CHE 514, Descriptive Inorganic Chemistry
Spring, 2005
Problem Set 1 key

Points: 6 + 3+ 15 + 5 + 9 + 5 + 10 + 15 + 10 + 5 + 10 = 93 for undergraduates, 93 + 10 + 10 = 113 for graduates

1. (6 total) Why did the discovery of the noble gases end significant changes in the main block of the periodic table? Was there any later change in the overall structure of the periodic table?

The noble gases provided the zerovalent elements to provide a "spacer" between the characteristically –1 halogens and +1 alkali metals. There were no more groups to fill in the spd block of the periodic table once they were discovered.
The significant later changes were the additions of the lanthanoid and actinoid groups between the s and d elements of the 6^{th} and 7^{th} periods. The post-actinoid elements continue to fill in the d and p block of the 7^{th} period and may eventually "round the corner" to the 8^{th} period.

2. (3) Modern texts usually refer to "lanthanoids and actinoids" rather than lanthanides and actinide. Why?

The "-ide" ending is usually applied to an element in its negative oxidation state (oxide, chloride), and the f metals do not display negative oxidation states. The "-oid" ending means, more appropriately, "-like".

3. (15= 5 each for any reasonable answers) Identify three elements that are found in nature almost entirely as a single isotope. Suggest for each a reason why there is only a single isotope.

Numbers of nucleons to complete shells ("magic numbers") are 2, 8, 20, 28, 50, 82 and 126.
Possible answers:
^{1}H 99.985%, ^{2}H and ^{3}H have low binding energies
^{4}He, 100%, stable w/ filled proton and neutron shells, abundant because the nucleus = alpha particle
^{9}Be, 100%, ^{8}Be breaks down very easily into 2 alpha particles, but I'm not sure why there is no natural ^{10}Be – probably related to details of its x-process formation.
^{16}O 99.76%, doubly "magic"
^{19}F 100%, again I'm not sure since it's odd-odd
^{23}Na, ^{27}Al, ^{31}P, several others.

4. (5 for any reasonable answer) Why are polonium-210 and astatine-211 the longest-lived isotopes of those elements?

The question has two errors. The three longest-lived isotopes of Po and At are:

^{208}Po has $t_{1/2}$ = 2.898 y, 84 protons, 124 neutrons
^{209}Po has $t_{1/2}$ = 102 y, 84 protons, 125 neutrons
^{210}Po has $t_{1/2}$ = 138.38 d, 84 protons, 126 neutrons

^{209}At has $t_{1/2}$ = 5.4 h, 85 protons, 124 neutrons
^{210}At has $t_{1/2}$ = 8.1 h, 85 protons, 125 neutrons
^{211}At has $t_{1/2}$ = 7.21 h, 85 protons, 126 neutrons

Filled nuclear shells hold 126 nucleons, so the observed lifetimes do <u>not</u> agree with the simple filled-shell model. [Proving that the instructor should not use textbook questions without checking the data.]

5. (9) Which element of each pair has the larger atomic radius? Explain.
   K, Ca; Cl, Br; Pr, Tm

K > Ca, as the effective atomic charge on the outermost electrons increases across a period, so the covalent radius will decrease, resulting in a smaller radius for calcium.
Br > Cl, larger principal quantum number
Pr > Tm, "lanthanoid contraction", i.e. f-electrons are poorly shielding so the effective atomic charge on the outermost electrons increases across the lanthanoid group, resulting in a decreasing radius

6. (5) Why do the atomic radii of Al and Ga differ so little?

Al and Ga both have a s^2 p^1 configuration in their highest n level. Ga should be larger because n = 4 rather than 3 for Al, but the 10 3d electrons shield the valence electrons very poorly, resulting in a higher Z_{eff} and smaller radius than expected for Ga.

7. (10) Calculate the effective nuclear charge on a 3*p* electron in (a) Al and (b) Cl. How does this affect the relative atomic radii and first ionization enthalpies of the two elements?

Effective nuclear charge on 3*p* electrons in aluminum = 3.50, in chlorine = 6.10. The higher effective nuclear charge on the outermost electrons in chlorine results in that element having the smaller atomic radius of the two and the higher first ionization energy.

8. (15) Explain the very small electron affinities of Be, N and Ne.

Be is $1s^2$ $2s^2$ – the s electrons shield the nucleus so effectively that an added electron would "feel" Zeff of nearly zero
N is $1s^2$ $2s^2$ $2p^3$ – adding a 4th electron to the $2p^3$ introduces a significant (unfavorable) pairing energy that almost overcomes the favorable addition of an electron
Ne is $1s^2$ $2s^2$ $2p^6$ – the n = 2 level is complete, so the added electron would go into a 3s orbital that is very high in energy, so the addition is not favorable

9. (10) Predict some key qualitative properties of element 114.

Element 114 (X) would be a member of the carbon group. Aside from a very short half-life and radioactive behavior, it should resemble lead. It should be a low-melting metallic solid at room temperature. It should favor positive oxidation states, particularly +2 and +4. The divalent ion should be very stable and the tetravalent ion very strongly oxidizing. It should form very weak covalent bonds with any elements except perhaps F and O.

10. (5) Why are isotopes with atomic numbers divisible by four more abundant than neighboring isotopes?

Elements with atomic weights divisible by 4 arise from several α-particle-based processes such as helium burning and α-process that occur in the evolution of all stars.

11. (10) Provide evidence that our solar system did not arise from a first-generation protostar (in the "big bang" model).

Heavy elements (Z>26) are much more abundant on earth (and other parts of the solar system) than in the universe as a whole. Thus, the matter in our solar system must have been through more than one cycle of star formation, evolution and death (supernova) to enrich these elements.

Problems 12 and 13 are required for graduate students, optional for undergraduates

12. (10) Why are there significant amounts of uranium and thorium in the earth's crust even though all isotopes of these elements are unstable? Why are there traces of technetium (with no stable isotopes) found in the earth's crust?

(See Greenwood page 13) The age of the universe is about 1.5×10^{10} y, and the age of our solar system about 5×10^9 y. The longest-lived thorium isotope is ^{232}Th with $t_{1/2} = 1.4 \times 10^{10}$ y, so there is no problem with significant amounts of it remaining in the earth's crust. Uranium has two long-lived isotopes, ^{235}U with $t_{1/2} = 7.0 \times 10^8$ y and ^{238}U with $t_{1/2} = 4.5 \times 10^9$ y. These isotopes of uranium and thorium are long-lived enough that the amounts found on earth were probably formed by the r-process in supernova events starting about 10^{10} y ago. Small amounts of less stable isotopes, e.g. ^{234}U with $t_{1/2} = 2.4 \times 10^5$ y, are formed in natural radioactive decay chains of heavier elements. Because the earth formed from elements "born" about 10^9 y ago, there is virtually no "original" Tc with isotopic half-lives of 10^6 y or much shorter. Traces of ^{99}Tc with $t_{1/2} = 2.1 \times 10^5$ y are found in the earth's crust as a result of spontaneous fission of uranium. There is a lot of technetium produced as waste from nuclear reactors, and some of this could accidentally migrate into the earth's crust.

13. (10) Distinguish between the *s*-process and the *r*-process in the formation of elements within a star. Why does the *s*-process only form elements up to bismuth, whereas the *r*-process can form heavier elements?

The *s*-process is slow neutron addition. One neutron is added at a time, typically followed by beta emission before another neutron adds. The net effect is increase of one proton (both Z and A increase by one) each time the process occurs.

The *r*-process is rapid neutron addition. Many neutrons, up to 30, are added very quickly, before the nucleus has time to decay. At the number of neutrons approaches a "magic number" (N = 2, 8, 20, 28, 50, 82, 126; usually the last three for r-process to be significant), the neutron cross-section decreases and the nucleus has time to undergo decay to a stable one. Decay takes place by a cascade of beta losses.

The *s*-process only forms elements up to bismuth because bismuth (Z = 83, A = 209) has a full neutron shell and therefore a low neutron cross-section. This nucleus simply stops growing under s-process conditions. Under *r*-process conditions, the neutron flux is much higher and even "magic number" nuclei can add neutrons, leading to heavier elements.