5.111 Principles of Chemical Science
Fall 2008

First Hour Exam **5.111**

Write your name below**. Do not open the exam until the start of the exam is announced.** The exam is closed notes and closed book.

1. Read each part of each problem carefully and thoroughly.
2. Read all parts of each problem. MANY OF THE LATTER PARTS OF A PROBLEM CAN BE SOLVED WITHOUT HAVING SOLVED EARLIER PARTS. However, if you need a numerical result that you were not successful in obtaining for the computation of a latter part, make a physically reasonable approximation for that quantity (and indicate it as such) and use it to solve the latter parts.
3. A problem that requests you to "calculate" implies that several calculation steps may be necessary for the problem's solution. You must show these steps clearly and indicate all values, including physical constants used to obtain your quantitative result. Significant figures must be correct.
4. If you don't understand what the problem is requesting, raise your hand and a proctor will come to your desk.
5. Physical constants, formulas and a periodic table are given on the last page. You may detach this page **once the exam has started**.

	Suggested time		
1.	12 minutes	(22 points)	______________
2.	10 minutes	(16 points)	______________
3.	19 minutes	(38 points)	______________
4.	9 minutes	(24 points)	______________

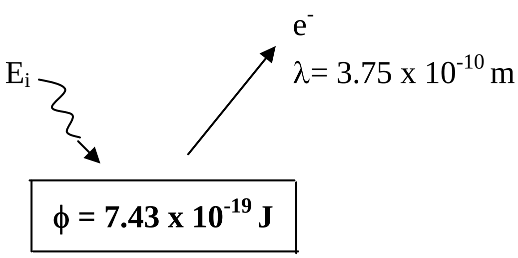
Total (100 points) ________________

Name ____________________________________

1. (22 points) **The photoelectric effect**

A beam of light with an intensity of 15 W is incident on a copper plate ($\phi = 7.43 \times 10^{-19}$ J). Electrons with a minimum wavelength of 3.75×10^{-10} m are ejected from the surface of the copper.

(a) (12 points) Calculate the frequency of the incident light.



K.E. of electron:

$$\lambda = \frac{h}{p} \qquad p = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34}\ \text{Js}}{3.75 \times 10^{-10}\ \text{m}} = 1.7\underline{6}7 \times 10^{-24}\ \text{kgms}^{-1}$$

$\text{Js} \leftarrow \text{kgm}^2\text{s}^{-2}$

$$E = \frac{p^2}{2m_e} = \frac{(1.7\underline{6}7 \times 10^{-24}\ \text{kgms}^{-1})^2}{2\,(9.109 \times 10^{-31}\ \text{kg})} = 1.7\underline{1}38 \times 10^{-18}\ \text{J}$$

$$E_i = \phi + KE$$
$$= 0.74\underline{3} \times 10^{-18} + 1.7\underline{1}4 \times 10^{-18}\ \text{J} = 2.4\underline{5}7 \times 10^{-18}\ \text{J}$$

$$E = h\nu \qquad \nu = \frac{2.4\underline{5}7 \times 10^{-18}\ \text{J}}{6.626 \times 10^{-34}\ \text{J}} = 3.7\underline{0}8 \times 10^{15}\ \text{s}^{-1}$$
$$\nu = \frac{E}{h}$$

$\boldsymbol{\nu = 3.71 \times 10^{15}\ \text{s}^{-1}}$ or 3.71×10^{15} Hz

A beam of light with an intensity of 15 W is incident on a copper plate (ϕ = 7.43 x 10^{-19} J). Electrons with a minimum wavelength of 3.75 x 10^{-10} m are ejected from the surface of the copper.

(b) (6 points) Calculate the maximum number of electrons that can be ejected by a 3.0-second pulse of the incident light.

1 W = 1 J/s

$$3.0\ \text{s} \times \frac{1\underline{5}\ \text{J}}{\text{s}} \times \frac{(\text{photon})}{2.4\underline{5}7 \times 10^{-18}\ \text{J}} = 1.\underline{8}3 \times 10^{19}$$

E per photon calc. in part (a)

1.8 x 10^{19} electrons

(c) (4 points) If a new light source (E_i = 7.19 x 10^{-19} J) with an intensity of 35 W is incident on the copper surface, what is the maximum number of electrons that can be ejected from a 6.0 second pulse of light?

$E_i < \phi$ for copper

zero

2. (16 points) **One-electron atoms:**

Consider a Ca^{19+} ion with its electron in the 5^{th} excited state. ← n = 6 state

(a) (12 points) Calculate the longest wavelength of light that could be emitted when the Ca^{19+} electron transitions to a lower energy state. Report your answer with three significant figures.

longest λ = smallest E
$n_i = 6$ (5^{th} excited state)
$n_f = 5$

$$\nu = Z^2\Re\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = (20)^2\, 3.2898 \times 10^{15}\ s^{-1}\left(\frac{1}{25} - \frac{1}{36}\right)$$

$$\nu = 1.608 \times 10^{16}\ s^{-1}$$

$c = \lambda\nu$ $\qquad \lambda = \dfrac{c}{\nu} = \dfrac{2.9979 \times 10^{8}\ m/s}{1.608 \times 10^{16}\ s^{-1}}$

$\lambda = 1.864 \times 10^{-8}$ m

$\boldsymbol{\lambda = 1.86 \times 10^{-8}}$ m or 18.6 nm

(b) (4 points) Suppose the same transition as in part (a) took place in a **hydrogen atom**. Would the wavelength of emission be longer than, shorter than, or the same as your answer to part (a). Very briefly explain why. *(Note: This question does NOT require a calculation. Also, you do not need to use the answer to part (a) to answer this question.)*

n = 6 to n = 5 in H atom
For H atom, Z =1, so the ν of the emitted light would be lower. Since $\nu = c/\lambda$, the wavelength of the emitted light would be **longer than** the answer to part (a).

3. (32 points) **Multi-electron atoms**

(**a**) (16 points) An x-ray photoelectron spectroscopy experiment with an unidentified element, **X**, displays an emission spectrum with four distinct kinetic energies: 5.9×10^{-17} J, 2.53×10^{-18} J, 2.59×10^{-20} J, and 2.67×10^{-20} J. (Assume the incident light has sufficient energy to eject any electron in the atom.)

(i) (4 points) Name all of the possible ground state atoms that could yield this spectrum.

4 orbitals: 1s, 2s, 2p, 3s

Na or **Mg**

(**ii**) (8 points) Calculate the **binding energy** of an electron in the 2p orbital of element **X** if the x-rays used for the spectroscopy experiment had an energy of 2.68×10^{-16} J.

2p orbital: 2nd lowest IE, so 2nd highest KE.

$KE = 2.53 \times 10^{-18}$ J

$E_i = IE + KE$

$IE = E_i - KE$

$IE = 2.6\underline{8} \times 10^{-16}\ J - 0.0253 \times 10^{-16}\ J$

$IE = 2.6\underline{5}47 \times 10^{-16}\ J$

BE = -IE = **-2.65×10^{-16} J** (also accept -2.66×10^{-16} J)

(**iii**) (4 points) Consider both the filled and unfilled orbitals of element **X**. Determine the number of:

total nodes in a 4d orbital:

n – 1 4 – 1 = **3** total nodes

angular nodes in the $2p_y$ orbital:

ℓ p orbitals have $\ell = 1$ **1** angular node

degenerate 5p orbitals:

same energy

$$\left.\begin{array}{l} 5p_x \\ 5p_y \\ 5p_z \end{array}\right\} \textbf{3}\text{ orbitals}$$

(b) (22 points) The first, second, and third ionization energies of phosphorus are 1011 kJ/mol, 1903 kJ/mol, and 2912 kJ/mol respectively.

$[Ne]3s^2 3p^3$

(i) (8 points) Calculate the effective nuclear charge (Z_{eff}) experienced by a 3p electron in phosphorus.

$$IE = -E_{n,l} = \frac{Z_{eff}^2 R_H}{n^2} \qquad Z_{eff} = \left[\frac{n^2 IE}{R_H}\right]^{1/2}$$

$$IE = \frac{1011k\ J}{mol} \times \frac{1000\ J}{kJ} \times \frac{mol}{6.022 \times 10^{23}} = 1.67\underline{8}8 \times 10^{-18}\ J$$

$$Z_{eff} = \left[\frac{(3)^2 (1.6788 \times 10^{-18}\ J)}{2.1799 \times 10^{-18}\ J}\right]^{1/2} = (6.93\underline{1}1)^{1/2}$$

$\mathbf{Z_{eff} = 2.633}$

(ii) (4 points) Would it be expected that the minimum energy necessary to eject a 3s electron from phosphorus in a photoelectron spectroscopy experiment be **larger**, **smaller**, or **the same** as the 4th ionization energy (IE_4) of phosphorus? Briefly explain your answer.

$$[Ne]\ 3s^2 3p^3 \longrightarrow [Ne]\ 3s^1 3p^3 + e^-$$

The E to eject a 3s electron from P would be **smaller** than the 4th IE because there are more electrons in P, meaning more shielding and a lower Z_{eff}.

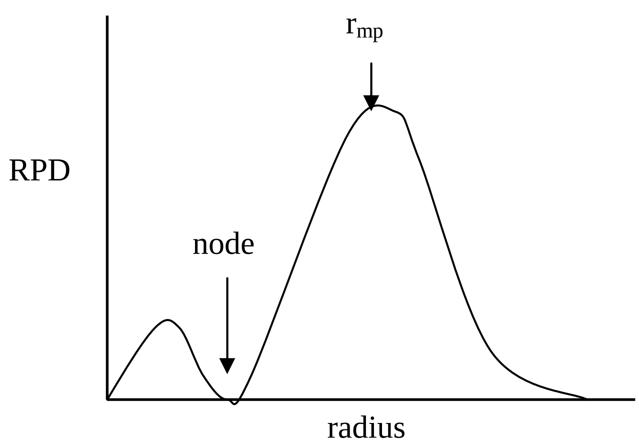
(**iii**) (4 points) Which experience **less** shielding, 3s-electrons or 3p-electrons in phosphorus? Very briefly explain why.

3s 3s e^{-}s penetrate closer to the nucleus, so Z_{eff} avg for 3s > Z_{eff} avg for 3p.

(**iv**) (4 points) On the plot below, graph the radial probability distribution for a phosphorus 3p orbital with a solid line. Label the r_{mp}, and point to each node with an arrow. Label the axes, but do not include numbers or units.

radial nodes: $n - 1 - \ell$

$3 - 1 - 1 = 1$



(**v**) (2 points) Is the r_{mp} for a **hydrogen** 3p orbital **longer** or **shorter** than the r_{mp} for a 3p phosphorus orbital? Very briefly explain why.

r_{mp} for a H 3p orbital is **longer** because Z_{eff} is smaller for the H atom (because Z is less).

4. (24 points) **Periodic trends and miscellaneous short answer**

(**a**) (5 points) Consider the **second** ionization energies (IE_2) for the following 3rd row elements: Si, S, Mg, Al.

(**i**) Which has the highest IE_2?

S

(**ii**) Which has the third highest IE_2?

Si

(**b**) (5 points) Order the following atoms and ions in order of **increasing** atomic radius: Cl, Te, Te^{2-}, S. Note: use the < symbol for clarity.

$Cl < S < Te < Te^{2-}$

(**c**) (6 points) Give the electron configuration expected for the following atoms or ions. *(You may use the noble gas configuration as a means to abbreviate the full configuration.)*

(**i**) Pb (Z = 82)

$[Xe]6s^2 4f^{14} 5d^{10} 6p^2$

(**ii**) Mo (Z = 42)

$[Kr]5s^1 4d^5$ or $\mathbf{[Kr]4d^5 5s^1}$

(**iii**) Zr^+ (Z = 40)

Zr: $[Kr]5s^2 4d^2$ $[Kr]4d^2 5s^2$

Zr^+: $\mathbf{[Kr]4d^2 5s^1}$

(**d**) (4 points) In one sentence (or less!), briefly explain the physical interpretation of $\mathbf{\Psi^2}$ for a hydrogen atom.

probability density of finding the electron

(**e**) (4 points) How many **electrons** in a single atom can have the following two quantum numbers: $n = 7$, $m_l = -3$?

$$\left.\begin{array}{lll} n = 7 & \ell = 6 & m_e = -3 \\ & 5 & -3 \\ & 4 & -3 \\ & 3 & -3 \end{array}\right\} \text{4 orbitals} \rightarrow \textbf{8 electrons}$$

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18[a] VIIIA b
The Active Metals																	Noble Gases
1 H 1.008													The Nonmetals				2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.990	12 Mg 24.305	Transition Elements										13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.29
55 Cs 132.905	56 Ba 137.33	57 La 138.905	* 72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.966	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 Ac 227.028	† 104 Unq (261)	105 Unp (262)	106 Unh (263)												

Inner Transition Metals

* Lanthanides	58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
† Actinides	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Image by MIT OpenCourseWare

$c = 2.9979 \times 10^{8}$ m/s

$h = 6.6261 \times 10^{-34}$ J s

$N_A = 6.022 \times 10^{23}$ mol^{-1}

$m_e = 9.1094 \times 10^{-31}$ kg

$a_o = 5.292 \times 10^{-11}$ m

1 amu $= 1.66 \times 10^{-27}$ kg

$$\lambda = \frac{h}{p}$$

$R_H = 2.1799 \times 10^{-18}$ J

$\Re = R_H/h = 3.2898 \times 10^{15}$ Hz

$$E = \frac{p^2}{2m}$$

$$E_n = -\frac{Z^2 R_H}{n^2}$$

$$E_{nl} = -\frac{Z_{eff}{}^2 R_H}{n^2}$$

1W = 1 J s^{-1}

1 J = 1 kgm^{2}s^{-2}

1 eV $= 1.6022 \times 10^{-19}$ J

for s wavefunction:

RPD $= 4\pi r^2 \Psi^2 dr$

for $n_f < n_i$……

$$v = \frac{Z^2 R_H}{h}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

for $n_f > n_i$…..

$$v = \frac{Z^2 R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$