Chem 1A, Fall 2015, Final Exam

December 14, 2015

(Prof. Head-Gordon)^2

Name: ______________________________

Student ID:____________________________ TA: ______________________

Contents: 14 pages

1. Multiple choice (15 points)
2. Molecular orbitals and quantum mechanics (12 points)
3. Acid-Base Equilibria (13 points)
4. Electrochemistry (12 points)
5. Thermochemistry (12 points)
6. Chemical Kinetics (8 points)

Total Points: 72 points (+ 2 bonus points)

Instructions: Closed book exam. Basic scientific calculators are OK. Set brains in high gear and go! Thanks for taking our class, and best wishes for success today, and beyond.

Some possibly useful facts.

$N_0 = 6.02214 \times 10^{23}$ mol^{-1}

$R_y = 2.179874 \times 10^{-18}$ J = 1312 kJ mol^{-1}

$R_y = 3.28984 \times 10^{15}$ Hz

$k = 1.38066 \times 10^{-23}$ J K^{-1}

$h = 6.62608 \times 10^{-34}$ J s

$\hbar = h / 2\pi$

$m_e = 9.101939 \times 10^{-31}$ kg

$c = 2.99792 \times 10^{8}$ m s^{-1}

$R_\infty = 2.18 \times 10^{-18} J$

1eV = 1.602×10^{-19} J

1 J = 1 kg m^2 s^{-2}

Molar volume at STP = 22.4 L

1 V = 1 J / C

1 nm = 10^{-9} m

1 kJ = 1000 J

1 atm = 760 mm Hg = 760 torr ≈ 1 bar

1 L atm ≈ 100 J

T (K) = T (C) + 273.15

F = 96,485 C / mol

$K_w = 1.0 \times 10^{-14}$ (at 25C)

Gas Constant: R = 8.31451 J K^{-1} mol^{-1} or

R = 8.20578×10^{-2} L atm K^{-1} mol^{-1}

Some possibly relevant equations:

Quantum:

$E = h\nu$ $\lambda\nu = c$ $E_n = -\frac{Z^2}{n^2} R_\infty$

$\lambda_{\text{deBroglie}} = h/p = h/mv$
$E_{\text{kin}} (e^-) = h\nu - \Phi = h\nu - h\nu_0$

$\Delta p \Delta x \geq \hbar / 2$ $p = mv$ $KE = \frac{1}{2} m v^2$

Particle in a box (1-D Quantum):

$E_n = h^2 n^2 / 8mL^2$; $n = 1, 2, 3...$

$$\Psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

Vibrational:

$$V(x) = \frac{1}{2} k x^2; \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$E_v = (v + ½)\, hA/2\pi$; $A = (k/m)^{½}$

Rotational:

$$E_{\text{rot}} = hBJ(J+1) \qquad J = 0,1,2...$$

$m = m_A m_B / (m_A + m_B)$

Gases:

$$P = \frac{F}{A} = \frac{mg}{A} = \frac{mgh}{V} = \rho g h$$

$$P_{\text{ideal}} V_{\text{ideal}} = nRT \qquad V_{\text{ideal}} = V - nb$$

$$E_{kin} = \frac{3}{2} RT \qquad \text{v}_{\text{rms}} = \sqrt{\frac{3\text{RT}}{\text{M}}}$$

$$\frac{\text{rate}_A}{\text{rate}_B} = \frac{n_A}{n_B} \sqrt{\frac{M_B}{M_A}} \qquad P_{\text{ideal}} = P + a\left(\frac{n}{V}\right)^2$$

$$f(v) = \left(\frac{2\pi kT}{m}\right)^{-3/2} 4\pi v^2 \exp\left(-mv^2/2kT\right)$$

Acid Base, Solubility, Electrochemistry:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] \qquad pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$K_w = K_a K_b \qquad \text{K}_{\text{sp}} = \left[\text{X}_{(\text{aq})}\right]\left[\text{Y}_{(\text{aq})}\right]$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{nF} \ln Q$$

$$\Delta G^0 = -n\, \mathcal{E}^0\, \mathcal{F}$$

Thermodynamics:

$$\Delta U = q + w \quad w_{irr} = -P_{ex} \Delta V \quad w_{rev} = -nRT \ln\left(V_f / V_i\right)$$

$$\varepsilon = \frac{T_h - T_c}{T_h} = -\frac{w_{net}}{q_{in}} \qquad q = C\Delta T \qquad H = U + PV$$

$$\Delta S = \frac{q_{rev}}{T} \qquad \Omega = CV^N E^{3N/2} \qquad S = k \ln \Omega$$

$\Delta G = \Delta H - T\Delta S$ $\Delta G° = \Delta H° - T\Delta S°$

$\Delta H° = \Sigma\, \Delta H°_f$ (products) - $\Sigma\, \Delta H°_f$ (reactants)

$\Delta S° = \Sigma\, S°$ (products) - $\Sigma\, S°$ (reactants)

$\Delta G° = \Sigma\, \Delta G°_f$ (products) - $\Sigma\, \Delta G°_f$ (reactants)

Equilibrium:

for $aA + bB \rightleftharpoons cC + dD$ $\Delta G = \Delta G° + RT\ln Q$

$$K = \frac{[\text{C}]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b} \quad Q = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad \Delta G° = -RT\ln K$$

Temperature dependence

$$\ln K = -\frac{\Delta H°}{R} \frac{1}{T} + \frac{\Delta S°}{R} \qquad \ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H^{\text{o}}_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Colligative properties:

$$P = x_{\text{solvent}} P_{\text{pure}} \quad \Delta T_{\text{b}} = ik_{\text{b}} \times b \quad \Pi = iRTc \quad P_A = x_{\text{A}} P_{\text{A}}^{\text{o}}$$

Kinetics:

$$\text{rate} = -\frac{1}{a} \frac{d[\text{A}]}{dt} = k[\text{A}]^m [\text{B}]^n$$

0th, 1st, 2nd:

$$[\text{A}] = [\text{A}]_0 - kt \quad [\text{A}] = [\text{A}]_0 \exp(-kt) \quad \frac{1}{[\text{A}]} - \frac{1}{[\text{A}]_0} = kt$$

Temperature dependence:

$$k = \frac{kT}{h} e^{\Delta S^{\circ\dagger}/R} e^{-\Delta H^{\circ\dagger}/RT} \qquad \frac{k_1}{k_2} = \exp\left[-\Delta E_a / RT\right]$$

Michaelis-Menten

$$\text{rate} = \frac{d[\text{P}]}{dt} = \frac{k_2[\text{E}_0][\text{S}]}{K_M + [\text{S}]} \qquad K_M = \frac{k_{-1} + k_2}{k_1}$$

1. Multiple choice (15 points): ***there may be one or more correct solutions, so circle all that apply***

1-1. Using molecular orbitals, which properties is the O_2 molecule predicted to have

(a) 0 unpaired electrons
(b) magnetism
(c) 2 unpaired electrons
(d) no magnetism

1-2. Which sets of hydrogenic atomic orbital quantum numbers (n,l,m) are valid?

(a) (0,0,0)
(b) (1,1,1)
(c) (1,0,-1)
(d) (3,2,1)

1-3. Which molecule(s) would be expected to have an allowed transition in infrared spectroscopy?

(a) N_2
(b) CO_2
(c) HF
(d) F_2

1-4. Consider two reactions, 1 and 2, with $\Delta G_1 < \Delta G_2 < 0$

(a) Reaction 1 is faster
(b) They both proceed at the same rate
(c) Reaction 2 is faster
(d) insufficient information

1-5. The order of this elementary reaction: $A + B \rightarrow C$ is

(a) can't be determined without experiment
(b) 1st order
(c) 2nd order
(d) none of the above

1-6. After spontaneous heat transfer between two systems, the overall multiplicity of the two systems is

(a) minimized
(b) maximized
(c) unity
(d) none of the above

1-7. Which must be independent of temperature when applying the van't Hoff equation?

(a) ΔS^0
(b) a and c
(c) ΔH^0
(d) none of the above

1-8. The units of the rate constant for a second-order elementary reaction is

(a) $\sec^{-1}$
(b) $M^{-1} \bullet \sec^{-1}$
(c) $M \bullet \sec^{-1}$
(d) none of the above

------------------------work space--------------------------

1-9. Which transition in the Li$^{(2+)}$ ion would be expected to have the same frequency as the n=1 → n=2 transition in the H atom?

(a) n=2 → n=3
(b) n=3 → n=4
(c) n=3 → n=5
(d) n=4 → n=6

1-10. Catalysts can work by changing the

(a) reaction mechanism
(b) decreasing the activation energy
(c) decreasing the pre-exponential factor
(d) all of the above

1-11. For a situation where $[E]_0 << [S] << K_M$, the initial rate observed in Michaelis-Menten kinetics

(a) is first order in [E]
(b) plateaus to a maximum rate
(c) is first order in [S]
(d) none of the above

1-12. How much energy is required to raise the temperature of 500g of liquid water by 20°C (its heat capacity is 4.2 J g^{-1} K^{-1})?

(a) 4.2 kJ
(b) 42 kJ
(c) 420 kJ
(d) 4200 kJ

1-13. What is the standard heat of formation of oxygen atoms?

(a) -250 kJ/mol
(b) 0 kJ/mol
(c) +250 kJ/mol
(d) none of the above

1-14. What is the critical temperature of water?

(a) -196°C
(b) 0°C
(c) 100°C
(d) 374°C

1-15. Which of the following correctly describes the interconversion $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$?

(a) $\Delta H<0, \Delta S<0$
(b) $\Delta H>0, \Delta S<0$
(c) $\Delta H<0, \Delta S>0$
(d) $\Delta H>0, \Delta S>0$

-----------------------work space-------------------------

2. (12 points) Molecular orbitals & quantum mechanics.

(a) (2 points) Flame tests identify the metal in a salt by the color of emission when the compound is vaporized in a Bunsen burner. Sodium salts typically show a yellow flame with λ=580nm. What is the energy difference between the levels involved in this emission (in eV)?

Workspace	Answer

(b) (2 points) Suppose an electron in the H atom is at a distance of about 1 Bohr radius from the nucleus. Estimate its minimum kinetic energy using the uncertainty principle.

Workspace	Answer

(c) (2 points) In the left box, draw a molecular orbital energy level diagram for the helium dimer, using the 1s atomic orbitals of each helium atom. Show the AO of each atom clearly on the left and the right, and the MOs clearly in the middle. In the right box, sketch the shape of each MO.

Energy level diagram	Sketch of each MO

(d) (2 points) Use your molecular orbital diagram from part (c) above to predict whether or not the He_2^+ molecular ion would be stable (bound) relative to He + He^+, giving your logic for credit.

Logic	Answer

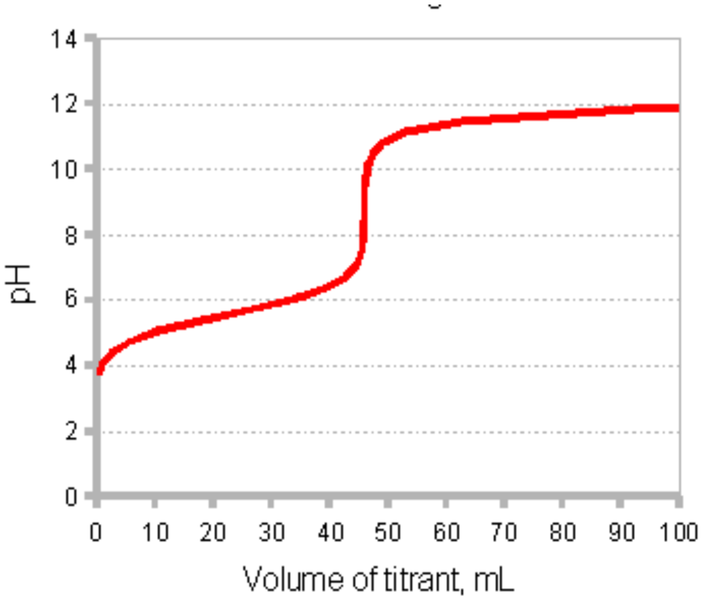
(e) (2 points) What is the structure of the water molecule (left box), and hence what type of hybrid molecular orbitals would you use to describe the molecular orbitals?

Structure of the water molecule (draw and describe)	Type of hybrid orbitals

(f) (2 points) Draw a molecular orbital energy level diagram for the water molecule, showing the energy levels of the hybrid AOs in the left box, the energy levels of the 2 H atoms in the right box, and how they interact to make MOs in the middle box. Label each MO as bonding (σ), antibonding (σ*) or lone-pair (n).

O energy levels	MO energy levels of water	H energy levels

3. (13 points) Acid-base equilibria. A sample of acid is titrated with 0.1M strong base (NaOH) to yield the titration curve shown on right



(a) (1.5 points) Roughly (to +/-3mL) how many mL of strong base (to an accuracy) must be added to reach the stoichiometric point?

(b) (1.5 points) Roughly (give 1 significant figure) what is the pH at the stoichiometric point?

(c) (2 points) Explain clearly why your answer is or is not neutral pH. What is the significance of the value?

(d) (2 points) What is the pKa (to accuracy of +/- 0.5) for this acid? Explain your logic for full credit.

Logic	pK_a

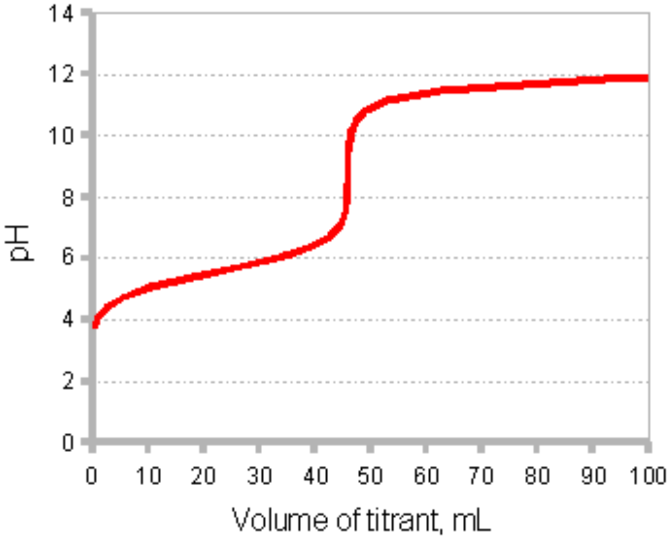
(e) (2 points) Evaluate the number of moles of HA and A^- at the half-equivalence point, giving 1 significant figure in your answer.

workspace	n(HA)	n(A^-)

(f) (2 points) Evaluate the concentration of H^+ and OH^- at the half-equivalence point, giving 1 significant figure in your answer, and showing the units.

workspace	$[H^+]$	$[OH^-]$

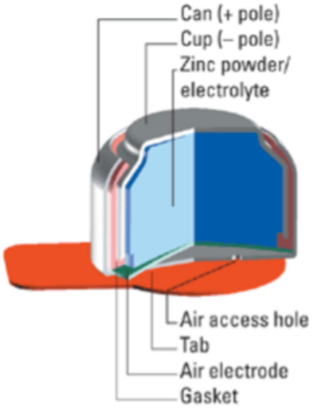
(g) (2 points) Sketch the form of the titration curve on the figure if the initial acid concentration was made two times smaller.



4. Electrochemistry (12 points).

One type of battery that has high energy density is the "zinc-air" battery, which is used in size and weight-sensitive applications such as hearing aids. It uses zinc particles mixed with a damp alkaline electrolyte, and carbon covered by a gas-permeable (but water impermeable) Teflon membrane. The battery is covered by an airtight seal that is removed prior to use. (see diagram)

half-cell reaction	$\mathcal{E}^o$ (V)
$O_{3(aq)} + H_2O_{(l)} + 2e^- \rightarrow O_{2(g)} + 2OH^-_{(aq)}$	1.25
$O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}$	1.23
$O_{2(g)} + 2H_2O_{(l)} + 4e- \rightarrow 4OH^-_{(aq)}$	0.40
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	0.34
$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$	0
$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$	-0.08
$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$	-0.76
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.36



(a) (2 points) Write the half-reaction that is most likely to occur for Zn in the battery, state whether it is oxidation or reduction, and give the name of the electrode at which it occurs.

Reaction:	Oxidation or reduction?	Electrode?

(b) (2 points) The reaction at the other electrode consumes oxygen from the air, and water from the electrolyte at basic pH. Write the half-reaction, state whether it is oxidation or reduction, and give the name of the electrode at which it occurs.

Reaction:	Oxidation or reduction?	Electrode?

(c) (2 points) Use the provided tables of data to evaluate the cell voltage under standard conditions and 25°C.

Workspace	Answer

(d) (2 points) While your reaction from (b) appears to consume water, another reaction also occurs in the Zn-air cell, which is the formation of nearly insoluble ZnO due to hydroxide reacting with zinc ions. Write a balanced equation for this reaction.

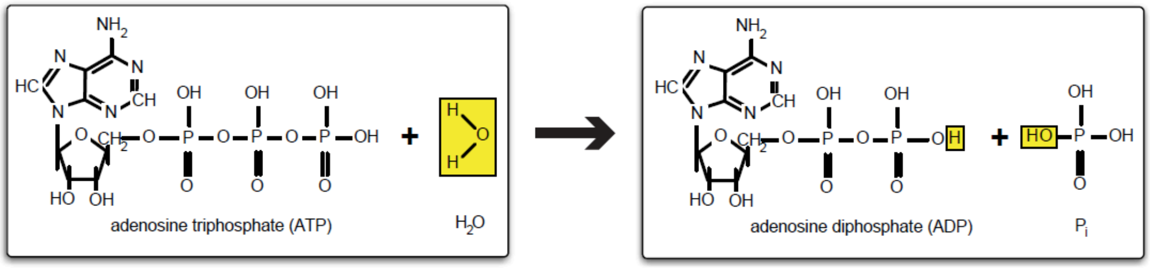
(e) (2 points) Rewrite your reactions from (a) and (b), and combine with reaction (d) to predict the overall stoichiometry of the reaction. Show work for full credit.

Reactions from (a), (b), (d)	
Overall reaction	

(f) (2 points) Suggest (briefly) why the energy density of the zinc-air battery is high relative to a standard alkaline battery (which also uses zinc as one electrode).

5. (12 points) Thermodynamics and Equilibrium. ATP hydrolysis is the reaction by which chemical energy that has been stored in ATP's high-energy bonds is released in order to do useful work by the body.

$$\mathbf{ATP+H_2O \rightarrow ADP+P_i} \qquad \textbf{where } \Delta G^\circ = -31\,\mathrm{kJ/mol}$$



(a) (2 points) Draw resonance structures of H_3PO_4. (labeled as P_i in the equation & diagram above)

(b) (2 points) In light of (a), discuss briefly how this could explain the free energy of hydrolysis.

(c) (2 points) Evaluate the equilibrium constant for ATP hydrolysis.

Workspace	Answer

(d) (2 points) A solution contains [ATP]=30 mM, [ADP]=20 mM ADP, and $[P_i]$=0.25 M. Using your result from part (c), will the reaction proceed spontaneously at room temperature? **You must show your work for credit.**

(e) (2 points) In fact the polyprotic acid H_3PO_4 can dissociate in solution and exhibits 3 pK_as: $pK_{a1}=2.0$, $pK_{a2}=6.6$, $pK_{a3}=12.0$. Write the chemical formulas that correspond to the equilibrium for each pK_a.

pK_{a1}	
pK_{a2}	
pK_{a3}	

(f) (2 points) Using your result (e) (or otherwise), suggest which species is dominant at neutral pH. Give your working for full credit.

Working	Dominant species

6. (8 points) Chemical kinetics. Ozone (O_3) decomposition in the presence of oxygen (O_2) is studied using the method of initial rates. The overall reaction is $2O_3 \rightarrow 3O_2$.

(a) (1.5 points) Doubling the initial O_3 concentration causes the rate to become 4 times **faster**. What is the order of reaction with respect to O_3?

Workspace	Order of reaction

(b) (1.5 points) Doubling the initial O_2 concentration causes the rate to become 2 times **slower**. What is the order of reaction with respect to O_2? (hint: this result will be important for part (d) below)

Workspace	Order of reaction

(c) (1 point) What is experimentally derived expression for the overall reaction rate?

(d) (2 points) How can you tell that this reaction cannot proceed via a single elementary step?

(e) (2 points) The accepted mechanism for this reaction has two steps:

$$\text{(i) } \mathrm{O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2 + O} \qquad \text{(ii) } \mathrm{O_3 + O \xrightarrow{k_2} O_2 + O_2}$$

Suppose the rate of reaction (ii) is slow compared to forward and reverse rates of reaction (i) so that reaction (i) exists as a pre-equilibrium. Show that this mechanism is consistent with your result from (c) and give an expression for the rate constant in terms of k_1, k_{-1}, and k_2.

Derivation	
Rate constant expression	

(f) (Bonus – 2 points – do this only if you are confident and have time!). Analyze the mechanism from (e) applying the steady state approximation to the reactive intermediate, O, to derive a more complex expression for the rate law. Due to our time constraints on grading, credit can only be given for the correct answer – after all it is bonus credit anyway!

Rate equation expression	