CHEMISTRY 135
ATOMIC PROPERTIES, BONDING AND SHAPES OF MOLECULES

1) a) Write out the electronic configurations of the following atoms showing occupancy of orbitals: Be, B, C, O, Ne, K, Zn, Sr, Cd, Xe.
   b) Write out the electronic configurations of the following ions: Be^{2+}, F^-, Na^+, Ca^{2+}, Cd^{2+}.
2) Briefly explain what is meant by each of the following terms, giving examples where appropriate:
   a) i) Atomic radius
      ii) Ionic radius
      iii) Metallic radius
      iv) Van der Waals radius
      v) Covalent radius
   b) i) Ionization energy
      ii) Electron affinity
   c) i) Electropositivity
      ii) Electronegativity
3) Explain briefly, in terms of electronic structures, the occurrence of periods, groups and transition series in the periodic table.
4) Explain, using the electronic structure of oxygen as an example, what is meant by (a) the Pauli exclusion principle, and (b) Hund's rule.
5) Without referring to the periodic table name the elements, give the electronic structure, and name the group in the periodic table to which elements with the following atomic numbers belong: 4, 9, 15, 17, 20, 28, and 37.
6) a) How does the atomic radius vary (i) going down a group, (ii) going left to right across a period, and (iii) going left to right across the first transition series of elements (ie. the elements scandium to copper) in the periodic table.
   b) Describe the basic trends encountered in (i) ionization energy and (ii) electron affinity in the periodic table.
   c) The radius of an ion is roughly one third of the radius of the original atom. What can you say about the identity of this atom? How does the ***volume*** of the ion compare with that of the atom?
   d) Explain how the radius of an anion compares with that of the atom from which it is formed.
7) Place the following species in order of increasing radius:
   a) F_2, F, and F^-.
   b) Fe, Fe^{3+}, and Fe^{2+}.
   c) Br, F, Cl, I
   d) Cl, Si, O, Na, Mg,
8) The P-Cl bond length in PCl_3 is 0·204nm. The bond length in Cl_2 is 0·198nm. Calculate the atomic radii of chlorine and phosphorus, and the probable bond length in PF_3 given that the fluorine atom has radius 0·071nm. Calculate also the bond length in ClF and comment on your result given that the actual value is 0·164nm.
9) a) Write down the electronic structures of Li, Al, O and F. Show how these structures are changed when these atoms form ions.
   b) Explain the meaning of the term ***isoelectronic***. With what atoms are the above ions isoelectronic?
10) Carefully and fully explain the meaning of each of the following terms.
   a) Valence electron
   b) Ionic bond

c) Covalent bond
d) Dative covalent bond
e) Polar covalent bond
f) Polarisability
g) Polarising power
h) Dipole moment
i) Percentage ionic character
j) Macromolecule
k) Bond
l) Intermolecular force
m) Van der Waals Forces
n) Dipole/dipole interaction
o) London dispersion force
p) Hydrogen bond

11) Draw diagrams to show how the following compounds are produced from atoms of their elements. In each case show how the outer shell electrons are affected.
a) sodium chloride
b) calcium fluoride
c) aluminium oxide

12) Determine which of the following statements is true and state why.
a) Ionization energy increases down a group.
b) Ionization energies decrease from right to left across a period.
c) All the halogens have higher first-ionization energies than all the noble gases.
d) One reason why helium is unreactive is that its ionization energy is very high.

13) Determine which of the following statements is true and state why.
a) More energy is released when a chlorine atom gains an electron than when a bromine atom gains an electron.
b) The electron affinity of a singly-charged cation is greater than that of the parent atom.
c) The electron affinity of a singly-charged anion is greater than that of the parent atom.
d) The first electron affinity of an atom is numerically equal to the first ionization energy of the resulting ion.
e) An F^- ion is of lower energy than a widely separated F atom and electron.

14) What is meant by the ionization energy of an element? The first three ionization energies of sodium are 494, 4564, and 6924 kJ mol^{-1}; those for magnesium are 744, 1464, and 7750 kJ mol^{-1}; similarly the first four ionization energies for aluminium are 578, 1811, 2745, and 11540 kJ mol^{-1}. Plot the logarithm of these successive ionization energies against the number of the ionization (ie. 1, 2, 3, or 4) and comment on your results by referring to the usual ions that these elements form.

15) Arrange the following elements in order of increasing electronegativity.
a) B, Al, C, Si
b) O, F, Cl, N
c) Na, K, Mg, Ca
d) Al, Mg, Li, Be

16) a) Which one of each pair would be expected to have the higher first ionization energy?
i) Li or Cs
ii) Li or F
iii) Cs or F
iv) F or I
b) Which one of each pair would be expected to have the (numerically) higher first electron affinity?
i) C or F
ii) F or I
iii) Te or I
iv) C or Si
v) F or Cl
vi) Cl or Br
vii) O or S
viii) S or Se

17) a) Rank the following in order of increasing ionic character.

i) HCl, NaCl, LiCl, $AlCl_3$, Cl_2

ii) IF, ClF, F_2, BrF,

iii) $FeCl_2$, $FeCl_3$

b) In each of the above cases suggest which substance or molecule is expected to:

i) have the highest melting and boiling points.

ii) have the lowest dipole moment. (Molecules only.)

c) Which of the substances NaCl and LiCl would you expect to be the most soluble in alcohol? Explain your answer.

18) Use figures from your text book to calculate the charge/radius ratio of each of the following ions and so rank them in order of increasing polarizing power: Na^+, Mg^{2+}, Al^{3+}, B^{3+}, Pb^{4+}. (B^{3+} and Pb^{4+} have been estimated as 0·020 and 0·084 nm respectively.) On this basis, which one of their chlorides should possess the most covalent character and which the least?

The boiling points of the above chlorides are: 1465, 1437, 181, 12, and 105°C respectively. Discuss these values in the light of your conclusions.

19) Discuss the nature of metallic bond and show how it accounts for the physical properties of metals.

20) Explain the meaning of the term ***ionic bonding*** and briefly describe the typical properties of an ionic compound. What sorts of element combine to form ionic compounds? Interpret your answer in terms of electronegativity values.

The formation of a cation is an endothermic process and the formation of an anion is often so, and yet the formation of an ionic compound from its elements is always exothermic. Where is the energy coming from?

21) Using diagrams explain the meaning of the term ***metallic bond***. What properties does this bond confer on metals?

22) Silica is a high-melting solid, whilst carbon dioxide is a gas at room temperature. Account for this difference in properties in terms of structure and bonding.

23) Draw valence bond diagrams (Lewis electron-dot diagrams) to explain the bonding in each of the following. Show ALL outer shell electrons.

a) the hydrogen molecule

b) the chlorine molecule

c) the oxygen molecule

d) the nitrogen molecule

e) the water molecule

f) the ammonia molecule

g) the methane molecule

h) the ethane molecule

i) the ethene molecule

j) the ethyne molecule

k) the methanol molecule

24) Draw valence bond diagrams (Lewis electron-dot diagrams) to explain the bonding in each of the following. Show ALL outer shell electrons.

a) beryllium dichloride

b) boron trifluoride

c) sulfur hexafluoride

d) sulfur trioxide

e) sulfur dioxide

f) hydrogen sulfide

g) sulfur tetrachloride

h) xenon tetrafluoride

i) iodine pentafluoride

j) nitrogen monoxide

k) nitrogen dioxide

l) dinitrogen trioxide

m) dinitrogen pentoxide

n) dinitrogen monoxide (NNO)

25) Draw valence bond diagrams (Lewis electron-dot diagrams) to explain the bonding in each of the following. Show ALL outer shell electrons.

a) the sulfate ion

b) the sulfite ion
c) the carbonate ion
d) the hydrogencarbonate ion
e) the hydroxide ion
f) the ammonium ion
g) the hydronium ion
h) the boron trifluoride-ammonia complex
i) the nitrate ion
j) the nitrite ion
k) the thiosulfate ion
l) the peroxydisulfate ion (S2O82-)
m) the orthophosphate ion (PO43-)
n) The tetra-aquocopper(II) ion ([Cu(H2O)4]2+)

26) Explain the meaning of the term ***resonance*** in valence bond theory. What features of molecules are explained by the concept of resonance? How many of the molecules or ions of questions 5 and 6 can you find which require resonance to explain their properties? Draw three canonical forms for the nitrate ion. In what way do the canonical forms of a molecule differ from each other?

27) The geometry of a molecule is determined by the number of atoms or groups and the number of pairs of electrons surrounding the central atom. The arrangement of electron pairs must be distinguished from the arrangement of the nuclei, which determines overall molecular shape. Sketch the orientation of electron pairs and the shapes of the molecules in the following cases. Name the geometry of both the arrangement of electron pairs and the molecule as a whole in each case. Give an actual example of such a molecule and draw a diagram of it.

a) 2 bonding pairs of electrons only.
b) i) 3 bonding pairs of electrons only.
ii) one lone pair and 2 bonding pairs.
c) i) 4 bonding pairs of electrons only
ii) one lone pair and 3 bonding pairs.
iii) two lone pairs and 2 bonding pairs.
iv) three lone pairs and 1 bonding pair.
d) i) 5 bonding pairs of electrons only.
ii) one lone pair and 4 bonding pairs.
iii) two lone pairs and 3 bonding pairs.
iv) three lone pairs and 1 bonding pair.
e) i) 6 bonding pairs of electrons only.
ii) one lone pair and five bonding pairs.
iii) two lone pairs and four bonding pairs.
iv) three lone pairs and three bonding pairs.
v) four lone pairs and two bonding pairs.

28) Use VSEPR theory to predict the shapes of each of the following species:

a) H_2O	b) H_2S	c) F_2O
d) H_3O^+	e) I_3^-	f) SiH_4
g) SF_6	h) IO_4^-	i) NCl_3
j) ICl_4^-	k) CO_2	l) AlH_4^-
m) ClO_3^-	n) SeF_6	o) X eF_2
p) XeF_4	q) ClO_4^-	r) $+C(CH_4)_3$
s) H_2Se	t) PH_3	u) ClOCl
v) BF_3	w) NF_3	x) SCl_4
y) ICl_3	z) ICl_2^+	α) ICl_2^-
β) $BeCl_2$	γ) $MgF_2(g)$	δ) BrCl
ε) SiF_4	ζ) PO_4^{3-}	η) PO_3^{3-}
θ) NO_2^-	ι) XeO_3	

29) Predict which of the following molecules would be expected to possess a dipole moment and (if appropriate) draw diagrams of the molecules with the positive and negative parts marked with δ+ and δ- respectively.

a) nitrogen
b) hydrogen sulfide
c) ammonia
d) germanium(IV) chloride
e) iodine trichloride
f) xenon difluoride

30) What types of bonding and intermolecular forces (as appropriate) are present in each of the following substances:

a) sodium chloride
b) potassium nitrate
c) solid neon
d) gaseous neon
e) solid carbon dioxide
f) copper(II) sulfate 5-water
g) silica
h) sodium
i) liquid hydrogen fluoride
j) liquid hydrogen iodide
k) liquid natural gas (a mixture of hydrocarbons)
l) DNA

31) What conditions are necessary for the formation of hydrogen bonds? How do hydrogen bonds contribute to the structure of ice? How do we know that hydrogen bonding is present in water? If water were not hydrogen-bonded, what would you expect for its boiling temperature and melting temperature and the relative densities of the liquid and solid states?

32) What reasons do we have for postulating the existence of Van der Walls forces? What is responsible for the van der Waals attractive forces, and what gives rise to repulsion?

33) On the basis of the probable intermolecular forces which operate, put the following in order of increasing boiling temperature, giving reasons for your choice:

C_4H_9OH, $CH_3CH_2CH_2CH_2CH_3$, $(CH_3)_3CCH_3$, N_2

34) Which member of each of the following pairs would you expect to have the higher boiling temperature? Give reasons for your choices.

a) C_3H_8 and CH_3OCH_3
b) $CH_3CH_2NH_2$ and CH_3CH_2OH
c) CH_3CH_2OH and C_2H_6
d) C_3H_8 and $(CH_3)_2C=O$

35) Sketch a graph of the boiling points of the hydrides of the group VI elements against proton number. Comment on the form of the graph with reference to hydrogen bonding.

36) Explain why and how hydrogen bonding is important in each of the following cases. Illustrate your answers with diagrams.

a) The fact that water boils at 100°C whereas hydrogen sulphide boils at -60·33°C.
b) The fact that ethanol (CH_3CH_2OH) is freely soluble in water whereas chloroethane (CH_3CH_2Cl) is not.
c) The fact that ice is less dense than water at 0°C.
d) The fact that the RMM of ethanoic acid vapour just above its boiling point is about twice what is expected.

37) The boiling points of the hydrides SiH_4, PH_3, H_2S, show an increasing trend and yet the relative molecular masses are similar. The dipole moments of these molecules are: 0, 0·58, and 0·97 Debye units respectively. Do you think there is any connection between these facts, and if so what?