Felker F15

Second Midterm Examination, CH20A-1, Fall 2015

Thursday, November 19, 7 to 8:50 pm

NAME: Owen Hemminger

This examination is composed of four problems. Do all parts of all the problems. You have one hour and fifty minutes to complete the exam. You may use three pages of notes (front and back), and a noncommunicating calculator of your choice in working the exam. Only exams **worked in pen** will be eligible for any possible regrades.

Possibly useful physical constants:

Avogadro's number: $N_A = 6.022 \times 10^{23}$ mol^{-1}
Electron charge: $-e = -1.602 \times 10^{-19}$ C
Permittivity of vacuum: $\epsilon_0 = 8.854 \times 10^{-12}$ C^{2}J^{-1}m^{-1}
Speed of light: $c = 2.9979 \times 10^8$ m/s
Planck's constant: $h = 6.626 \times 10^{-34}$ J s

A periodic table is reproduced on the following page.

Problem 1: 22 of 25 points

Problem 2: 22 of 30 points

Problem 3: 22 of 24 points

Problem 4: 15 of 21 points

1(a) (12 points) A hydrogen atom in its ground state is photoionized by light with wavelength equal to 90 nm (9.0×10^{-8} m). Determine the de Broglie wavelength of the photoelectron produced in this process.

(b) A particle in a one-dimensional box of length equal to L (inside the box corresponds to $0 \leq x \leq L$) is in the first state higher in energy than the ground state. (i) (5 points) Write the wavefunction for the particle in this state. (ii) (8 points) At what position(s) in the box (what value(s) of x) is the probability of finding the particle greatest?

a) $IE = E_1 = \frac{(2.1799 \times 10^{-18})}{n^2} Z^2 = (2.1799 \times 10^{-18} J) \frac{1^2}{1^2} = 2.1799 \times 10^{-18} J$

$E_{photon} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} J \cdot s)(2.9979 \times 10^8 m/s)}{(9.0 \times 10^{-8} m)} = 2.20712 \times 10^{-18} J$

$KE = E_{photon} - IE$

$\frac{1}{2}(9.1094 \times 10^{-31} kg) v^2 = (2.20712 - 2.1799) \times 10^{-18} J$

$v = \sqrt{\frac{2 \cdot (2.20712 - 2.1799) \times 10^{-18} J}{9.1094 \times 10^{-31} kg}}$

$v = 2.44466 \times 10^5 m/s$

$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} J \cdot s)}{(9.1094 \times 10^{-31} kg)(2.44466 \times 10^5 m/s)}$

$= \boxed{2.975 \times 10^{-9} m}$ ✓ +12

b) i) $n = 2$ state since $n = 1$ is ground ✓ +2

$\frac{h^2}{8mL^2} = E$

$\lambda = \frac{2L}{n} = \frac{2L}{2} = L$ because 1 nodes → One wavelength contained in box

$\Psi(x) =$

ii) Ψ^2 gives probability

Want $\Psi^2(x) =$ +8

$x = \frac{L}{4}$ and $\frac{3L}{4}$ since these are antinodes → where wave function has max amplitude (where $\Psi(x)$ is max or min, $\Psi^2(x)$ has a max)

2(a) (15 points) The highest-energy electron in an alkali-metal atom behaves very much like an electron in the corresponding state of a one-electron atom. Compare the first ionization energy of potassium (418.8 kJ/mol from Appendix F of Oxtoby) with the binding energy of a 4*s* electron in a one-electron atom that has nuclear charge eZ_{eff} (where e is the fundamental charge) and determine the value of Z_{eff} that is necessary for the two energies to be the same.

(b) Aluminum in its ground state is excited such that the ground state's highest-energy electron is promoted to the 4*s* orbital. The wavelength of the light emitted when this 4*s* electron falls back to re-achieve the ground-state configuration is about 395 nm. In a similar experiment the ground state's highest-energy electron is promoted to a 3*d* orbital. The wavelength of light emitted when this electron falls back to achieve the ground-state configuration is 310 nm. (i) (3 points) Write down the configurations for the Al ground state and the two excited states referred to above. (ii) (8 points) Given that the first ionization energy of Al is 577.6 kJ/mol, draw an energy-level diagram depicting the three electronic states of Al described here and label the energies of the three states (in joules) relative to the energy of infinitely separated $Al^+(g) + e^-(g)$. (iii) (4 points) On the diagram in part (ii) draw arrows indicating the two emission transitions described above.

a) IE of potassium = 418.8 kJ/mol +2

If nuclear charge is equal to eZ_{eff}, then $Z_{eff} = Z$ in [illegible] energy equation

$IE = \frac{418.8\ kJ}{1\ mol} \cdot \frac{1\ mol}{6.022 \times 10^{23}\ atoms} \cdot \frac{1000\ J}{1\ kJ} = 6.9545 \times 10^{-19}\ J/atom$

$E_4 = (2.1799 \times 10^{-18}\ J)\frac{(Z_{eff})^2}{4^2}$ = Binding energy for 4s electron

$E_4 = (1.3624 \times 10^{-19}\ J)(Z_{eff})^2$ +4

$1.3624 \times 10^{-19}\ J$ $6.9545 \times 10^{-19}\ J$

Binding energy of 4s e⁻ less than IE of potassium for small Z_{eff}

$IE = \Delta B = 0 - E_{4s}$

$(1.3624 \times 10^{-19}\ J)(Z_{eff})^2 = 6.9545 \times 10^{-19}\ J$ +2

$Z_{eff}^2 = 5.1045$ +5

$Z_{eff} = 2.259$ to make the two energies equal

Part b on next page

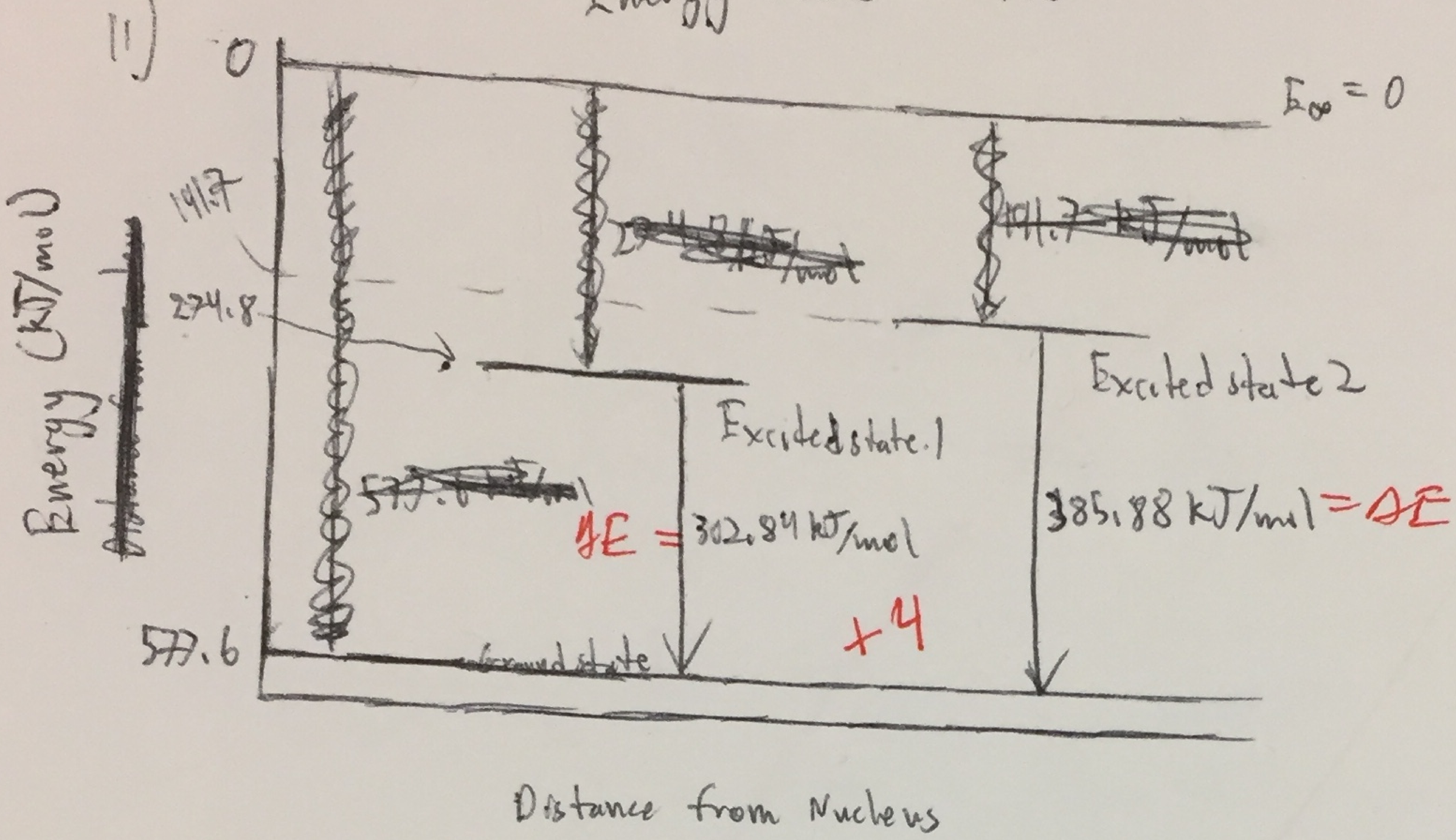
+13

b) i) Ground state: [Ne] $3s^2 3p^1$ +1

Excited state 1 (4s): ~~[Ne] $3s^2 4$~~ [Ne] $3s^2 4s^1$ +1

Excited state 2 (3d): [Ne] $3s^2 3d^1$ +1

ii) Energy levels for Al



+2

$\Delta E_2 = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,J\cdot s)(2.9979\times10^8\,m/s)}{3.95\times10^{-7}\,m} = \frac{5.02888\,J}{atom}\cdot\frac{1\,kJ}{1000\,J}\cdot\frac{6.022\times10^{23}\,atoms}{mol} = 302.84\,\frac{kJ}{mol}$

$\Delta E_1 = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,J\cdot s)(2.9979\times10^8\,m/s)}{3.10\times10^{-7}\,m} = \frac{6.4078\,J}{atom}\cdot\frac{1\,kJ}{1000\,J}\cdot\frac{6.022\times10^{23}\,atoms}{mol} = 385.88\,\frac{kJ}{mol}$

$E_{tot} = IE - \Delta E$

$E_{tot_1} = 577.6\,\frac{kJ}{mol} - 302.84\,\frac{kJ}{mol} = 274.8\,kJ/mol$ $E_{tot_2} = 577.6\,kJ/mol - 385.88\,\frac{kJ}{mol} = 191.7\,\frac{kJ}{mol}$

iii) See above

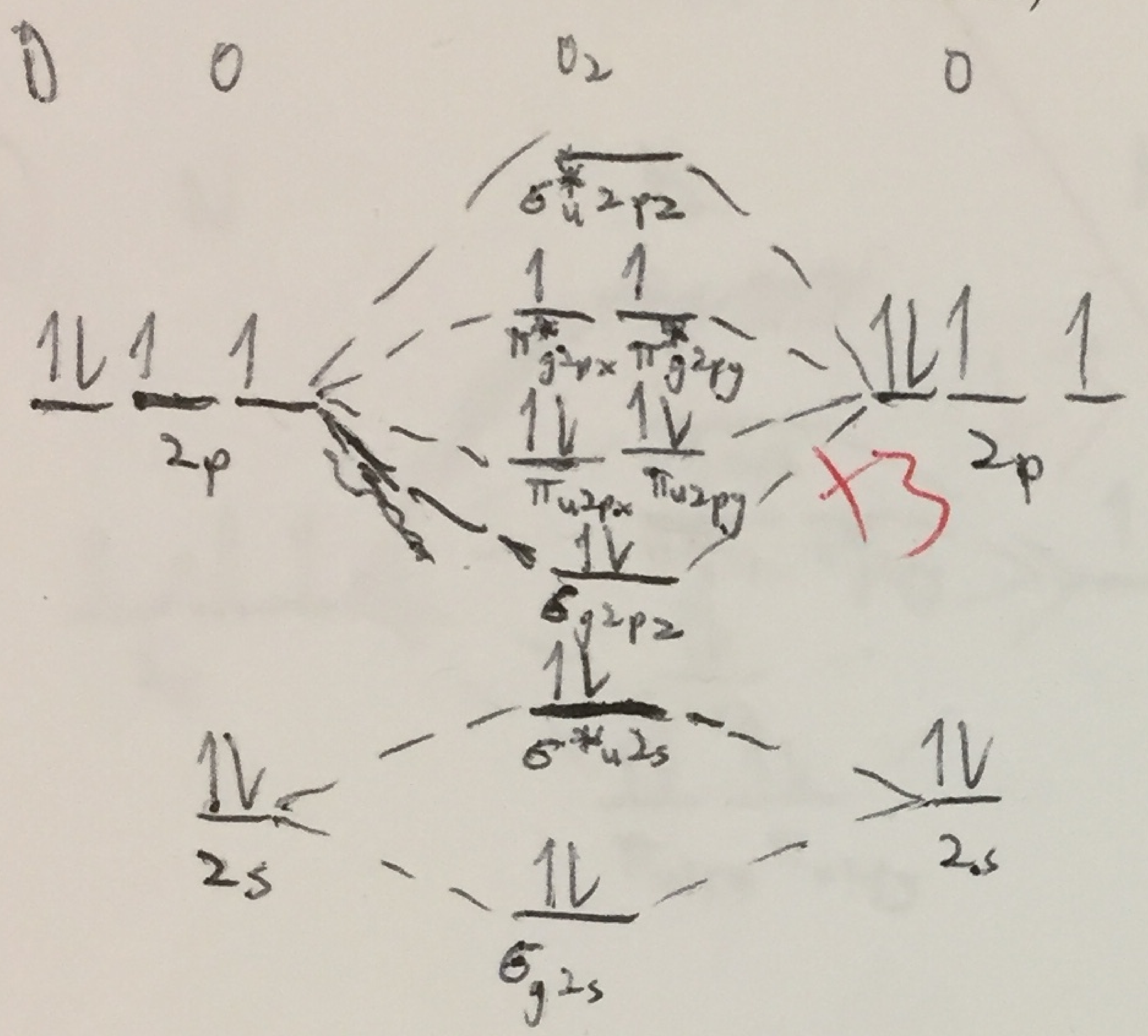
Looking for answer in Joules and want E not ΔE

+9

3(a) The homonuclear diatomic A_2 will generally have a different first ionization energy than atom A. Given what you know about the MO correlation diagrams and electron configurations of the 2nd-row homonuclear diatomics predict whether the molecule or the atom will have the larger first ionization energy for (i) (4 points) O_2 vs. O, (ii) (4 points) Li_2 vs Li, (iii) (4 points) Be_2 vs Be, and (iv) (4 points) N_2 vs N. Be sure to fully explain your answers. (Correlation diagrams will prove useful.)

(b) (8 points) For each of the following species formulate the appropriate hybridization of the central atom based on its Lewis structure and a VSEPR analysis of its geometry. (i) CO_2, (ii) PH_3, (iii) CH_3^+, and (iv) BF_3. (In all cases the central atom is the first one listed in the molecular formula.)

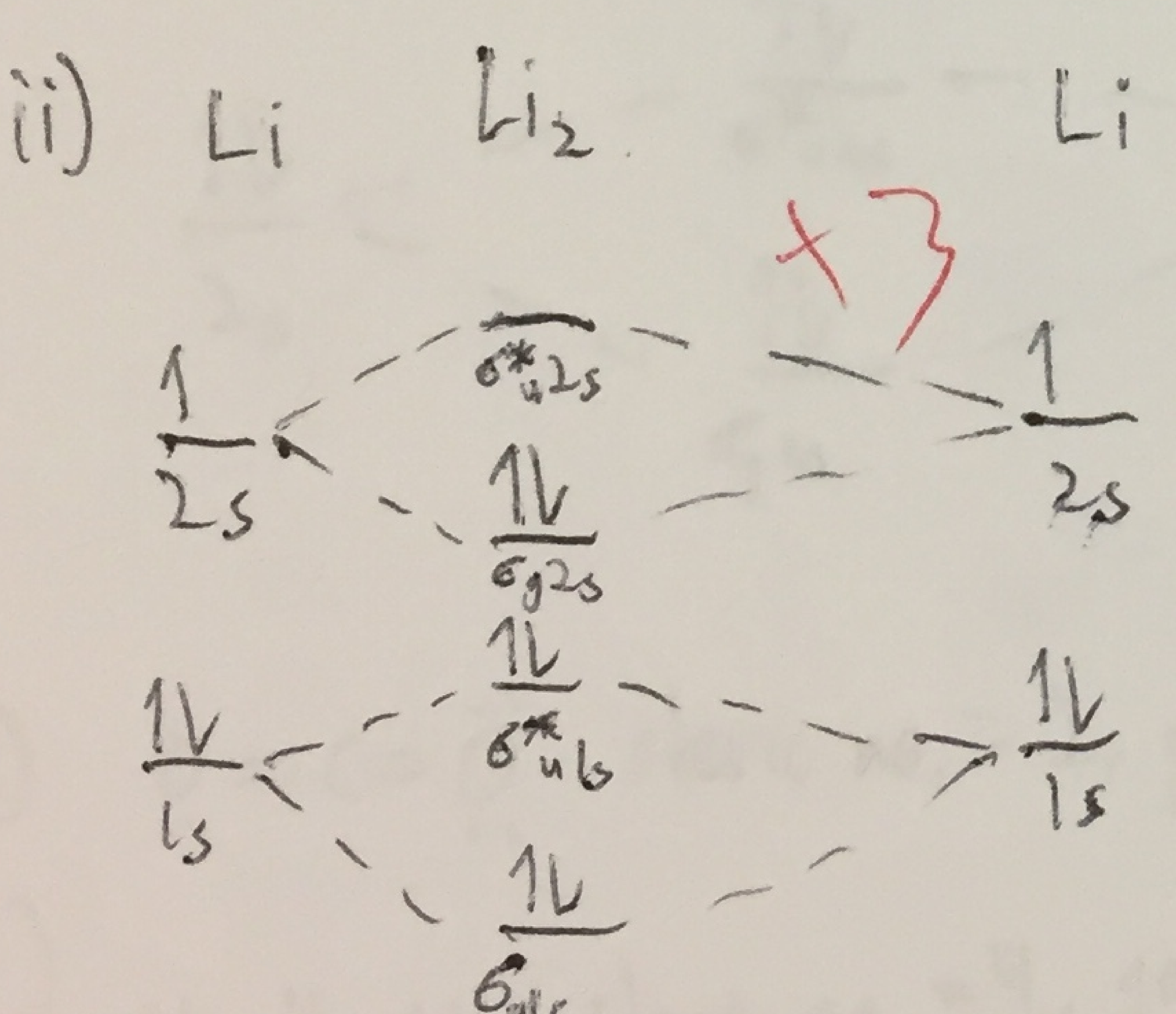
a) i)



+1

O will have the greater first ionization energy. O_2 has 2 unpaired electrons in higher energy π^*_{g2p} orbitals, meaning they are more easily removed than the 2p electrons in O. Thus, O_2 will have a lower ionization energy than O, giving O the greater ionization energy

ii)



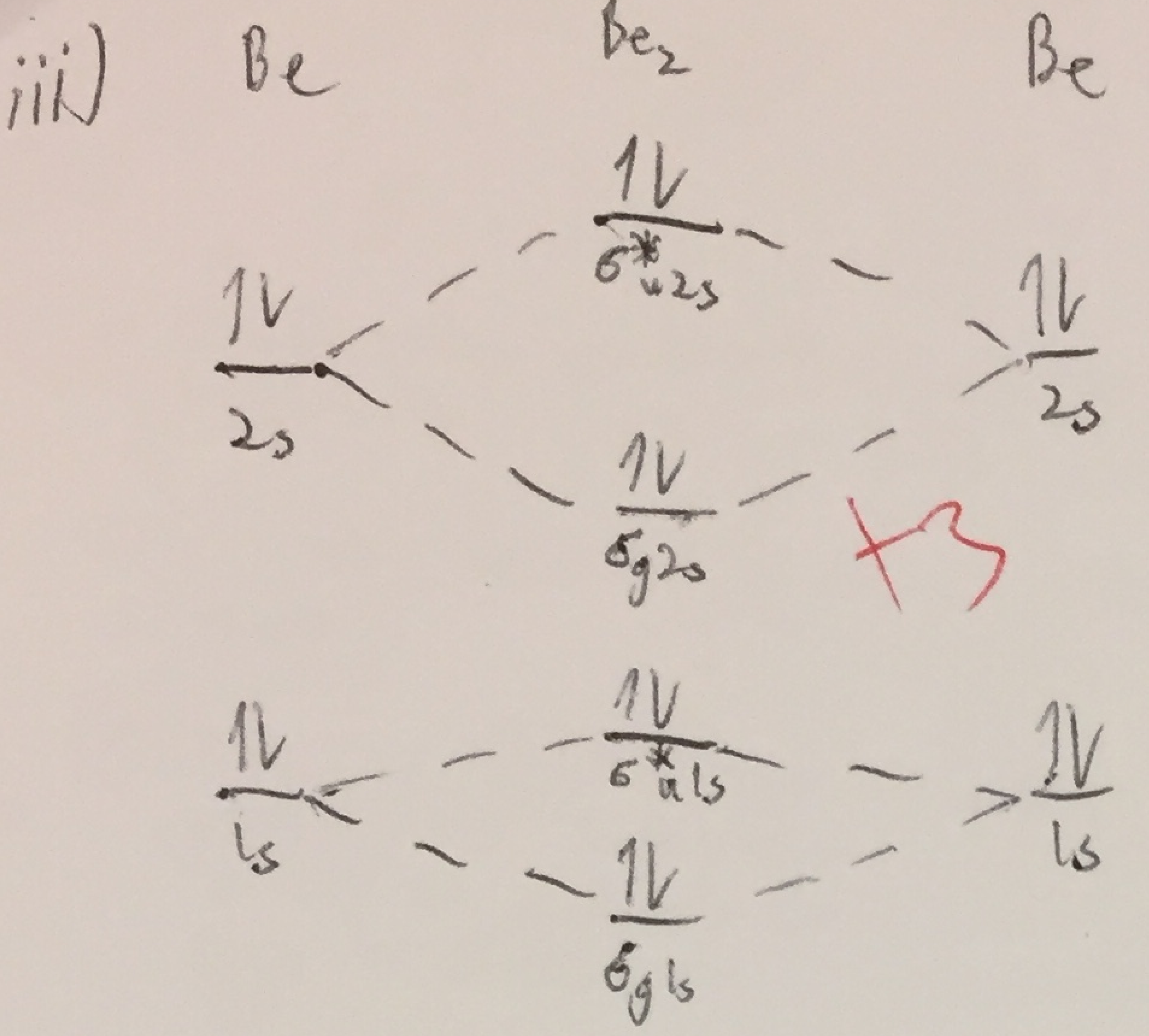
+1

Li_2 will have the greater first ionization energy. Its highest energy electrons are in the σ_{g2s} orbital, which is at a lower energy than the 2s orbital in which Li has its highest energy electron. This means the outermost electron of Li_2 will be harder to remove than that of Li, giving it the greater first ionization energy.

Cont. on next page

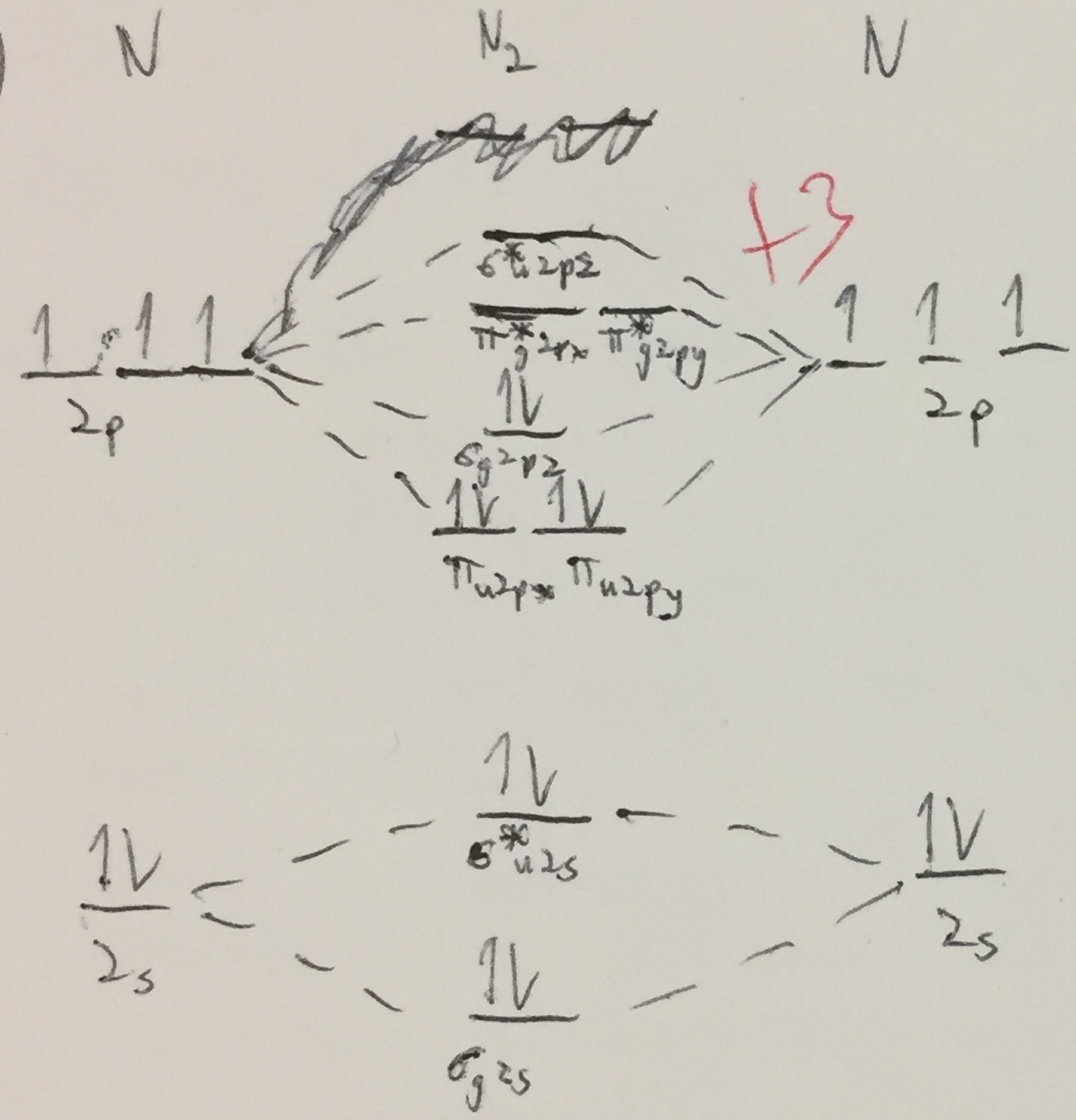
8

iii)



~~Be~~ will have the greater first ionization energy since its highest energy electrons are in the 2s orbital and thus at a lower energy than the electrons in Be_2's σ^*_{u2s} orbital. This means more energy will be required to remove an electron from Be, giving it the greater ionization energy

iv)



+1

N_2 will have the greater first ionization energy. Its highest energy electrons are in the σ_{g2p_z} orbital which is at a lower energy than the 2p orbital in which the highest energy electrons of N reside. As such, more energy is required to remove the outermost electron from N_2, giving it the greater first ionization energy.

(14)

b) i) Ö=C=Ö steric no. = 2, geometry is linear, so C is sp hybridized. +1 +1

ii) H–P̈–H (with H below P) steric no. = 4, geometry is ~~trigonal~~ planar, so P is sp^3 hybridized. +1

iii) $[H–C–H]^+$ (with H below C) steric no. = 3, geometry is trigonal planar, so C is sp^2 hybridized. +1 +1

iv) F–B–F (with F below B) steric no. = 3, geometry is trigonal planar, so B is sp^2 hybridized. +1 +1

4. The neutral atoms of three elements have ground-state electronic configurations given by $1s^22s^22p^63s^23p^64s^1$, $1s^22s^22p^63s^23p^6$, and $1s^22s^22p^63s^2$, respectively.

(a) (3 points) What are the elements that correspond to these ground-state configurations?

(b) (10 points) The first ionization energies of the three elements (not necessarily in the same order as the electronic configurations given above) are 1.5×10^6, 4.2×10^5, and 7.4×10^5 J/mol. Match these values to the elements to which they correspond by using reasoning based on the electronic configurations. Be sure to explain your reasoning fully.

(c) (8 points) By using reasoning based on the electronic configurations, order the three elements in terms of increasing atomic radius and explain the trend in atomic size.

a) $1s^22s^22p^63s^23p^64s^1$ = K (Potassium); $1s^22s^22p^63s^23p^6$ = Ar (Argon); $1s^22s^22p^63s^2$ = Mg (Magnesium)

b) 4.2×10^5 J/mol corresponds to Potassium. Potassium should have the lowest ionization energy of the three since its outermost electron is unpaired and one full shell farther from the nucleus than the other two. This, combined with the increased shielding from its larger core of electrons, make its outermost electron the most loosely held and thus easiest to remove, giving it the lowest ionization energy.

1.5×10^6 J/mol corresponds to Argon. Argon has its entire third shell filled, indicating it is the most stable. Additionally, its outermost electrons experience less shielding from core electrons than Potassium since it has fewer, meaning each outer electron will experience a greater Coulombic attraction to the nucleus due to fewer $e^- - e^-$ repulsions. Also, though its outermost electrons are farther from the nucleus than the 3s electrons of magnesium, Argon's greater number of protons yield a greater effective nuclear charge on each of its electrons, causing them to be held more tightly. All of this corresponds to argon having the highest first ionization energy.

perfect!

7.4×10^5 J/mol corresponds to magnesium. Its outermost electrons, those in its 3s orbital, are paired, making it more stable compared to potassium, whose outermost electron is unpaired. Additionally, its valence electrons are in the third shell, meaning its valence electrons experience a greater Coulombic attraction and fewer repulsions from core electrons than the valence electrons in potassium's fourth shell. This gives it a higher first IE than potassium. However, magnesium's lack of an octet and weaker nucleus mean it is less stable and less effective at attracting its electrons than Argon, making its valence electrons easier to remove. This lands its ionization energy in the middle of potassium and argon.

(c on next page

c) Mg < Ar < K

increasing atomic radius.

Argon's outermost electrons lie in the 3p orbital. P orbitals are farther from the nucleus than s orbitals, so its 3p electrons are farther from the nucleus than the 3s electrons in Mg. Additionally, Potassium's valence electrons lie in the fourth shell, meaning they are farther from the nucleus than the valence electrons of Mg and Ar, which lie in the third shell. The farther away an element's valence electrons are from the nucleus, the larger its atomic radius, so K > Ar > Mg in terms of atomic radius.

Shielding (-2)