

University of Massachusetts Boston
Department of Chemistry
Chemistry Doctoral Program
Green Chemistry Track
Written Qualifying Exam
June 18, 2007

Inorganic Chemistry II

The following questions are based on the paper:

“The Geometry of Nonmetal Hydrides and the Ligand Radius of Hydrogen” E. A. Robinson and R. J. Gillespie. *Inorganic Chemistry*, **2004**, 43(7), 2318-2323.

Answer any five (5) of the following questions (2 points each) plus the Green Chemistry question (2 points). *Be sure to indicate which question you are answering in each case.* If you answer more than five of the following eight questions, only your first five responses will be graded. Your answer for each question should consist of at least one or two paragraphs (always using complete sentences), which fully explore the issues being addressed and indicate your comprehension of the underlying concepts and theories.

1. What are the fundamental bases of the VSEPR and LCP theories? What geometries about a central atom (A) are predicted for various numbers of ligands (X) and non-bonding electrons (E) in AX_nE_m cases for which $2 \leq (n + m) \leq 6$? In what ways do the predictions from these theories agree with one another? What advantage, if any, does LCP theory have over VSEPR theory? Give specific examples.
2. What is the definition of the ligand radius? What data are used to calculate ligand radii and how are they obtained? What underlying assumptions are made in these calculations? In the case of ligand hydrogen, what challenges exist to obtaining the necessary data? How are these challenges addressed?
3. Most ligands (X) have a single, relatively constant ligand radius when bonded to a certain central atom (A). The paper lists two values of the hydrogen ligand radius with carbon (89 pm and 94 pm). Why are there two values in this case? Why is the one value so much larger than the other? What conclusions can be drawn about the hydrogen ligand in the kinds of structures to which each value pertains?
4. In all cases the ligand radius of X decreases with increasing electronegativity of the central atom A. For ligand hydrogen, the radii with B, C, N, and O are 102, 89, 82, and 76 pm, respectively. What is the underlying reason for the decline in ligand radius of X with increasing electronegativity of A? How does this trend account for the difference in the bond angle of H_2O versus NH_3 ? (Do not use VSEPR arguments here.)

5. A plot of hydrogen ligand radius versus ligand charge, $q(\text{H})$, is linear for the cases BH_3 , BH_4^- , CH_4 , NH_3 , and H_2O . A number of other cases, such as SiH_4 , PH_3 , CH_3^+ , and NH_4^+ fall slightly or significantly above this line. How are the charges on the ligands obtained? What can be inferred about the hydrogen ligands in these two kinds of cases?
6. In VSEPR theory, bond angles in molecules of the type AX_nE_m are predicted to decline with increasing ligand electronegativity or decreasing central atom electronegativity. For example, compare PI_3 (102°) to PF_3 (97.8°), in which the electronegativity of X increases, and NF_3 (102.3°) to SbF_3 (87.3°), in which the electronegativity of A decreases. What reason is given in VSEPR theory for this trend? How does LCP theory account for this trend? How does LCP theory (but not VSEPR theory) successfully account for the following observed angles: HOF (97.2°), H_2O (104.5°), F_2O (103.3°)?
7. Bond angles of period 3 hydrides are much smaller than their period 2 analogues, and are also somewhat smaller than the corresponding period 3 fluorides. For example, consider the following data: NH_3 (107°), H_2O (104.5°), PH_3 (93.3°), H_2S (92.1°), PF_3 (97.8°), SF_2 (98.0°). Account for these data on the basis of LCP theory. In which cases can or cannot the ligands be assumed to be close packed. In those cases where close packing cannot be assumed, how are the ligand radii estimated?
8. Figure 2 of the paper shows a plot of ligand charge versus electronegativity for the period 2 and 3 hydrides. Describe the observed trends. The figure caption indicates that Allred-Rochow values are being used, rather than Pauling values. What are the underlying bases of the two sets of electronegativity values? What exactly is electronegativity? Is electronegativity a measurable quantity? What is the origin of the scale of values used for electronegativity? Why would Allred-Rochow values be preferred in this paper? (Disregard the fact that Allred-Rochow values were calculated more recently; Pauling values exist that have been recalculated with more recent data, too.)

Green Chemistry Question (*This question must be answered.*)

The assigned paper deals with predicting and understanding distances of ligand-ligand interactions and bond angles among similar compounds. How could these considerations, based on LCP theory, be applied to the practice of green chemistry, particularly including the practice of benign synthesis?