First Hour Exam

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 x 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:

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

$$E = p^{2} = \frac{(1.7\underline{6}7 \times 10^{-24} \text{ kgms}^{-1})^{2}}{2m_{e}} = 1.7\underline{1}38 \times 10^{-18} \text{ J}$$

$$\begin{split} E_i &= \varphi + KE \\ &= 0.74\underline{3} \ x \ 10^{-18} \ + \ 1.7\underline{1}4 \ x \ 10^{-18} \ J \ = 2.4\underline{5}7 \ x \ 10^{-18} \ J \end{split}$$

$$E = hv \qquad v = 2.457 \times 10^{-18} \text{ J} = 3.708 \times 10^{15} \text{ s}^{-1}$$

$$v = E \qquad 6.626 \times 10^{-34} \text{ J}$$

 $\mathbf{v} = 3.71 \text{ x } 10^{15} \text{ s}^{-1}$ or $3.71 \text{ x } 10^{15} \text{ Hz}$

A beam of light with an intensity of 15 W is incident on a copper plate ($\phi = 7.43 \times 10^{-19} \text{ J}$). 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.

$$1 \text{ W} = 1 \text{ J/s}$$

3.0 s x $\underline{15}$ J x (photon) = $1.\underline{8}3 \times 10^{19}$ s $2.4\underline{5}7 \times 10^{-18}$ J = $1.\underline{8}3 \times 10^{19}$ f E per photon calc. in part (a)

(c) (4 points) If a new light source ($E_i = 7.19 \times 10^{-19} \text{ J}$) 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 5th 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.

 $\begin{array}{l} longest \; \lambda \; = smallest \; E \\ n_i = 6 \; (5^{th} \; excited \; state) \\ n_f = 5 \end{array}$

$$v = Z^{2} \Re \left[\frac{1}{n_{f}^{2}} - \frac{1}{n_{i}^{2}} \right] = (20)^{2} \ 3.2898 \ x \ 10^{15} \ s^{-1} \left[\frac{1}{25} - \frac{1}{36} \right]$$
$$v = 1.608 \ x \ 10^{16} \ s^{-1}$$

c =
$$\lambda v$$

 $\lambda = \frac{c}{v} = \frac{2.9979 \times 10^8 \text{ m/s}}{1.608 \times 10^{16} \text{ s}^{-1}}$
 $\lambda = 1.864 \times 10^{-8} \text{ m}$
 $\lambda = 1.866 \times 10^{-8} \text{ m}$ 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 v of the emitted light would be lower. Since $v = c/\lambda$, 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 x 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: 2^{nd} lowest IE, so 2^{nd} highest KE. KE = 2.53 x 10^{-18} J

$$\begin{split} E_i = IE \ + \ KE & IE \ = E_i - KE \\ IE \ = 2.6\underline{8} \ x \ 10^{\text{-16}} \ J - 0.0253 \ x \ 10^{\text{-16}} \ J \\ IE \ = 2.6\underline{5}47 \ x \ 10^{\text{-16}} \ J \end{split}$$

BE = -IE = -2.65 x 10^{-16} J (also accept -2.66 x 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 2py orbital:

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

degenerate 5p orbitals:

$$\left\{\begin{array}{c} \text{same energy} & 5p_x \\ 5p_y \\ 5p_z \end{array}\right\} \quad \textbf{3 orbitals}$$

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

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

$$IE = -E_{n,l} = \frac{Z_{eff}^{2}R_{H}}{n^{2}} \qquad Z_{eff} = \left[\begin{array}{c}n^{2}IE\\ \hline R_{H}\end{array}\right]^{1/2}$$

$$IE = \frac{1011 \text{ k J}}{\text{mol}} \times \frac{1000 \text{ J}}{\text{ kJ}} \times \frac{\text{mol}}{6.022 \text{ x } 10^{23}} = 1.67\underline{88} \text{ x } 10^{-18} \text{ J}$$

$$Z_{eff} = \left[\begin{array}{c}(3)^{2} (1.6788 \text{ x } 10^{-18} \text{ J})\\ \hline 2.1799 \text{ x } 10^{-18} \text{ J}\end{array}\right]^{1/2} = (6.93\underline{1}1)^{1/2}$$

$$Z_{eff} = 2.633$$

(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 (IE₄) of phosphorus? Briefly explain your answer.

[Ne] $3s^2 3p^3$ [Ne] $3s^1 3p^3 + e^{-3}$

The E to eject a 3s electron from P would be **smaller** than the 4^{th} 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.



(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 (IE₂) for the following 3^{rd} 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, Te²⁻, S. Note: use the < symbol for clarity.

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

(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 $[Kr]4d^{5}5s^{1}$

(iii)
$$Zr^{+} (Z = 40)$$

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

(d) (4 points) In one sentence (or less!), briefly explain the physical interpretation of Ψ^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, $m_l = -3$?

$$n = 7 \qquad \ell = 6 \qquad m_e = -3$$

$$5 \qquad -3$$

$$4 \qquad -3$$

$$3 \qquad -3$$

$$4 \text{ orbitals} \rightarrow 8 \text{ electrons}$$

															$h = 6.6261 \text{ x } 10^{-34} \text{ J s}$
18 ^a VIIIA b	Voble Gases	ر He 4.003	10 Ne 0 170	18	Ar 9.948	36 Kr	83.80	54 Xe 31.29	86 Rn	(777)					$N_A = 6.022 \text{ x } 10^{23} \text{ mol}^{-1}$
VIIA V			9 F	17	U 35.453 3	35 Br	79.904	53 I 126.904	85 At	(017)			71 Lu 174.967	103 Lr (260)	$m_e = 9.1094 \text{ x } 10^{-31} \text{ kg}$
16 VIA		tals	8 0 15 000	16	32.06	34 Se	78.96	52 Te 127.60	Po Po	(607)			70 Yb 173.04	102 No (259)	$a_0 = 5.292 \text{ x } 10^{-11} \text{ m}$
15 VA		e Nonme	7 N 14.007	15 15	г 30.974	33 As	74.922	51 Sb 121.75	83 Bi	06.007			69 Tm 168,934	101 Md (258)	1 amu = 1.66 x 10 ⁻²⁷ kg
14 IVA		The	6 C C	14	28.086	32 Ge	72.59	50 Sn 118.69	82 Pb	7107			68 Er 167.26	100 Fm (257)	$\lambda = \frac{h}{p}$
13 IIIA			5 B 10.81	13	AI 26.982	31 Ga	69.72	49 In 114.82	81 TI	00.402			67 Ho 164.930	99 Es (252)	$\mathbf{R}_{\rm H} = 2.1799 \text{ x } 10^{-18} \text{ J}$
12 IIB					30 Zn	65.38	48 Cd 112.41	80 Hg	60.002		etals	66 Dy 162.50	98 Cf (251)	$\Re = R_{\rm H}/h = 3.2898 \text{ x } 10^{15} \text{ Hz}$	
B							63.546	47 Ag 107.868	79 10	006'061		sition M	65 Tb 158.925	97 Bk (247)	$E=\frac{p^2}{2}$
10						28 Ni 58.69 58.69 58.69 76 76 76 76 76 195.08 195.08 195.08 195.08 26 54 54 54 55 54 54 55 55 56 54 56 56 56 56 56 56 56 56 56 56 56 56 56			96 Cm (247)	2m					
9 VIIIB				nts	27 Co	58.933	45 Rh 102.906	77 Ir 192.22	77.761		Ini	63 Eu 151.96	95 Am (243)	$\mathbf{E}_{n} = -\frac{\mathbf{Z}^{2}\mathbf{R}_{H}}{n^{2}}$	
∞						26 Fe	55.847	44 Ru 101.07	97 SO	7'041			62 Sm 150.36	94 Pu 8 (244)	$\mathbf{E}_{\rm nl} = -\frac{\mathbf{Z}_{\rm eff}^2 \mathbf{R}_{\rm H}}{n^2}$
7 VIIB							54.938	43 Tc (98)	75 Re	17:001			61 Pm (145)	93 Np 237.048	$1W - 1 L s^{-1}$
6 VIB						24 C	51.996	42 Mo 95.94	74 W	106 106 Unh	(263)		60 Nd 144.24	92 U 238.029	$1 \text{ W} = 13 \text{ S}^{-1}$ $1 \text{ J} = 1 \text{ kgm}^2 \text{s}^{-2}$ $1 \text{ eV} = 1.6022 \text{ x} 10^{-19} \text{ J}$
5 VB					l	۲3 >	50.942	41 Nb 92.906	73 Ta	105 105 Unp	(262)		59 Pr 140.90	91 Pa 231.030	$1 \text{ CV} = 1.0022 \times 10^{-3}$
4 IVB						7 T	47.88	40 Zr 91.224	* 72 Hf	† 104 Unq	3 (261)		58 Ce 140.12	90 Th 232.038	for s wavefunction: RPD = $4\pi r^2 \Psi^2 dr$
3 IIIB			_	_		21 Sc	44.956	39 Y 88.906	57 La	-06.901 89 Ac	227.028		ides	SS	
2 IIA	Active etals		4 Be 0.017	12	Mg 24.305	20 Ca	40.08	38 Sr 87.62	56 Ba	88 88 Ra	226.025		Lanthan	Actinide	for $n_f < n_i$
1 IA	The	H 1.008	3 Li 6041		22.990	19 K	39.098	37 Rb 85.468	55 Cs 112 005	87 Fr	(223)		*	+	$v = \frac{\Sigma \kappa_{\rm H}}{h} \left(\frac{1}{n_{\rm f}^2} - \frac{1}{n_{\rm i}^2} \right)$

Image by MIT OpenCourseWare

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

for $n_f > n_i \dots$

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

MIT OpenCourseWare <u>http://ocw.mit.edu</u>

5.111 Principles of Chemical Science Fall 2008

For information about citing these materials or our Terms of Use, visit: http://ocw.mit.edu/terms.