CHEM 2351 --- SECTION 1 --- TEXTBOOK SOLUTIONS

1.3 Cr^+ has electron configuration $[Ar]4s^1 3d^5$
Mn^+ has configuration $[Ar]4s^2 3d^5$ OR $[Ar]4s^1 3d^6$
No matter how the electronic configuration of Mn+ is written, there must be a paired electron. Therefore the 2nd ionization energy (to go to Mn^{2+}) will come from an orbital that is relatively destabilized orbital, so it's easier to ionize Mn^+ to Mn^{2+}. Cr^+'s electron comes from a more stabilized orbital with no e¯ pairing energy and so is harder to remove.

1.17 The outer shell electrons are being shielded by electrons lower in energy (lower principle quantum number *n*). So, in the case of Be, there are 1*s* electrons and 2*s* electrons. The 1*s* electrons form a "shell" that the 2*s* electrons are outside of. Thus, a 2*s* electron "looking toward" the nucleus will see the 4+ Be nucleus plus two 1*s* electrons with 2- charge overall. The effective charge seen by the outer shell 2*s* electrons will then be 4 – 2 = 2.

1.19 Ca (6 eV) has a lower 1st ionization potential than Zn (8 eV) (these are estimates looking at Fig. 1.25). Ca has a lower Z_{eff} than Zn (the outer shell electrons see +2 for Ca and +12 for Zn), thus it is harder to remove an electron from a +12 charge than a +2 charge.

1.20 Sr, Ba, and Ra are all in Group 2 (in order of increasing atomic number). Thus, they all have the same Z_{eff}, but with successive, larger outer shells (Sr's valence electrons are 5*s*, Ba's are 6*s*, Ra's are 7*s*). Therefore, they are farther from the nucleus as you increase *n*, therefore they are easier to remove.

1.22 (a) $1s^2 2s^2 2p^2$ (b) $1s^2 2s^2 2p^5$ (c) $[Ar]4s^2$ (d) $[Ar]3d^{10}$
(e) $[Xe]\ 5d^{10} 6s^2 6p^3$ (f) $[Xe]5d^{10} 6s^2$

1.27 The trends all generally relate to effective nuclear charge Z_{eff}. The larger the Z_{eff}, the greater the pull of electrons to the nucleus. This makes (a) increasing ionization energy across the row, the atom harder to ionize (electrons have greater attraction to nucleus, therefore harder to remove); (b) increasing electron affinity across a row, easier to reduce (adding an electron is more favourable the higher the positive charge the incoming electron sees); and (c) increases electronegativity across a row, electrons in bonds have the same attraction to a higher-charged nucleus as any other electron.

1.28 This is probably due to the extra contraction of the orbitals brought on by relativistic effects – as the lower-level electrons approach the speed of light, they increase in mass, which further contracts their orbitals (they "fall" towards the nuclear centre). These effects kick in around the *n* = 6 level of atoms, so the effect is very obvious in Ta, so it shrinks to the size of Nb.

1.29 The frontier orbitals are the 2*s* (HOMO) and 2*p* (LUMO).

1.p4 Because of the conservation of energy law, the energy of the photon is transferred to the electron that is ejected. The energy that is not used in removing the electron is turned into the kinetic energy of the now-freed electron.

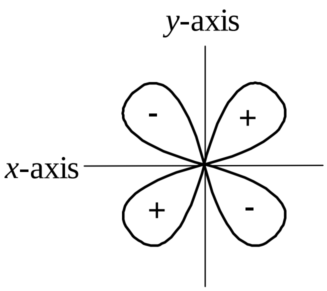
$E_{\text{photon}} = \text{hc}/\lambda = (6.626\text{x}10^{-34}\text{Js})(2.9979\text{x}10^{8}\text{ms}^{-1})/(58.4\text{x}10^{-9}\text{m}) = 3.401\text{x}10^{-18}\text{J}$

K.E. of $e^{-}_{\text{Kr}} = \frac{1}{2}m_e v^2 = (0.5)(9.109\text{x}10^{-31}\text{kg})(1.59\text{x}10^{6}\text{ms}^{-1})^2 = 1.15\text{x}10^{-18}\text{J}$
$\text{I.E.}_{\text{Kr}} = 3.401\text{x}10^{-18} - 1.15\text{x}10^{-18} = 2.25\text{x}10^{-18}\text{J} = 14.1\text{ eV}$

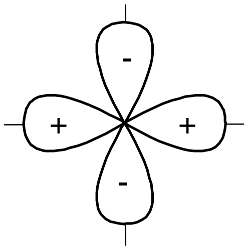
K.E. of $e^{-}_{\text{Rb}} = (0.5)(9.109\text{x}10^{-31}\text{kg})(2.45\text{x}10^{6}\text{ms}^{-1})^2 = 2.73\text{x}10^{-18}\text{J}$
$\text{I.E.}_{\text{Rb}} = 3.401\text{x}10^{-18} - 2.73\text{x}10^{-18} = 0.67\text{x}10^{-18}\text{J} = 4.2\text{ eV}$

Note that these answers are right based on the values in Figure 1.25.

1.p7



d_{xy}



$d_{x^2-y^2}$

2.6 simply add the radii: (a) C-Cl = 77+99 = 176 pm (b) Si-Cl = 118+99 = 217 pm
(c) Ge-Cl = 122+99 = 221 pm

2.11 AD > BD > AC > AB

9.1 Maximum stable oxidation state is (usually) loss of all valence electrons, *i.e.*,
(a) Ba^{2+} (b) As^{5+} (c) P^{5+} (d) Cl^{7+}

For (c) and (d), it is unlikely that either of these would exist as stand-alone ions (P^{3-} and Cl^{-} would be more likely) but as “formal” oxidation states in a molecular compound, these positive oxidation states are not unknown.

9.3 The +5/+3 oxidation state limits the choices to Groups 5 (V) and 15 (N). Of those two choices, Group 15 is more likely (forms gaseous hydrides) because Group 5 hydrides are likely to be salts, not molecular compounds.

9.5 The heavier elements Po (Group 16) and At (Group 17) are radioactive, but probably Po^{4+} would be more stable than Po^{6+}. With At, being on the non-metal side of the metalloid line, it’s likely that At^{-} is still the most common ionic state of At, but perhaps, for example, the complex ion AtO_4^{-} (At^{7+}) might not be easily accessible, unlike the equivalent ClO_4^{-}, BrO_4^{-}, or IO_4^{-}. Similarly, the interhalogen AtX_5 might be the most readily accessible interhalogen, as opposed to, for example, ICl_7.