PROBLEMS IN PHYSICAL CHEMISTRY

by

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PREFACE

This collection of questions was originally compiled to help those studying an up-dated Chemistry syllabus introduced by the Irish Department of Education in 1964, and was published by A. Folens Ltd. With some modifications it is now offered in the hope of being of wider assistance to those following advanced or modern courses of Chemistry in schools.

A. ATOMS, ORBITALS, VALENCY AND THE PERIODIC TABLE

Note. Questions in which a knowledge of orbital nomenclature is required or desirable are marked ‡

1. Which are the three main fundamental particles of which all atoms are composed? Compare their masses and electrical charges, and show how they are distributed within atoms.
2. Of what fundamental particles are atoms composed? Why is it that many elements, but not all, have atomic weights that are not whole numbers or nearly whole numbers?
3. The mass of the electron is 9×10^{-28} gram; the proton and neutron weigh approximately 2000 times as much. If the radius of a nucleus of mass number 10 is 10^{-13} cm, calculate the approximate density of nuclear matter.
4. "For all chemical purposes we can ignore the mass of an electron, but we cannot ignore its electric charge." Comment on this statement.
5. Distinguish between the terms "atomic number", "mass number", "atomic weight". Indicate what each term means.
6. What are isotopes? An element of atomic number 27 has only two isotopes. These isotopes are of equal abundance, one containing 25 neutrons and the other 27. What will be the chemical atomic weight? (Assume the neutron and proton have the same mass.)
7. The atomic number of fluorine is 9 and the mass number is 19. Say what these terms mean. What kind of particles compose the nucleus, and how many of each are there?
8. What are isotopes? A certain element has a chemical atomic weight of 63·57. It consists of two isotopes, of mass numbers 63 and 65. Calculate the percentage of each isotope present (by

atoms). The atomic number is 29. How many neutrons are there in the atom of each isotope?

9. Boron has two isotopes. Boron-10 makes up 19 per cent and boron-11 81 per cent of the atoms of the natural element. What is the chemical atomic weight of boron?
10. The atomic weight of nickel is 58·69. The natural metal consists of two isotopes, in one of which there are 30 and the other 32 neutrons, the atomic number being 28. Calculate the percentage of each isotope present (by atoms).
11. In natural zinc there are four principal isotopes of mass numbers 64 (49 per cent), 66 (28 per cent), 67 (4 per cent), 68 (19 per cent). The atomic number is 30. Write down the numbers of protons and neutrons present in each kind of nucleus, and estimate the atomic weight of zinc.
12. "It is quite possible to have two nuclei of different elements which have the same mass number (isobars)." How can this statement be reconciled with the uniqueness of an element's atomic weight? Suggest two possible cases of isobars.
13. "The properties of elements are a periodic property of their atomic weights." Comment on this statement, giving examples from among the first twenty elements in order of atomic number.

‡14. State the rules governing the four quantum numbers *n*, *l*, *m* and *s*. Show how these rules and numbers interpret the general shape of the periodic table.

‡15. State Hund's rule of maximum multiplicity. Indicate the electronic structure of atoms of nitrogen and phosphorus. Show how these underlie the chemical similarities and differences between these elements. If bismuth is known to be chemically similar to phosphorus, what could you infer about its electronic arrangement?

16. The maximum valency of oxygen is 2, but of sulphur it is 6. Write down the electronic structures of these two atoms, and describe why sulphur can expand its valency shell readily whereas oxygen cannot do so.
17. What is the electronic arrangement in the valency shell of a halogen? Why would you expect that iodine would form a negative ion much less readily than does chlorine?

‡18. What is an electronic orbital? The atomic number of oxygen is 8. Which orbitals would you expect to find filled in the ground state of the atom? How many unpaired electrons should there be?

19. What are the essential electronic differences between the atoms of transitional and non-transitional elements? Give some ex-

amples of each type, and indicate some chemical differences resulting from them.

20. In any given group of the periodic table, elements become more metallic as atomic number increases. In what way would you account for this in terms of atomic size and the general electronic nature of metals?

‡21. An element has an atomic number of 6. Write out its electronic structure. Do you think the majority of its compounds will be electrovalent or covalent? Give reasons for your answer.

‡22. An element has an atomic number of 17. Write out its electronic structure in full. Hence deduce its valency, tendency to form ions, metallic or non-metallic character, and most probable type of compound formed. (You are not asked to identify it.)

23. What is an "atomic volume"? What information would you require to calculate one? The atomic weight of caesium is 133, and its density in the solid state $1{\cdot}87$ g cm^{-3}. Calculate its atomic volume. Comment on the fact that the element of next higher atomic weight, barium, has A.W. 137 and density $3{\cdot}5$ g cm^{-3}.

24. The elements gallium, germanium, and arsenic are adjacent to one another in the periodic table. Their atomic weights are Ga 70, Ge 73, As 75; and densities Ga $5{\cdot}91$, Ge $5{\cdot}36$, As $5{\cdot}73$ g cm^{-3}. In each case calculate the atomic volume, and comment on what the values reveal.

25. What is meant by the statement "zinc is electropositive with respect to copper"? Describe the various chemical and electrical changes that occur when a zinc plate and a copper plate are joined by a wire and dipped into dilute sulphuric acid.

26. Arrange the following elements in the order of their position in the electrochemical series:

K Cu Mg Au Pb Fe.

It is often said that the position of an element in the series is a guide to its chemical reactivity. Discuss this in terms of the reactions of these metals with oxygen, water, and dilute acid.

27. The elements sodium, calcium, iron and lead occur in that order in the electrochemical series. Show how their reactivity towards oxygen, water, and dilute acids is graduated in the same order.

28. State the positions of beryllium, boron, magnesium, and aluminium in the periodic table. In terms of atomic size and the electrical forces within the atom, indicate why you would expect the electronegativities of beryllium and aluminium to be more similar than those of beryllium and magnesium or boron and

aluminium. Can you suggest other examples of this "diagonal relationship"?

29. What is the electrochemical series? Why would you regard aluminium as a good metal with which to coat iron to prevent corrosion?
30. Steel pipelines buried in the ground are often protected against corrosion by "sacrificial anodes", which are frequently pieces of magnesium in good metallic contact with the pipe. What are the reasons underlying this? Why is it essential to make *good* metallic contact between the pipe and the anode?
31. When iron coated with zinc (galvanized iron) is exposed to rain water, the iron is protected even if the zinc is scratched, but iron coated with tin (tinplate) is rapidly corroded when the tin is damaged. Explain this in terms of the electrochemical series. Why is zinc plate not used for canning food?
32. Describe an experiment to establish whether a given metal was electropositive to iron or otherwise.
33. In metallic corrosion, the anode (the point at which electrons leave the solution) is usually dissolved. Give two examples. In many cases it is wiser to leave a metal surface exposed to moist soil unpainted than to cover it with paint; can you suggest a reason for this?
34. In older motor cars, the negative pole of the battery was connected to the chassis, but the modern practice is to connect the positive to the chassis. This reduces corrosion damage in the electrical circuits: how?

‡35. What do you understand by an electronic orbital? How many electrons can any one orbital hold? Sketch the shapes of an *s* orbital and a *p* orbital. What bearing has the shape of orbitals on the shape of molecules?

‡36. An electronic orbital in an atom may be occupied by 0, 1, or 2 electrons. Taking sulphur as an example, show how it forms compounds by using orbitals so occupied in the free atom. (Hint: suitable compounds are SF_6, SO_2, SO_3.)

‡37. The greatest number of covalencies that a nitrogen atom can form is three but for phosphorus it is five. Yet both elements are in the same periodic group. Why is this?

38. Discuss, with examples, the differences between electrovalent and covalent bonds. How are these differences reflected in the physical and chemical properties of the compounds?
39. A pure metal tends to conduct electricity, whereas most non-metals do not. How is this related to the atomic and crystal

structures of these substances? Is there any relation between this fact and the tendency of non-metals to be more volatile than metals?

40. Chlorine is a gas, carbon tetrachloride a liquid, and potassium chloride a solid. Discuss this in terms of the bonds present in the molecules of these substances and the links between molecules.
41. Write electronic structures for the following molecules: carbonate ion, nitrate ion, phosphate ion (number of valency electrons around P is 10 in phosphate). Indicate to what extent the structures you have drawn fail to account for the symmetry of these molecules, and how this is overcome by the concept of resonance.
42. Write down the electronic structures of sodium and chlorine. Outline the processes which occur when sodium chloride is formed from these elements. What kind of bond is formed? Is it correct to speak of a molecule of sodium chloride? If so, when?
43. "It is meaningless to talk about a molecule of potassium iodide." Discuss this statement in the light of what you know of this material.
44. What do you understand by a "crystal lattice"? Give an example of any crystal lattice you like, and sketch the arrangement.
45. What are the essential differences between the crystal structure of a typical salt and that of a metal? Can you suggest any reason why a crystal of sodium chloride should break more readily than a crystal of a metal?
46. What is a co-ordinate (dative) bond? Give two examples of molecules in which there is such a bond. In what ways are such bonds (a) similar to (b) different from an ordinary covalent bond?
47. The solid salt ammonium sulphate contains different types of bond. Detail the types present, and indicate where each can be found.
48. Write a note about dipole moments, showing how they are caused. Methane and carbon tetrachloride have zero dipole moment, whereas chloromethane, dichloromethane, and chloroform have dipole moments. Discuss why this should be so: if dichloromethane had zero moment, why would this prove that the carbon atom was not tetrahedral?
49. The molecule HCl is covalent, but the solution in water does not contain this molecule. Describe the changes occurring during the formation of this solution.

    Would you expect gaseous HCl to show a dipole moment? In what sense would it be polarized?

50. The sulphate ion can be regarded as constructed from a sulphide ion and four oxygen atoms, but the sulphur atom cannot contain more than twelve valency electrons. Draw an electronic arrangement for the ion, and say to what extent this structure interprets the true shape of the ion.

51. Consider a central point, and imagine that you have to draw three lines from it so that these lines are as far from each other as possible. By drawing or some other method show that the lines will point from the centre to the three corners of an equilateral triangle.

If the problem is extended to four or six directions (three dimensional), draw diagrams to show the "tetrahedral" and "octahedral" arrangements of lines that result.

52. "Covalent bonds round a central atom tend to repel one another, and in this respect a lone pair of electrons behaves much like a covalent bond." Write down the electronic arrangements in BF_3, SO_2, SO_3, and use the ideas of Q.51 to predict the shape of these molecules.

53. Write electronic structures for the nitrate ion, nitrite ion, and ammonium ion. Using the electron-pair repulsion theory (Q.51 and Q.52), predict the shape of these ions.

54. Write electronic structures for carbon dioxide and the carbonate ion, and say what shape you would expect them to have. See Q.51 and Q.52.

55. Write electronic structures for, and predict shapes of, sulphur hexafluoride, SF_6, sulphuryl chloride, SO_2Cl_2, and phosphate ion, PO_4^{3-}.

‡56. Distinguish between σ bonds and π bonds. Give examples in which a σ bond is formed between two *s* orbitals; and between an *s* and a *p* orbital. What is required for the production of a π bond?

‡57. The two carbon atoms in ethane are bound by a σ bond, but in ethylene a π bond is present also. Show why this restricts relative rotation of the groups at each end of the bond, and discuss the consequences of this for organic chemistry. Why should restricted rotation about a triple bond be of less interest than that about a double bond?

B. THERMOCHEMISTRY, HEATS OF REACTION AND BOND ENERGIES

58. What is an exothermic reaction? Give two examples. The heat of combustion of sulphur is $-71 \cdot 68$ kcal mole^{-1} (evolved), and the heat of formation of sulphur trioxide is $-91 \cdot 52$ kcal mole^{-1} (evolved). How much heat will be given out when 1 kilogram of sulphur dioxide is converted into sulphur trioxide? ($S = 32$, $O = 16$.)

59. Calculate the heat of formation of ammonia from nitrogen and hydrogen molecules. You are given that

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O; \; \triangle H = -364 \text{ kcal}$$

and the heat of combustion of hydrogen is -68 kcal mole^{-1} (evolved).

60. Calculate the heat of the reaction

$$Al_2O_3 + 6Na = 2Al + 3Na_2O.$$

You are given that

$$2Al + \tfrac{3}{2}O_2 = Al_2O_3; \; \triangle H = -380 \text{ kcal.}$$

$$2Na + \tfrac{1}{2}O_2 = Na_2O; \; \triangle H = -101 \text{ kcal.}$$

61. State Hess's law. Calculate the heat of formation of zinc sulphate from its elements, $Zn + S + 2O_2$, given that the heat of combustion of zinc (to ZnO) is -85 kcal mole^{-1} (evolved); the heat of combustion of sulphur (S to SO_2) is -72 kcal mole^{-1} (evolved); the heat of conversion of SO_2 into SO_3 is $+20$ kcal mole^{-1} (absorbed) and

$$ZnO + SO_3 = ZnSO_4; \; \triangle H = -53 \text{ kcal.}$$

62. What is the heat of neutralization of an acid? The heats of neutralization of sulphuric, hydrochloric, and nitric acids are all about $-13 \cdot 5$ kcal equivalent^{-1}, but for acetic acid the value is only about -12 kcal equivalent^{-1}. Comment on these observations, and draw what conclusions you can about the nature of acetic acid. *Note:* 1 equivalent of an acid is that weight which contains 1 g of replaceable hydrogen.

63. What is the difference between an endothermic reaction and an exothermic one? Which type would you expect to occur most readily?

Explain carefully the meaning of the statement

$$C(\text{solid}) + O_2(\text{gas}) = CO_2(\text{gas}); \ \Delta H = -94 \text{ kcal}.$$

64. Calculate the heat of formation of propane, given that its heat of combustion is -529 kcal mole^{-1} (evolved). The heat of combustion of carbon is -94 kcal mole^{-1} and of hydrogen -68 kcal mole^{-1}, (both evolved).
65. What is the heat of formation of a compound? Calculate the heat of formation of glucose, $C_6H_{12}O_6$. The heat of combustion of carbon is -94 kcal mole^{-1} (evolved) and of hydrogen -68 kcal mole^{-1} (evolved), and the heat of combustion of glucose is -673 kcal mole^{-1} (evolved).
66. When 1 mole of Na_2HPO_4 dissolves in a large volume of water, 5·64 kcal are evolved. When 1 mole of $Na_2HPO_4,2H_2O$ dissolves in a large volume of water, 0·39 kcal are absorbed. Calculate the heat of hydration of Na_2HPO_4 in this case, i.e., ΔH for the reaction:

$$Na_2HPO_4 + 2H_2O = Na_2HPO_4,2H_2O.$$

67. When 16 g of anhydrous copper sulphate are dissolved in water, 1·589 kcal are evolved. When 25 g of the pentahydrate are dissolved to give the same volume of solution, 0·278 kcal are absorbed. Calculate ΔH, in kcal mole^{-1}, for the reaction

$$CuSO_4 + 5H_2O = CuSO_4,5H_2O$$

(Take Cu = 64, S = 32, O = 16, H = 1.)

68. Calculate the heat of hydrogenation of ethylene, i.e.: ΔH for the reaction

$$C_2H_4 + H_2 = C_2H_6.$$

The heats of combustion of ethylene and ethane respectively are -341 and -372 kcal mole^{-1} (evolved), and the heat of formation of water is -68 kcal mole^{-1}.

69. What is meant by bond energy? Outline the method of calculation, and list the pieces of information you would need, to calculate the bond energy of the C=C double bond.
70. The heats of atomization of solid carbon, gaseous hydrogen, and gaseous oxygen are $+170·4$, $+51·7$ and $+59·1$ kcal g-atom^{-1} respectively. The heat of formation of ethyl alcohol from its elements in their standard states is $-57·0$ kcal mole^{-1}. Calculate the heat of formation of ethyl alcohol from its atoms. Compare