

CHEM 20100 (Inorganic Chemistry I) Problem Sets

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0 Course Prep Problems

9/13: **2.8** The details of several steps in the particle-in-a-box model in this chapter have been omitted. Work out the details of the following steps:

- a. Show that if $\Psi = A \sin rx + B \cos sx$ (A , B , r , and s are constants) is a solution to the wave equation for the one-dimensional box, then

$$r = s = \sqrt{2mE} \left(\frac{2\pi}{h} \right)$$

Solution.

$$\begin{aligned} \frac{-h^2}{8\pi^2m} \cdot \frac{\partial^2 \Psi(x)}{\partial x^2} &= E\Psi(x) \\ \frac{-h^2}{8\pi^2m} \cdot \frac{\partial^2}{\partial x^2} (A \sin rx + B \cos sx) &= E(A \sin rx + B \cos sx) \\ \frac{-h^2}{8\pi^2m} \cdot \frac{\partial}{\partial x} (Ar \cos rx - Bs \sin sx) &= E(A \sin rx + B \cos sx) \\ \frac{-h^2}{8\pi^2m} \cdot (-Ar^2 \sin rx - Bs^2 \cos sx) &= E(A \sin rx + B \cos sx) \\ \frac{Ar^2 h^2}{8\pi^2m} \sin rx + \frac{Bs^2 h^2}{8\pi^2m} \cos sx &= AE \sin rx + BE \cos sx \\ 0 &= \left(\frac{Ar^2 h^2}{8\pi^2m} - AE \right) \sin rx + \left(\frac{Bs^2 h^2}{8\pi^2m} - BE \right) \cos sx \end{aligned}$$

Choose $x = 0$.

$$\begin{aligned} &= \frac{Bs^2 h^2}{8\pi^2m} - BE \\ E &= \frac{s^2 h^2}{8\pi^2m} \\ \frac{8\pi^2mE}{h^2} &= s^2 \\ s &= \sqrt{\frac{8\pi^2mE}{h^2}} \\ \boxed{s = \sqrt{2mE} \frac{2\pi}{h}} \end{aligned}$$

With this result ...

$$\begin{aligned} 0 &= \left(\frac{Ar^2 h^2}{8\pi^2m} - AE \right) \sin rx + \left(\frac{Bs^2 h^2}{8\pi^2m} - BE \right) \cos sx \\ &= \left(\frac{Ar^2 h^2}{8\pi^2m} - AE \right) \sin rx + \left(B \left(\frac{s^2 h^2}{8\pi^2m} \right) - BE \right) \cos sx \\ &= \left(\frac{Ar^2 h^2}{8\pi^2m} - AE \right) \sin rx + (BE - BE) \cos sx \\ &= \left(\frac{Ar^2 h^2}{8\pi^2m} - AE \right) \sin rx \end{aligned}$$

Choose $x = \frac{\pi}{2r}$.

$$= \frac{Ar^2 h^2}{8\pi^2m} - AE$$

$$r = \sqrt{2mE} \frac{2\pi}{h}$$

□

- d. Show that substituting the value of r given in part c into $\Psi = A \sin rx$ and applying the normalizing requirement gives $A = \sqrt{2/a}$.

Solution.

$$\begin{aligned} 1 &= \int_{\text{all space}} \Psi \Psi^* d\tau \\ &= \int_0^a \left(A \sin \frac{n\pi x}{a} \right) \left(A \sin \frac{n\pi x}{a} \right) dx \\ &= \int_0^a A^2 \sin^2 \frac{n\pi x}{a} dx \end{aligned}$$

Use $\sin^2 u = \frac{1 - \cos 2u}{2}$.

$$\begin{aligned} &= A^2 \int_0^a \frac{1 - \cos \frac{2n\pi x}{a}}{2} dx \\ &= \frac{A^2}{2} \left(\int_0^a dx - \int_0^a \cos \frac{2n\pi x}{a} dx \right) \\ &= \frac{A^2}{2} \left([x]_0^a - \left[\frac{a}{2n\pi} \sin \frac{2n\pi x}{a} \right]_0^a \right) \\ &= \frac{A^2}{2} \left((a - 0) - \left(\frac{a}{2n\pi} \sin 2n\pi - \frac{a}{2n\pi} \sin 0 \right) \right) \\ &= \frac{A^2}{2} \left(a - \left(\frac{a}{2n\pi} \sin 2n\pi \right) \right) \end{aligned}$$

Since n is an integer, $\sin 2n\pi = 0$.

$$\begin{aligned} &= \frac{aA^2}{2} \\ \frac{2}{a} &= A^2 \\ A &= \sqrt{\frac{2}{a}} \end{aligned}$$

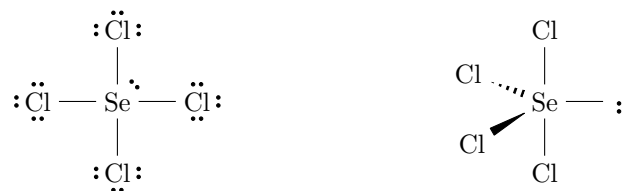
□

1 VSEPR and Point Groups

1/21: I) Do the following (VSEPR) problems from your text (Miessler et al. (2014)): Chapter 3: #8, 9f-i, 20, 29.

3.8 Give Lewis dot structures and sketch the shapes of the following:

a. SeCl_4



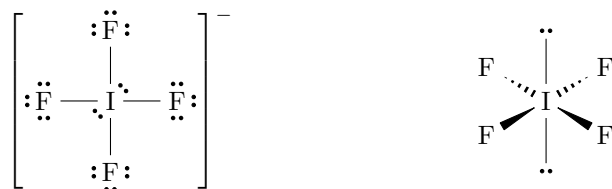
b. I_3^-



c. PSCl_3



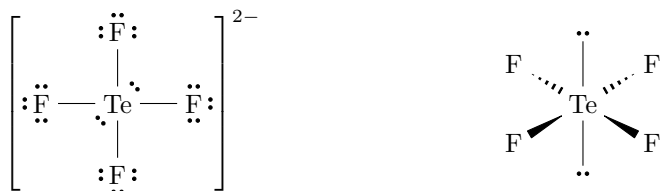
d. IF_4^-



e. PH_2^-

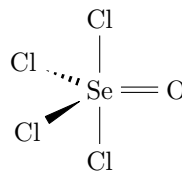
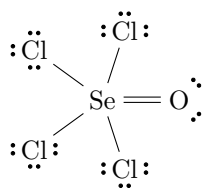
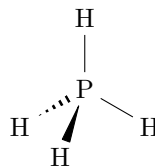
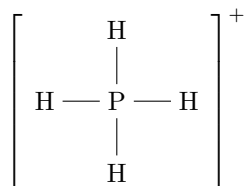
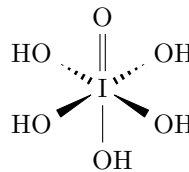
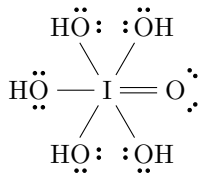
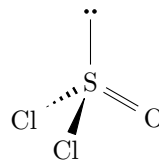
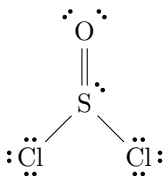
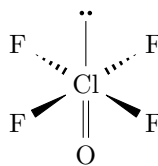
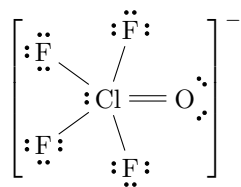
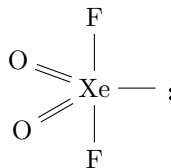
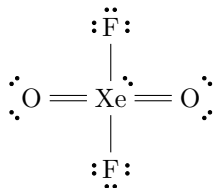


f. TeF_4^{2-}

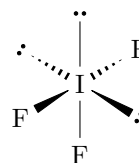
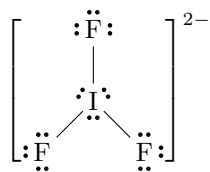


g. N_3^-

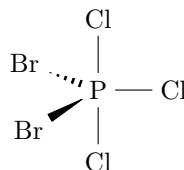


h. SeOCl_4 i. PH_4^+ **3.9** Give Lewis dot structures and sketch the shapes of the following.f. $\text{IO}(\text{OH})_5$ g. SOCl_2 h. ClOF_4^- i. XeO_2F_2 

3.20 Predict and sketch the structure of the (as yet) hypothetical ion IF_3^{2-} .



3.29 Sketch the most likely structure of PCl_3Br_2 and explain your reasoning.



Answer. Bromine is more electropositive than chlorine. Thus, by Bent's rule, the bromines will bond to the hybrid orbitals with greater s -character (the equatorial sp^2 ones) first. \square

II) Assign the symmetry point group to the 13 ions and molecules in problems #8, 9f-i in Chapter 3 of your text.

3.8**a. SeCl₄**

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes.

Therefore, SeCl₄ is of the C_{2v} point group. ☐

b. I₃⁻

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes.

Therefore, I₃⁻ is of the C_{2v} point group. ☐

c. PSCl₃

Answer. Not low or high symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h . Has three σ_v planes all offset by 60°.

Therefore, PSCl₃ is of the C_{3v} point group. ☐

d. IF₄⁻

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h .

Therefore, IF₄⁻ is of the D_{4h} point group. ☐

e. PH₂⁻

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes.

Therefore, PH₂⁻ is of the C_{2v} point group. ☐

f. TeF₄²⁻

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h .

Therefore, TeF₄²⁻ is of the D_{4h} point group. ☐

g. N₃⁻

Answer. N₃⁻ is of the $D_{\infty h}$ point group. ☐

h. SeOCl₄

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes.

Therefore, SeOCl₄ is of the C_{2v} point group. ☐

i. PH₄⁺

Answer. PH₄⁺ is of the T_d point group. ☐

3.9**f. IO(OH)₅**

Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes and two perpendicular σ_d planes.

Therefore, IO(OH)₅ is of the C_{4v} point group. ☐

g. SOCl₂

Answer. SOCl₂ is of the C_s point group. ☐

h. ClOF₄⁻

Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes and two perpendicular σ_d planes.

Therefore, ClOF₄⁻ is of the C_{4v} point group. ☐

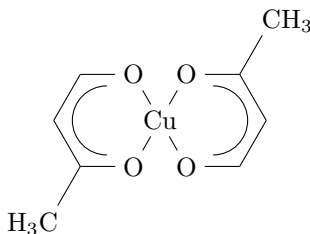
i. XeO₂F₂

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes.

Therefore, XeO₂F₂ is of the C_{2v} point group. ☐

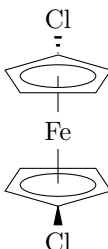
III) Assign the symmetry point group of the following molecules and objects. Ignore the H atoms in (a), (e), and (g). Note that (e) has pseudooctahedral geometry and (g) is square-planar.

a) The molecule pictured below.



Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. Has a σ_h .
Therefore, the above molecule is of the C_{2h} point group. ☐

b) The molecule pictured below.



Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. Has a σ_h .
Therefore, the above molecule is of the C_{2h} point group. ☐

c) POCl_3

Answer. Not low or high symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h . Has three σ_v planes all offset by 60° .
Therefore, POCl_3 is of the C_{3v} point group. ☐

d) Tennis ball (including the seam)

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes.
Therefore, a tennis ball is of the C_{2v} point group. ☐

e) $\text{trans}[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h .
Therefore, $\text{trans}[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ is of the D_{4h} point group. ☐

f) 1,3,5-trichlorobenzene.

Answer. Not low or high symmetry. Has a C_3 axis. Has 3 perpendicular C_2 axes. Has σ_h .
Therefore, 1,3,5-trichlorobenzene is of the D_{3h} point group. ☐

g) $\text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$

Answer. Not low or high symmetry. Has a C_2 axis. Has 2 perpendicular C_2 axes. Has σ_h .
Therefore, TeF_4^{2-} is of the D_{2h} point group. ☐

h) SF_5Cl

Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes and two perpendicular σ_d planes.

Therefore, SF_5Cl is of the C_{4v} point group. □

i) BFClBr

Answer. BFClBr is of the C_s point group. □

j) PF_2^+

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes.

Therefore, PF_2^+ is of the C_{2v} point group. □

- IV) In the octahedral ion FeF_6^{3-} , what symmetry elements are destroyed if two *trans* F ions are moved away from the Fe^{3+} center in an equidistant fashion?

Answer. If the described change is made, the point group changes from O_h to D_{4h} . In this change, every C_3 and S_6 axis, two of the three C_4 axes, and every σ_d that does not contain the axis along which the F ions are stretched are destroyed. \square