

2015 USNCO National Part 2

7. [12] Chlorine is an industrially and biologically important element.
- Give the ground state electron configuration for gas-phase atomic Cl.
 - Draw a Lewis structure for molecular chlorine, including all lone pairs and any formal charges.
 - Which would have a greater first ionization energy, atomic Cl or molecular chlorine? Justify your answer.
 - Which would have a larger radius, atomic Cl or the chloride ion (Cl^-)? Justify your answer.
 - Explain why the oxoanions ClO^- , ClO_2^- , ClO_3^- , and ClO_4^- all form stable salts, but the oxoanion ClO_5^- is unknown.

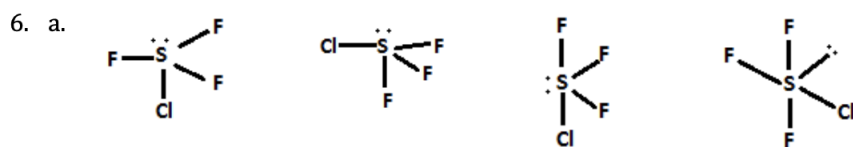
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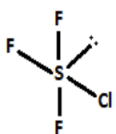
6. [13] Consider the highly reactive molecule SF_3Cl .
- Draw all of the possible structures of SF_3Cl with S as the central atom.
 - Use VSEPR theory to predict the most stable structure in a. and justify your answer.
 - Recent calculations predict that the two structures that are lowest in energy differ by about 0.2 kJ/mol. Identify the second lowest energy structure and justify your answer.
 - While selenium and tellurium can potentially form SeF_3Cl and TeF_3Cl , an OF_3Cl species is not known even though oxygen has the same valence electron configuration. Account for this difference in the behavior of oxygen.

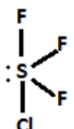
(Part d. Omitted)

Answer Key**2015 USNCO National Part 2**

7. [12 pts.]
- a. $1s^2 2s^2 2p^6 3s^2 3p^5$ or $[\text{Ne}] 3s^2 3p^5$
- b. $:\ddot{\text{Cl}}-\ddot{\text{Cl}}:$
- c. Cl has a higher ionization energy than Cl_2 . The highest-lying electrons in Cl_2 are π^* , so they are higher in energy, and hence require less energy to ionize, than the $3p$ electrons in atomic chlorine. (The experimental values are 13.0 eV for Cl, 11.5 eV for Cl_2 [Frost, D. C.; McDowell, C. A.; Vroom, D. A. *J. Chem. Phys.* **1967**, *46*, 4255-4259].)
- d. Cl^- would have a larger radius, since it has an additional electron.
- e. Cl has 7 valence electrons. An oxoanion with the formula ClO_5^- would require an oxidation state of +9 for Cl, which would require removing core electrons. This is not energetically feasible.

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- b.  Structure is correct for most stable. Lone pair of electrons and the least electronegative atom (Cl) are in the equatorial plane at 120 degrees apart with very electronegative F atoms in axial positions, drawing bonding pairs of electrons away from S.

- c.  Structure is correct for second most stable. Cl is in an apical position but the lone pair is still in the equatorial plane, minimizing its repulsion of the bonding pairs of electrons.

- e. The central atom in SF_3Cl has ten electrons around it. While S , Se and Te can all accommodate ten electrons, O (with fewer orbitals available) cannot do so.