112 \text{ M}, \)

and \([\text{H}_2\text{O}] = 55 \text{ M} \). What is the magnitude of the equilibrium constant \( K \)?

A.) \(2.57 \times 10^{-5} \)  B.) \(1.25 \times 10^{-4} \)  C.) \(1.4 \times 10^{-3} \)  D.) \(8.88 \times 10^{-2} \)  E.) \(1.26 \times 10^{-1} \)

19.) Air contains approximately 20 mole percent oxygen and 80 mole percent nitrogen. How many millimoles of molecular oxygen (Henry’s Law constant: \( K = 1.3 \text{ mM/atm} \)) are dissolved in a glass of water (~200mL) at atmospheric pressure?

A.) 32.5  B.) 6.5  C.) 1.3  D.) 0.26  E.) 0.052

20.) For the reaction

\[ \text{CaO} (s) + \text{CO}_2 (g) \rightleftharpoons \text{CaCO}_3 (s) \]

\( \Delta H^\circ \sim -200 \text{ kJ/mol} \) and \( \Delta S^\circ \sim -200 \text{ J/K} \cdot \text{mol} \). At which temperatures is the reaction spontaneous at 1atm?

A.) above 1000 K  B.) below 1000 K  C.) only at 1000 K  D.) at all T  E.) at no T
21.) Consider the gas phase equilibrium reaction:

\[ \text{A(g)} \rightleftharpoons \text{B(g) + C(g)} \]

You decide to carry out this reaction in your flask. The equilibrium constant for this reaction is \( K \) and the reaction is known to be endothermic. Assume that you start with only gas A in your flask and you let the system come to equilibrium. Now, you place your flask in the refrigerator (i.e. you suddenly lower the temperature). In which direction will the reaction proceed?

A.) Right. \( Q \) is now less than \( K \).
B.) Right. \( Q \) is now greater than \( K \).
C.) No change. The system is already at equilibrium and \( Q \) is equal to \( K \).
D.) Left. \( Q \) is now less than \( K \).
E.) Left. \( Q \) is now greater than \( K \).

22.) The following figure shows the temperature dependence of the equilibrium constant, \( K \), for the equilibrium between the liquid and gas phases of an unknown alcohol.

![Temperature Dependence Graph](image)

What temperature is the normal boiling point of the alcohol (i.e. at sea level)?

A.) 0 °C  B.) 20 °C  C.) 40 °C  D.) 60 °C  E.) >60 °C
23.) 1.0 mole of ammonium nitrate (NH₄NO₃) is dissolved in 1.0 liter of water at 25°C. Using the data provided on Page 2, determine the final temperature of the solution.

A.) -6.7°C  B.) 6.7°C  C.) 18.3°C  D.) 28.0°C  E.) 31.7°C

24.) The acid ionization constants are $K_{a1}$ for NH₄⁺ and $K_{a2}$ for HAc. What is $K$ for the following reaction?

$\text{HAc (aq) + NH}_3\text{ (aq) }\rightleftharpoons \text{Ac}^-\text{ (aq) + NH}_4^+\text{ (aq)}$

A.) $K_w$  B.) $K_{a1} K_{a2}$  C.) $(K_{a1} K_{a2})/K_w$  D.) $K_{a1} / K_{a2}$  E.) $K_{a2} / K_{a1}$

25.) You dissolve 0.10 moles of an unknown acid in water and the resulting solution has a volume of 1.0 L. You measure the concentration of $\text{H}_3\text{O}^+$ in this solution and the pH is 3.0. Which of the following statements is true for this unknown acid?

A.) It is a strong acid because the relative Gibbs free energy of the products is higher than that of the reactants.

B.) It is a strong acid because the relative Gibbs free energy of the products is lower than that of the reactants.

C.) It is a weak acid because the relative Gibbs free energy of the products is higher than that of the reactants.

D.) It is a weak acid because the relative Gibbs free energy of the products is lower than that of the reactants.

E.) It is a weak acid because the relative Gibbs free energy of the products equals that of the reactants.

26.) A sample of formic acid (HA, a weak acid) is titrated to the equivalence point with 50 mL of 0.1 M NaOH. 25 mL of 0.1 M HCl are then added to the solution. What is the value of the ratio $[\text{A}^-]/[\text{HA}]$?

A.) 0  B.) 0.5  C.) 1  D.) 2  E.) $\infty$
27.) For the amino acid glycine the carboxyl group (COOH) has a pKₐ = 2.0 and the amino group (NH₃⁺) has a pKₐ = 9.0. Which is the dominant form of glycine in a solution with pH = 6.0?

A.) H₂NCH₂COOH  B.) +H₃NCH₂COOH  C.) H₂NCH₂COO⁻
D.) +H₃NCH₂COO⁻  E.) H₃NCH₂C(OH)₂⁺

For each of the following questions, choose the sketch which best represents the indicated relationship.

28.) ln K vs. 1/T for 2Al(s) + 3Br₂(g) ⇌ 2AlBr₃(s).  [C.]

29.) ∆G° vs. T for the reaction in Question 28.  [B.]

30.) P₉NO₂ vs. P₉N₂O₄ at constant T for N₂O₄(g) ⇌ 2NO₂(g).  [D.]

31.) [Ag⁺ (aq)] vs. [Cl⁻ (aq)] for a solution of 0.1M AgNO₃ titrated with HCl. [E.]

32.) Photon energy vs. wavelength (λ) for electromagnetic radiation.  [E.]

33.) UV absorbance vs. concentration of diluted sun screen lotion.  [A.]

34.) ∆T vs. mass of a metal for a given heat q.  [E.]

35.) Kinetic energy vs. T for an ideal gas.  [A.]
Part 2: Short Answer Problems (175 pts total)

Instructions: Enter answers in the boxes provided. Show your work. Where requested write explanations in fifteen words or less.

1.) (52 points)
There is strong evidence that chlorofluorocarbons (CFCs) are responsible for the “ozone hole” which has occurred in the stratosphere over the South Pole. The ClO radical is involved in this ozone destruction cycle. It is highly reactive and has a tendency to react with ozone (O₃) and oxygen atoms.

a.) The Lewis structure of the ClO radical is given below. Sketch the Lewis structures for the ClO⁺ and ClO⁻ ions.

```
ClO⁺ Structure: +
\:
\:Cl = O:
```

```
ClO⁻ Structure: −
\:
\:Cl - O:
```

b.) Considering the information on Page 2, would you expect a ClO radical to react with an O atom in the stratosphere to form an O₂ molecule and a chlorine atom. Circle your choice and explain.

YES  NO  Not enough information

Explanation: O=O bond energy greater than Cl–O, so the enthalpy contribution is favorable. Entropy change is negligible (unchanged number of gas moles).

c.) Using the data on Page 2, estimate the enthalpy change for the relevant reaction:

\[
\text{ClO}(g) + \text{O}(g) \rightleftharpoons \text{Cl}(g) + \text{O}_2(g).
\]

Cl-O bond enthalpy = 270 kJ/mol  O=O bond enthalpy = 497 kJ/mol

\[ \Delta H^\circ: -227 \text{ kJ/mol} \]

\[ \lambda_{\text{max}}: 308 \text{ nm} \]

C.) ClO radicals in the stratosphere are formed from the reaction of Cl atoms with O₃. The Cl atoms in turn are generated when sunlight hits CFCs like CF₂Cl₂ (also known as Freon-12). Calculate the maximum wavelength (in nanometers) required to break a C-Cl bond in CF₂Cl₂ using the data on Page 2.

C-Cl bond enthalpy = 389 kJ/mol

\[ \text{E}_{\text{photon}} = \frac{\hbar c}{\lambda} \]

\[ \text{Need } E_{\text{molephotons}} = 389 \text{ kJ/mol} = (hc/\lambda)N_0 \]

\[ \lambda = 3.075 \times 10^{-7} \text{ m} \]
2.) (75 points)

Consider the following five solutions in the titration of the weak acid formic acid (HA) with a strong base at 25°C. For this problem, explicitly calculate all quantities.

![Titration Curve for Formic Acid (HA)](image)

a.) Calculate the pH of a 100 mL solution of 0.100 M formic acid (HA, pKₐ = 3.75)?

\[
pK_a = -\log [3.75] \\
K_a = 1.78 \times 10^{-4} \\
HA + H_2O \rightleftharpoons H_3O^+ + A^- \\
K_a = \frac{[x]^2}{[0.100-x]} \text{ where } x \text{ is extent of reaction} \\
x = 4.13 \times 10^{-3} \text{ M using quadratic formula} \\
= 4.22 \times 10^{-3} \text{ M assuming } x \ll 0.100 \\
pH = -\log [H_3O^+] = -\log [4.13] = 2.38 \text{ or } 2.37
\]

b.) To a 100 mL solution of 0.100 M HA, 20 mL of 0.100 M NaOH are added. Calculate the pH of this solution.

NaOH fully dissociates. \([OH^-]_{init} = 0.0020 \text{ moles/120mL}\)

\[
1) HA + H_2O \rightleftharpoons H_3O^+ + A^- \\
2) H_3O^+ + OH^- \rightleftharpoons H_2O + H_2O \quad K = 10^{14} \\
[\text{A}^-]_{eq} = 0.0020 \text{ moles/120mL} = 0.0167 \text{ M} \\
[HA] = (0.00959 \text{ moles} - 0.0020 \text{ moles})/120 \text{mL} = 0.0632 \text{ M} \\
pH = pK_a + \log [\text{A}^-]/[HA] = 3.75 - 0.578 = 3.17
\]
c.) To a 100 mL solution of 0.100 M HA, 100 mL of 0.100 M NaOH are added. Calculate the pH of this solution.

NaOH fully dissociates. \([\text{OH}^-]_{\text{step 1}} = 0.010 \text{ moles/200mL}\]

\[
\begin{align*}
1) & \quad \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \\
2) & \quad \text{H}_3\text{O}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{H}_2\text{O} \quad K = 10^{14}
\end{align*}
\]

\([\text{A}^-]_{\text{step 2}} = 0.010 \text{ moles/200mL} = 0.050 \text{ M}\)

\([\text{HA}]_{\text{step 2}} = 0.000 \text{ moles/200mL} = 0.000 \text{ M}\)

Consider the conjugate base.

\[
\begin{align*}
3) & \quad \text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^- \\
& \quad K_b = Kw/K_a = 5.624 \times 10^{-11}
\end{align*}
\]

\[
K_b = \frac{x}{200\text{mL}}^2/[(0.0100 \text{ moles-x})/200\text{mL}] \quad \text{where x is extent of reaction}
\]

\[
x = 3.35 \times 10^{-7} \text{ moles assuming x } << 0.0100
\]

\[
\text{**pH} = - \log [\text{H}_3\text{O}^+] = - \log \left[\frac{K_w}{(3.35 \times 10^{-7}/200\text{mL})}\right] = - \log [5.97 \times 10^{-9}] = 8.22
\]

\[
\text{or} \quad \text{**[HA]}_{\text{step 3}} = 3.35 \times 10^{-7} \text{ moles/200mL} = 1.675 \times 10^{-6} \text{ M}
\]

\[
\text{[A}^-\text{]}_{\text{step 3}} = 0.010 - 3.35 \times 10^{-7} \text{moles/200mL} = 0.0500 \text{ M}
\]

\[
\text{pH} = pK_a + \log [\text{A}^-]/[\text{HA}] = 3.75 + 4.475 = 8.22
\]

d.) To a 100 mL solution of 0.100 M HA, 160 mL of 0.100 M NaOH are added. Calculate the pH of this solution.

Consider excess NaOH.

\[
\begin{align*}
\text{H}_2\text{O} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \quad K_w = 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-] \\
\text{pH} & = - \log \left[\frac{10^{-14}/(0.00600\text{moles/260mL})}{12.36}
\end{align*}
\]

e.) To a 100 mL solution of 0.100 M HA, 100 mL of 0.100 M NaOH and 40 mL of 0.100 M HCl are added. Calculate the pH of this solution.

one approach: calculate pH as if 60 mL of NaOH has been added (eqn 2) (and keep up with proper total volume).

NaOH fully dissociates. \([\text{OH}^-]_{\text{init}} = 0.0060 \text{ moles/240mL}\]

\[
\begin{align*}
1) & \quad \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \\
2) & \quad \text{H}_3\text{O}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{H}_2\text{O} \quad K = 10^{14}
\end{align*}
\]

\([\text{A}^-]_{\text{eqb}} = 0.0060\text{moles/240mL} = 0.025 \text{ M}\)

\([\text{HA}] = (0.00959\text{moles} - 0.0060\text{moles})/240\text{mL} = 0.0150 \text{ M}\)

\[
\text{pH} = pK_a + \log [\text{A}^-]/[\text{HA}] = 3.75 + 0.222 = 3.97
\]
3.) (2 pts each, 48 pts total)

A gas first expands isothermally against a vacuum (process I) and then is compressed isothermally and reversibly to its original volume and temperature (process II).

Determine the value \((0, < 0, > 0)\) for each of the quantities below for process I, process II, and the overall cyclic process \((I+II)\), and circle your choice. Each of the 24 boxes should have one choice circled.

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<th></th>
<th>I</th>
<th>II</th>
<th>I+II</th>
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<tbody>
<tr>
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<td>0</td>
<td>&lt; 0</td>
</tr>
<tr>
<td><strong>W</strong></td>
<td>&gt; 0</td>
<td>0</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>(\Delta E_{sys})</td>
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<td>&lt; 0</td>
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<tr>
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<tr>
<td>(\Delta S_{univ})</td>
<td>&gt; 0</td>
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