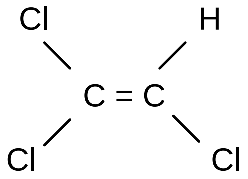
LN–2 IDLE MIND SOLUTIONS

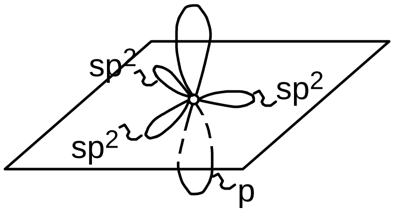
1. We recognize that, according to Pauling’s electronegativity scale, compounds with $\Delta x > 1.7$ are strongly ionic and exhibit properties which reflect the electrostatic interactions under conditions of energy minimization:
    (1) Non–directionality of the electrostatic forces will thus lead to an ordered solid (crystalline).
    (2) Octet stabilization makes the solid non–conducting (electrical insulator).
    (3) Stability will also most likely make the material transparent in the visible.
    (4) The magnitude of the attractive forces may make the solid melt at elevated temperature only.
    (5) Etc.

2. (a) C_2Cl_3H in Lewis notation:

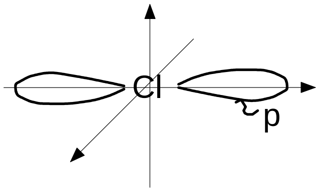


Note that the H may be located on any one of the 4 (sp^2) hybrid orbitals without changing the properties of the compound.

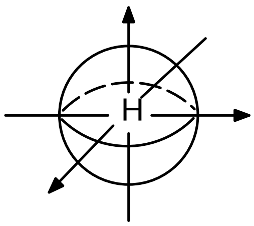
(b)



On each carbon there are:
three equivalent sp^2 bonding orbitals in a plane and one p orbital normal to the sp^2 plane.



On each chlorine there is:
one singly occupied p orbital.



On the hydrogen we have:
one singly occupied 1s orbital.

2. (c) $2\ sp^2\text{–}sp^2$ orbitals $\rightarrow$ $1\sigma\ \overset{\sigma}{C\text{–}C}$

2 p–p orbitals $\rightarrow$ $1\pi\ \overset{\pi}{C\text{–}C}$

$3\ sp^2\text{–}p$ orbitals $\rightarrow$ 3σ C–Cl

$1\ sp^2\text{–}s$ orbital $\rightarrow$ 1σ C–H

$\boxed{\text{6 bonds}}$

3. Silicon (Si) is a group 4 element like C (carbon) and wil also exhibit sp^3 hybridization: 4 sp^3 orbitals at B.A. = 109°. Unlike carbon, silicon cannot form double or triple bonds (by lateral p orbital overlap) because the atom is too large to permit lateral overlap!

(a) $Si + 2Cl_2 \rightarrow \boxed{SiCl_4}$

Si is in the center of a tetrahedron with the chlorine atoms as the four corners.

(b) $\Delta x = (x_{Cl} - x_{Si}) = 3.16 - 1.90 = 1.26$, which makes the compound $SiCl_4$ <u>a covalent material</u> (polar covalency). Since the bonding geometry is symmetric, the centers of fractional positive and negative charges coincide and the compound has <u>no dipole moment</u>. Intermolecular forces are therefore limited to London–Dispersion Forces which are weak. It is expected that the <u>material is a gas</u> at room temperature. It could also be a liquid, but definitely not a solid.

$SiCl_4$: $T_{boiling} = 57.6^oC$
$T_{freezing} = -70^oC$

4. (a) A give away!

$$E = h\nu = \frac{hc}{\lambda}\ J \times \frac{1\ eV}{1.6 \times 10^{-19}\ J}$$

$$E_1 = \frac{hc}{9.5 \times 10^{-6}} \times \frac{1}{1.6 \times 10^{-19}}\ eV = \boxed{0.13\ eV}$$

$$E_2 = \frac{hc}{0.1 \times 10^{-6}} \times \frac{1}{1.6 \times 10^{-19}}\ eV = \boxed{12.4\ eV}$$

4. (b) We have to determine the bond energy, Si–H (from the given data and from x values in the P.T.): $x_{Si} = 1.90$, $x_H = 2.20$

$$E_{Si-H} = \sqrt{E_{Si-Si} \times E_{H-H}} = k(x_H - x_{Si})^2$$

$$= \sqrt{180 \times 435} + 96.2(0.3)^2$$

$E_{Si-H} = 288.5$ kJ/mole

$$\text{To convert the energy into J/mole} = 288.5 \text{ kJ/mole} \times \frac{100}{k} \times \frac{1 \text{ mole}}{N_A}$$

$E_{Si-H} = 4.79 \times 10^{-19}$ J/bond

$$E_1 \text{ (laser photon energy)} = 0.13 \text{ eV} \times \frac{1.6 \times 10^{-19} \text{ J}}{\text{eV}}$$

$$= \boxed{2.08 \times 10^{-20} \text{ J}}$$

$$E_2 \text{ (laser photon energy)} = 12.4 \text{ eV} \times \frac{1.6 \times 10^{-18} \text{ J}}{\text{eV}}$$

$$= \boxed{1.98 \times 10^{-18} \text{ J}}$$

Only laser no. 2 has a photon energy (1.98×10^{-18} J) which is in excess of the bond energy Si–H (4.79×10^{-19}).

5. The bond energy for a LiF “molecule” is given as:

$$E = -\frac{e^2}{4\pi\varepsilon_o r_o}\left(1 - \frac{1}{n}\right)$$

We recognize that in this relationship the energy appears as the difference between the attractive and the repulsive term– where the repulsive term

$$E_{rep} = \frac{e^2}{4\pi\varepsilon_o r_o} \times \frac{1}{n}$$

The repulsive exponent n is unknown, but is expected to be around 10; this means that, neglecting shell repulsion, the calculated E value will be higher (by about 10%) than the actual value:

5. Continued:

$$E_{approximation} = +\frac{e^2}{4\pi\varepsilon_o r_o} = \frac{(1.6 \times 10^{-19})^2}{4\pi\ 8.85 \times 10^{-12} \times 1.52 \times 10^{-10}}$$

$$\boxed{E = +1.5 \times 10^{-18}\ \text{J}}$$

6. (a) Pure covalent bonds can only be formed by the interaction (overlap) of singly occupied orbitals and the maximum number of bonds is given by the number of existing singly occupied orbitals. With bond formation, molecular orbital formation, the bonding capability is saturated. In covalent bond formation, the charge distribution is axial between the reaction partners (σ bond) or lateral between the partners (π bond), the bonding is directional.

   Ionic bonds are the result of charge transfer which results in the formation of ions with opposite charge. The electric force fields associated with the ions are non–directional and therefore the bonding capability is not–saturated by the close proximity of oppositely charged species.

   (b) A direct consequence of the directional and saturated nature of covalent bonds is the formation of distinct species (molecule) with a limited number of atoms. (An exception is provided by Group IV elements, for example, where the number of spatial orientation of hybridized bonds permits the formation of covalent solids. A consequence of ion–formation (charge transfer) is in all instances the formation of a solid phase which, because of the principle of energy minimization, exhibits order on the atomic scale, i.e. crystalline structure.

7. This question was taken out of L. Pauling, General Chemistry; it cannot be solved without further information (there are three equations and five unknowns!). I apologize and hope you have learned something in attempting to find the solution.

8. Required: Periodic Table

(A look at the P.T. indicates that more than one oxidation state is encountered in Fe, Cu, Co, Te.)

1. $Ca \xrightarrow{2e^-} 2F = CaF_2$

2. $Al \xrightarrow{3e^-} 3Cl = AlCl_3$

3. $2K \xrightarrow{2e^-} S = K_2S$

4. $Fe \xrightarrow{2e^-} O = FeO$

   $2Fe \xrightarrow{6e^-} 3O = Fe_2O_3$

5. $Zn \xrightarrow{2e^-} 2Cl = ZnCl_2$

6. $Cs \xrightarrow{1e^-} Br = CsBr$

7. $Sr \xrightarrow{2e^-} Se = SrSe$

8. $Cu \xrightarrow{1e^-} Cl = CuCl$

   $Cu \xrightarrow{2e^-} 2Cl = CuCl_2$

9. $Co \xrightarrow{2e^-} 2F = CoF_2$

   $Co \xrightarrow{3e^-} 3F = CoF_3$

10. $Ti \xrightarrow{4e^-} 2O = TiO_2$

    $2Ti \xrightarrow{6e^-} 3O = Ti_2O_3$

    [$Ti \xrightarrow{2e^-} O = TiO$; very unstable and likely a mixture of ($Ti + TiO_2$)]

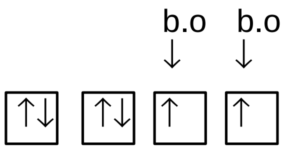
9. <u>Properties of Ionic Materials</u>:

   (a) <u>Transparent</u>: Ionic compounds are formed by charge transfer – which results in “stable” octets on both the cation and the anion. The energy gap between the valence shells (filled) and the next higher (empty) s orbital is so high (about 10 eV) that visible radiation cannot lead to electronic excitation; the radiation is not absorbed – the material appears transparent.

   (b) <u>Insulators</u>: There are no transparent electronic conductors. The argument made above applies here too. For conduction, the electrons under an applied potential must acquire energy – however, the lowest available empty energy states are separated by a large energy gap. No conduction can take place – ionic solids are insulators. The applied electric field exerts a force $q\varepsilon$ on each of the two types of ions in the crystal, but the ions are impeded from movement (ionic conduction) by the surrounding ions. Since, as we will see shortly, there are always some “vacancies” in the solids, small currents are observed. These are not electronic, but ionic, and therefore are associated with mass transport.

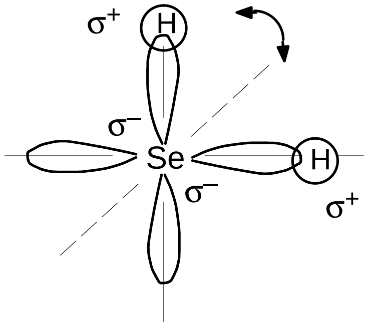
9. (c) <u>Conductors in the Molten State</u>: The phase transformation solid → liquid takes place when, through a temperature increase (at the melting point), the disruptive thermal forces exceed the attractive bonding forces which hold the "solid state" together. The phase transformation does not affect the electronic shell configurations – which remain octet–stabilized. Upon application of a potential, the anions will move to the anode ($2Cl^- \rightarrow Cl_2 + 2e^-$) and the cations will move to the cathode [$Na^+ + 1e^- \rightarrow Na(m)$].

10. (a) Se: $4s^2p^4$



2 bonding orbitals (like its homologue, O)

The relative electronegativity difference $\Delta X = (2.55 - 2.20) = 0.35$; the compound formed wil be covalent (polar).



The chemical formula is $\boxed{H_2Se.}$

(b) We have a discrete covalent molecule which is expected to be a gas at room temperature. A comparative analysis with H_2O (liquid at R.T.) indicates a decreased dipole moment and the absence of hydrogen bonding. This analysis cannot be quantitative without data – thus, if you make the above analysis and conclude the compound is liquid, you will get full credit. The decreased secondary bonding renders <u>H_2Se gaseous at room temperature</u>. (You could have found that out by a quick trip to the library – a good place to visit on–and–off.)

11. (a) The elements involved are $_{13}Al$, $_{19}K$, $_{26}Fe$, $_{35}Br$.

If we analyze for the possible valence states we find:

Al^{+++} , K^{+} , Fe^{++} and Fe^{+++} , Br^{-}

The only anion is Br, which appears in all compounds:	**B = Br**
There is only one AB compound:	**A = K**
One cation (D) appears with valencies +2 and +3:	**D = Fe**
This leaves C as Al:	**C = Al**

(b)

AB	= KBr	$\Delta x = (2.96–0.82) = 2.4$	ionic (some covalent contribution)
B_2	= Br_2	$\Delta x = 0$	covalent (pure)
CB_3	= $AlBr_3$	$\Delta x = (2.96–1.61) = 1.35$	covalent (polar)
DB_2	= $FeBr_2$	$\Delta x = (2.96–1.17) = 1.79$	ionic (some covalent contribution)
DB_3	= $FeBr_3$	$\Delta x = (2.96–1.17) = 1.79$	ionic (some covalent contribution)

12. (a) Sulfur is a homologue of oxygen; both are in Group VI: the valence shell has s^2p^4 configuration. There are two singly occupied p orbitals available for a σ bond formation with hydrogen:

chemical formula: H_2S

(b) Assuming (p–s) orbital overlap on compound formation and the establishment of polar covalencies ($\Delta x = 0.38$), we anticipate that the (non–polarized and non–hybridized) p–p bond angle is not 90^o but likely more, and 100^o appears a reasonable number for the B.A. (It is frequently stated that the large B.A. in H_2O and homologues can best be explained by involving sp^3 type hybridization.)

(c) The compound is expected to be a “gas” – not so much because of the smaller dipole moment compared to H_2O, but because of the absence of hydrogen bonding.

13. The key factor is the absence of hydrogen bonding – the dipole–dipole interaction is not enough to lead to condensation at R.T.

14. According to Pauling,the square of the difference in electronegativity for two elements $(X_A - X_B)^2$ is given by the following relationship:

$$(X_A - X_B)^2 = \left[\text{Bond energy (A – B)} - \sqrt{\text{Bond Energy AA} \cdot \text{Bond Energy BB}}\right] \times \frac{1}{96.3}$$

if bond energies are given in kJ.

(a) $$(X_H - X_F)^2 = \left[565 - \sqrt{436 \times 172}\right]\frac{1}{96.3} = 3.02$$

$$\boxed{(X_H - X_F) = \sqrt{3.02} = 1.7}$$

$$(X_C - X_H)^2 = \left[410 - \sqrt{335 \times 436}\right]\frac{1}{96.3} = 0.29$$

$$\boxed{(X_C - X_H) = \sqrt{0.29} = 0.54}$$

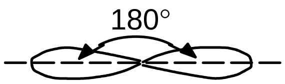
(b) Dilemma: $(2.1 - X_F) = 1.7$?
$(X_F - 2.1) = 1.7$?
We recognize that X_F may be either 3.8 or 0.4.

(This dilemma arises from the fact that Pauling had to operate with $(X_A–X_B)^2$ to avoid the appearance of a negative X value; the proper solution is always obvious considering the position of a given element in the Periodic Table.)

$\boxed{X_F = 3.8}$; the book value is 4.0.

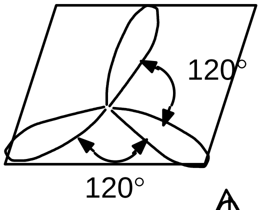
$(X_C - 2.1) = 0.54$ $\boxed{X_C = 2.64}$; the book value is 2.5.

15. sp hybrid



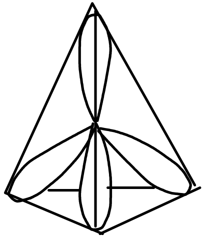
linear bonding orbital configuration; bond angle 180°

sp^2 hybrid



planar bonding orbital configuration; bond angle 120°

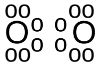
sp^3 hybrid



tetrahedral bonding orbital configuration; bond angle 109.5°

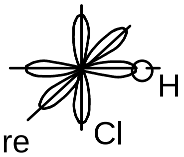
16. O_2 It is a gas at R.T. My apologies: you cannot be expected to find this answser (it is in fact not yet available).

It is customary to present the bonding as: $\overline{\underline{O}} = \overline{\underline{O}}$ or



the formation of two unspecified covalent bonds; this presentation is, however, inconsistent with the observed paramagnetism which demands the existence of an unpaired electron – consequently it is now frequently rewritten as: $|\overline{\underset{o}{O}} — \overline{\underset{o}{O}}|$ which in turn is not in line with the experimentally determined bond energy.

HCl H—Cl = H — $\overline{\underline{Cl}}|$ =



(p + s → σ orbital)

Δx = 0.9 polar covalency

a gas at room temperature

SiO2 Could be written as O=Si=O, but this would be incorrect!

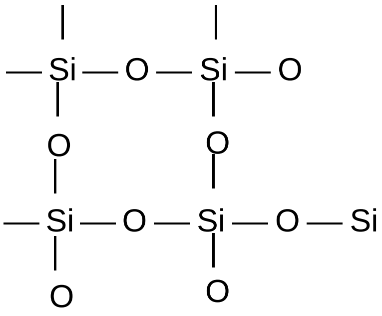
Si $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ $\boxed{}$

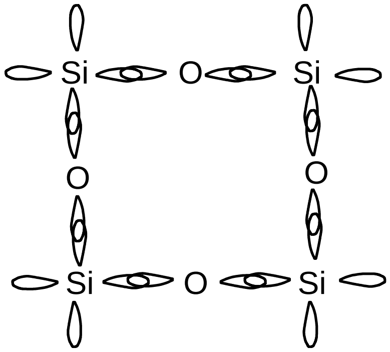
3s 3p

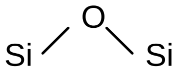
Si, like C, is subject to sp^3 hybridization and forms four equivalent hybrid orbitals directed with 109° bond angles at the corners of a <u>tetrahedron</u>. At each corner is located an oxygen atom which forms a bridge to another silicon with tetrahedral bond configuration – we obtain an ordered 3–dimensional structure.

16. Continued.

In <u>planar presentation</u> we would write:

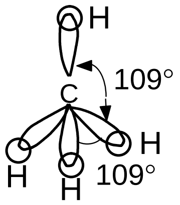




The Si–O bond is a polar covalency with the  bond angle being stressed out of their 90^o (p) configuration. SiO_2 is a solid at room temperature. (Your answer is acceptable if you say sp^3 hybridization leading to polar covalency.)

LiF Electron transfer and ionic bond formation: Li^+F^-. We have the formation of a solid at room temperature.

CH_4 sp^3 hybridization:



(planar presentation of a tetrahedron and 4 σ bonds are formed with l09^o bond angles)

The four σ bonds formed are polarized. CH_4 is a gas at room temperature.

17. $$\Delta E = \frac{e^2 N_A M}{4\pi\varepsilon_o r_o}\left(1 - \frac{1}{n}\right)$$

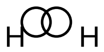
The assumption must be made that the distance of separation of Na–F is given by the sum of the ionic radii (that in a crystal they touch each other – a not unreasonable assumption). Thus, $r_o = 0.95 \times 10^{-10} + 1.36 \times 10^{-10}$ m = 2.31 Å and you must also assume M is the same as for NaCl = 1.747:

$$E_{cryst} = -\frac{(1.6 \times 10^{-19})^2\ 6.02 \times 10^{23} \times 1.747}{4\pi\ 8.85 \times 10^{-12} \times 2.31 \times 10^{-10}}\left(1 - \frac{1}{8.7}\right)$$

$$\boxed{E_{cryst} = 927.5\ \text{kJ/mole}}$$

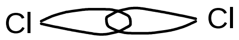
18. (a) σ bond:

s–s example H_2



s–p example HCl

p–p example Cl_2



hybrid orbitals – hybrid orbitals, example C–C

hybrid orbitals, s or p

or

(b) π orbitals cannot be formed if one of the partners is an s orbit.

19. $E_{cryst} = K(1 - 1/n) = K - 1/n\,K$ where $-1/n\,K$ is the repulsive contribution to $E_{cryst} \cdot 1/n \cong 1/8$. This means only ~12% of the total crystal energy.

20. (a) $H_2 + Br_2 \rightarrow 2HBr \qquad \Delta X = 0.7 \quad \boxed{\text{polar covalency}}$

(b) $E_T = \sqrt{E_{H_2} \times E_{Br_2}} + \Delta = 331 + 96.5 \times (0.7)^2 = \boxed{378 \text{ kJ/mole}}$

21. The energy of an electron (kinetic energy) under the influence of a potential drop (V) is given by:

$$E_{Kin} = (mv^2)/2 = eV \qquad (1)$$

The particle wavelength of such an electron is given by:

$$\lambda_{deBroglie} = h/mv \qquad (2)$$

Making use of (2), it is possible to substitute for v in (2):

$$\frac{mv^2}{2} = eV \qquad v = \sqrt{\frac{2eV}{m}} \qquad \text{and} \qquad \lambda_{deB.} = \frac{h}{m\sqrt{\frac{2eV}{m}}} = \frac{h}{\sqrt{2eV\ m}}$$

21. Continued

To solve the given problem, we take $\lambda = 0.1 \times 10^{-10}$ m and isolate V:

$$\sqrt{2eV\ m} = \frac{h}{\lambda}$$

$$V = \frac{h^2}{\lambda^2} \times \frac{1}{2em} = \frac{(6.62 \times 10^{-34})^2}{(10^{-11})^2 \times 2 \times 1.6 \times 10^{-19} \times 9.1 \times 10^{-31}}$$

$$= 15{,}050\ V = \boxed{15.05\ kV}$$

22. To calculate the particle wavelength for an electron ($\lambda = h/mv$) requires knowledge of its velocity:

$$eV = \frac{mv^2}{2} \quad ; \quad v = \sqrt{\frac{2eV}{m}}$$

By substitution we now obtain:

$$\lambda = \frac{h}{m\sqrt{\frac{2eV}{m}}} = \frac{h}{\sqrt{2eV\ m}}$$

$$= \frac{6.62 \times 10^{-34}}{\sqrt{2 \times 1.6 \times 10^{-19} \times 1.5 \times 10^4 \times 9.1 \times 10^{-31}}}$$

$$\lambda_{deB.} = \boxed{1 \times 10^{-11}\ m = 0.1\ Å}$$

23. Required: (a) $\lambda = h/mv$; $mvr = n(h/2\pi)$; $r = r_o n^2$; $r_o = 0.529$ Å
$m_c = 9.1 \times 10^{-31}$ kg
(b) The short way: $n\lambda = 2\pi r$; $r = r_o n^2$

(a) The long way:

$$\lambda_p = \frac{h}{mv} \quad ; \quad mvr = n\frac{h}{2\pi}$$

$$v = \frac{3h}{2\pi m \times 9r_o} = \frac{h}{6\pi m r_o}$$

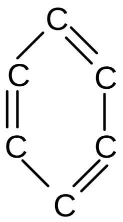
$$\lambda_p = \frac{h}{m\frac{h}{6\pi m r_o}} = 6\pi r_o = 6\pi \times 0.529 \times 10^{-10} = \boxed{9.971 \times 10^{-10}\ m}$$

23. (b) The short way:

$$n\lambda = 2\pi r = 18\pi r_o$$

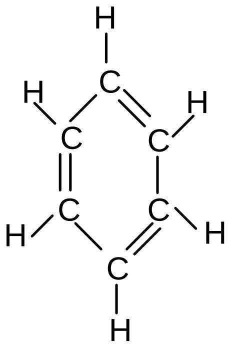
$$\lambda = \frac{18\pi r_o}{3} = 6\pi r_o \quad \text{(see above)}$$

24. (a)



From the schematic we recognize three single and three double carbon–to–carbon bonds which are respectively of the σ (sigma) and σ + π (sigma + pi) variety. Left out in the schematic are the six C–H bonds which are of the σ variety:

In C_6H_6, $\boxed{\text{we have 12 } \sigma \text{ and 3 } \pi \text{ bonds.}}$

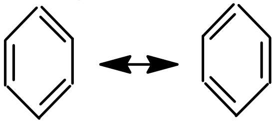


= C_6H_6

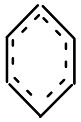
(b) In the ring structure of benzene we have three double bonds, which means that all six carbon atoms are sp^2 hybridized. Accordingly:

3 π bonds involve lateral (p–p) obrital overlap.
6 (C–C) σ bonds involve (sp^2–sp^2) orbital overlap.
6 (C–H) σ bonds involve (sp^2–s) orbital overlap.

(It should be noted that the experimentally determined bond energy for the carbon ring is larger than the sum of the bond energies of the double plus single bonds. This increased bond energy is attributed to the existence of alternating double bonds which permit the establishment of "equivalent resonance structures"



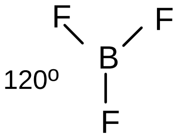
in which the double bonds are said to be delocalized:



25. Double bond formation, the result of lateral p orbital overlap, is contingent on close approach of the atoms. Such approach is possible for carbon with its K shell, but not for the larger germanium with its fully occupied M shell.

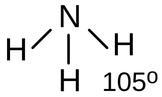
26. The answer to this question is found by looking at the valence shell configurations of B and N:
B: $2s^2p^1$
N: $2s^2p^3$

We realize that boron can hybridize into a planar sp^2 bonding configuration and form three σ bonds with fluorine. The compound is expected to be internally polarized, but no permanent dipole will thus result because of the bonding symmetry. Nitrogen has three singly occupied 2p orbitals directed at right angles to each other. Upon σ bond formation in NH_3, we anticipate a pyramidal configuration with nitrogen at the apex. Because of bond polarization ($\Delta x = 0.82$), mutual repulsion of the activated hydrogen atoms is anticipated to increase the bond angle (which is found to be 105^o). In fact, the large bond angle observed in NH^3 suggests sp^3 hybridization similar to that invoked in H_2O. In either case, the resulting molecule will exhibit a permanent dipole moment.



(planar)

non–polar



(sp^3 hybridization)

polar

27. (a) According to Pauling: $\text{B.E.}_{AB} = \sqrt{\text{B.E.}_{AA} \times \text{B.E.}_{BB}} = 96.3\ (X_A - X_B)^2$

$$\text{B.E.}_{C-Cl} = \sqrt{239 \times 334} + 96.3\ (3.16 - 2.55)^2$$

$$\boxed{\text{B.E.}_{C-Cl} = 318.4\ \text{kJ/mole}}$$

(b) The present ionicity can be obtained (by interpolation) of the table, Percent Ionic Character of a Single Chemical Bond, in the Periodic Table of the Elements. Accordingly, for $\Delta x = 0.61$, the percent ionic character is **9.3**.

Alternately, we can make use of the Pauling relationship:

$$\%\ \text{ionicity} = 18\ (\Delta x)^{1.4}$$

Accordingly:

$$\boxed{\%\ \text{ionicity} = 18 \times (0.61)^{1.4} = 9.0}$$

(The ~3% discrepancy can be attributed to the empirical nature of the approach taken by Pauling.)

28. To answer this question you need to know the distance travelled from 13–4134 to 10–250. Depending on time available and subjects to carry along, the lecturer walks along the peripheral corridor ($x \cong 60$ m) or takes a short–cut through the laboratories ($x \cong 45$ m). The velocity of your instructor is correspondingly:

$$v_{(1)} = 45/136 = 0.33 \text{ m/s} \quad \text{or} \quad v_{(2)} = 60/136 = 0.44 \text{ m/s}$$

Taking the weight:

$$m = 174 \text{ lb} \times \frac{1 \text{ kg}}{2.205 \text{ lb}} = 78.9 \text{ kg}$$

$$\lambda_1 = \frac{h}{mv_1} = \frac{6.63 \times 10^{-34}}{78.9 \times 0.33} = 2.54 \times 10^{-35} \text{ m}$$

$$\lambda_2 = \frac{h}{mv_2} = \frac{6.63 \times 10^{-34}}{78.9 \times 0.44} = 1.91 \times 10^{-35} \text{ m}$$

Any value from $\boxed{1 \times 10^{-35} \text{ to } 3 \times 10^{-35} \text{ m}}$ is acceptable.

29. According to deBroglie:

$$n\lambda_p = 2\pi r_n \qquad \text{(for the “O” shell, n=5)}$$

$$n\lambda_p = 2\pi n^2 r_o$$

$$\lambda_p = 2\pi n r_o = 10\pi \times 0.529 \times 10^{-10} \text{ m}$$

$$\boxed{\lambda_p = 1.66 \times 10^{-9} \text{ m}}$$

[You arrive at the same result by determining $E_K = (E_{total} - E_{Pot})$ for n=5 and from it deriving λ_p from $E_K = (mv^2)/2$ and $\lambda_p = h/(mv)$.]

30. To solve this problem we need to know the deBroglie relation:

$$\lambda_p = h/mv$$

$$v = h/(m\lambda_p) \qquad \lambda_p = 3v \cdot 2 = 6v[m/s \text{ x } s]$$

$$v = h/(6mv)$$

$$v^2 = h/6m \qquad v = \sqrt{h/6m}$$

$$= \sqrt{\frac{6.63 \text{ x } 10^{-34}}{6 \text{ x } 9.1 \text{ x } 10^{-31}}} = \boxed{0.011 \text{ ms}^{-1}}$$

31. (a) $E_{equ} = -3.84 \text{ eV} = -3.84 \text{ x } 1.6 \text{ x } 10^{-19} \text{ J} = -\frac{e^2}{4\pi\varepsilon_o r_o}(1 - \frac{1}{n})$

$$r_o = \frac{(1.6 \text{ x } 10^{-19})^2}{4\pi \text{ } 8.85 \text{ x } 10^{-12} \text{ x } 6.14 \text{ x } 10^{-19}}(1 - \frac{1}{8}) = \boxed{3.3 \text{ x } 10^{-10} \text{ m}}$$

(b) Shell “repulsion” obviously constitutes a “negative” contribution to the bond energy. Looking at the energy equation we find:

the attractive term as: –E x (1) = –E
the repulsion term as: –E x (–1/n) = E/n = E/8

The contribution to the bond energy by the repulsion term = 1/8 x 100 = **12.5%**.

(Since the bond energy is negative, the 12.5% constitute a reduction in bond strength.)

32. B: $1s^2 2s^2 2p^1$
Br: [Ar] $4s^2 3d^{10} 4p^5$

(a) If B shares its $2p^1$ electron with Br’s $4p^5$ shell, they will both obtain somewhat stable valence shells. However, BBr would be polar.

If B hybridizes and its electron shell changes to

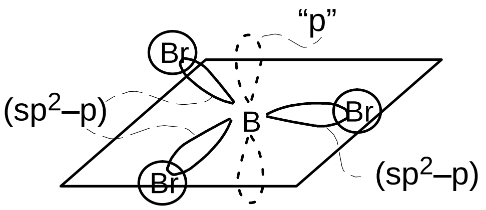
$$\overset{1s}{\boxed{\uparrow\downarrow}}\quad \overset{2sp^2}{\boxed{\uparrow}\,\boxed{\uparrow}\,\boxed{\uparrow}}\quad \overset{2p}{\boxed{}}$$

then the B can bond with 3 Br. **BBr_3: 3(sp^2–p overlap) σ bonds**

The symmetry of the hybridized (planar) molecule leads to coincidence of the centers of + and – charges — the molecule, in spite of three polar covalencies, does not exhibit a dipole moment.

(b)
$$\overset{1s}{\boxed{\uparrow\downarrow}}\quad \overset{2s}{\boxed{\uparrow\downarrow}}\quad \overset{2p}{\boxed{\uparrow}\,\boxed{}\,\boxed{}}\ \rightarrow\ \overset{1s}{\boxed{\uparrow\downarrow}}\quad \overset{2s}{\boxed{\uparrow}}\quad \overset{2p}{\boxed{\uparrow}\,\boxed{\uparrow}\,\boxed{}}$$

$$\rightarrow\ \overset{1s}{\boxed{\uparrow\downarrow}}\quad \overset{2sp^2}{\boxed{\uparrow}\,\boxed{\uparrow}\,\boxed{\uparrow}}\quad \overset{2p}{\boxed{}}$$



(c) All three bonds are based on sp^2 orbital overlap, leading to the formation of σ bonds.

(d) **Likely a liquid, or a gas.**
Even though the electronegativity difference is large (0.94), because of the planar bonding symmetry, the BBr_3 molecules will have no dipole moment. The only intermolecular force acting is too weak to form a solid!

33. The bonds in the material would be strongly ionic since the electronegativity difference is much greater than 1.7. It would probably be a crystalline solid since ionic materials are crystalline, and it would be an insulator because the electrons are bound tightly to the positively charged nucleus.

34. Because O and F are more electronegative than S and Cl, H_2O and HF form stronger hydrogen bonds than H_2S and HCl. These strong hydrogen bonds increase the intermolecular forces enough in H_2O and HF to more than compensate for the higher weight of H_2S and HCl, and cause H_2O and HF to have significantly higher boiling points than their homologues.

35. If we look at the information provided, we recognize: the photon energy is given through λ, the ionic component of the C–Cl bond can be determined from the Pauling series of the relative electronegativity. However, the pure covalent bonding contribution cannot be determined. You are marginally correct if you state:

the problem cannot be solved with the data given!

You will get full credit with this answer, but you can indeed solve the problem since:

B.E. C–C = 334 kJ/mole (class notes)
B.E. Cl–Cl = 239 kJ/mole (lecture notes)

$$\text{B.E. C} - \text{Cl} = \sqrt{334 \text{ x } 239} + 96.2\,(3.16 - 2.55)^2 = 318 \text{ kJ/mole}$$

$$= \boxed{5.29 \text{ x } 10^{-19} \text{ J/bond}}$$

Radiation energy is given as $E_{h\nu} = (hc)/\lambda = 6.63 \text{ x } 10^{-20}$ J/bond. We recognize that the radiation energy is by about one order of magnitude smaller than the bond energy.

CCl_4 will not decompose under irradiation by $\lambda = 3 \text{ x } 10^{-6}$ m.

36.

1.) $\mathrm{Ca(s)} \rightarrow \mathrm{Ca(v)}$	ΔH_{vap} (+)
2.) $\mathrm{Br_2\,(g)} \rightarrow 2\,\mathrm{Br}\bullet$	ΔH_{dissoc} (+)
3.) $\mathrm{Ca} \rightarrow \mathrm{Ca}^{++} + 2e^{-}$	
3a.) $\mathrm{Ca} \rightarrow \mathrm{Ca}^{+} + 1e^{-}$	ΔH_{ioniz} (+)
3b.) $\mathrm{Ca}^{+} \rightarrow \mathrm{Ca}^{++} + 1e^{-}$	ΔH_{ioniz} (+)
4.) $\mathrm{Br} + 1e^{-} \rightarrow \mathrm{Br}^{1-}$	EA (–) → exothermic
5.) $\mathrm{Ca}^{2+} + 2\mathrm{Br}^{1-} \rightarrow \mathrm{CaBr_2}$	DE_{cryst} (–) → exothermic

$$\Delta H_{reaction} = \Delta H_{vap} + \Delta H_{dissoc} + 1.\Delta H_{ioniz} + 2.\Delta H_{ioniz} + 2EA + \Delta E_{cryst}$$

(it is acceptable to note $\mathrm{Ca} \rightarrow \mathrm{Ca}^{++} + 2e^{-}$ if you realize that 1. and 2. ionization is involved)

37. $$\Delta E = \frac{-\,e^2 N_A M Q_1 Q_2}{4\pi E_o r_o}\left(1 - \frac{1}{n}\right)$$

1.) $$\left.\begin{array}{l}\mathrm{CaS} \rightarrow \mathrm{Ar}^{2+} + \mathrm{Ar}^{2-} \\ \mathrm{KCl} \rightarrow \mathrm{Ar}^{1+} + \mathrm{Ar}^{1-}\end{array}\right\} \left.\begin{array}{l} Q_1 = Q_2 = 2 \text{ for CaS} \\ Q_1 = Q_2 = 1 \text{ for KCl}\end{array}\right\} \rightarrow \left|\Delta E_{cryst}\right|_{CaS} > \left|\Delta E_{cryst}\right|_{KCl}$$

N.B. similar radius but different charge number.

2.) $$\left.\begin{array}{l}\mathrm{LiF} \rightarrow \mathrm{He}^{1+} + \mathrm{Ne}^{1-} \\ \mathrm{CsBr} \rightarrow \mathrm{Xe}^{1+} + \mathrm{Kr}^{1-}\end{array}\right] \begin{array}{l}\text{equal charge number but} \\ r_{o_{CsBr}} > r_{o_{LiF}} \rightarrow \left|\Delta E_{cryst}\right|_{LiF} > \left|\Delta E_{cryst}\right|_{CsBr}\end{array}$$

3.) $$\left.\begin{array}{l}\mathrm{MgO} \rightarrow \mathrm{Ne}^{2+} + \mathrm{Ne}^{2-} \\ \mathrm{MgS} \rightarrow \mathrm{Ne}^{2+} + \mathrm{Ar}^{2-}\end{array}\right] \begin{array}{l}\text{equal charge number but} \\ r_{o_{MgS}} > r_{o_{MgO}} \rightarrow \left|\Delta E_{cryst}\right|_{MgO} > \left|\Delta E_{cryst}\right|_{MgS}\end{array}$$

4.) $$\left.\begin{array}{l}\mathrm{MgO} \rightarrow \mathrm{Ne}^{2+} + \mathrm{Ne}^{2-} \\ \mathrm{BaO} \rightarrow \mathrm{Xe}^{2+} + \mathrm{Ne}^{2-}\end{array}\right] \begin{array}{l}\text{equal charge number but} \\ r_{o_{BaO}} > r_{o_{MgO}} \rightarrow \left|\Delta E_{cryst}\right|_{MgO} > \left|\Delta E_{cryst}\right|_{BaO}\end{array}$$

38.

1.) $Ca^{(s)} \rightarrow Ca(g)$	$\Delta H_{sublimation}$ (+)
2.) $1/2O_2 \rightarrow O$	$\Delta H_{dissociation}$ (+)
3.) $Ca(g) \rightarrow Ca^{2+} + 2e$	$\Delta H_{ionization}$ (+)
4.) $O + 2e^- \rightarrow O^{2-}$	E.A. (–)
5.) $Ca^{2+} + O^{2-} \rightarrow CaO(s)$	ΔE_{cryst} (–)
Total $Ca(s) + 1/2O_2(g) \rightarrow CaO(s)$	$\Delta H_{reaction} < 0$

The reason why CaO is more stable than its atomic components is because of its lower energy content.

$$\left|\Delta H_s + \Delta H_d + \Delta H_2\right| < \left|EA + \Delta E_{cryst}\right|$$

(The acquisition of 2 electrons by oxygen is not requiring energy – but the whole process: [$O_2 \rightarrow 2O$; $2O + 4e^- \rightarrow 2O^{--}$] requires energy!)

39. (a) Given the radii Cs^+ = 1.67Å and Cl^- = 1.81Å, we can assume that r_o is the sum of the two. However, we need to know the exponential constant of the repulsive term which is not provided. Considering only the attractive force:

$$\Delta E_{cryst} = \frac{-\ e^2 N_A M Q_1 Q_2}{4\pi\varepsilon_o r_o}$$

where: $Q_1 = Q_2 = 1$
$M = 1.763$
$N_A = 6.02 \times 10^{23}$ particle/mole

$$\Delta E_{cryst} = \frac{-\ (1.6 \times 10^{-19}\text{coul})^2 \times 6.02 \times 10^{23} \times 1.763 \times 1 \times 1}{4\pi \times 8.85 \times 10^{-12} \times (1.81 + 1.67) \times 10^{-10}\text{m}}$$

$$= \boxed{7.02 \times 10^{5} \text{ J/mole}}$$

(b) Because we didn't include the repulsive part, we expect the theoretical energy to be smaller by 1/n times that calculated above. Because n is in the range of 10 $\boxed{\text{we are off by around +10\%}}$

40. $$\lambda_p = \frac{h}{mv}$$

$$= \frac{6.63 \times 10^{-34}\ \text{Js}}{0.150[\text{kg}] \times 99\frac{\text{mi}}{\text{h}} \times \frac{1600\text{m}}{\text{mile}} \times \frac{\text{h}}{3600\text{s}}} = \boxed{1.00 \times 10^{-34}\ \text{m}}$$

40. Continued.

Playing rules for 1876: The Ball

The ball must weigh not less than 5 or more than 5 1/4 ounces, (avoirdupois). It must measure not less than 9, nor more than 9 1/4” in circumference. It must be of woolen yarn and shall not contain more than 1 ounce of vulcanized rubber in mold form and shall be covered with leather.

(1 ounce, avoirdupois = 28.350g)