Problems in Physical Chemistry

[FOR B.SC. (PASS AND HONS.) STUDENTS OF INDIAN UNIVERSITIES]

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PROBLEMS IN PHYSICAL CHEMISTRY

By the same author

A TEXTBOOK OF PHYSICAL CHEMISTRY (*2nd edition*) (*Co-author*)

PREFACE

In the study of Physical Chemistry, one comes across a large number of mathematical concepts that are introduced from time to time. Such concepts can better be clarified by solving numerical problems. This book is intended to help the student of physical chemistry clarify his concepts, by solving problems, which cannot be satisfactorily done in the textbook, due to the paucity of space. Each chapter begins with a brief introduction to the topic, laying special emphasis on mathematical relationship and units of the physical quantities. A large number of problems have been solved to illustrate the subject. This is then followed by exercises with the answers given at the end. Hints have also been given, wherever necessary.

Although SI units have been used very frequently, some non-SI units have also been retained because of their practical importance or use in the specialized fields.

The chapter on the mathematical methods apprises the student of the usage of slide rule and logarithmic tables.

This book, though meant primarily for B.Sc. pass and honours students of the Indian universities, will also be useful for engineering, pharmacy students, and those preparing for the competitive examinations.

The author is grateful to Dr. Dillip Singh Sharma, Lecturer in Chemistry, for his timely help and valuable suggestions.

Suggestions for the improvement of this book are welcome.

K.K. SHARMA

CONTENTS

1

MOLES, FORMULAS AND STOICHIOMETRY

The term stoichiometry, refers to relationships between quantities of reactants and products in chemical systems. The weight of each element present in a sample of a compound may be determined by analytical procedures. It is common to express this weight in terms of per cent. This is known as percentage composition.

$$\text{Percentage composition} = \frac{\text{Mass of element in sample}}{\text{Total mass of sample}} \times 100$$

Formulas, tell us the relative number of different atoms making up a chemical compound. One of the most important quantitative concepts in chemistry is the mole. Since individual atoms or molecules are so small as to be virtually impossible to work with, the idea of a large collection of atoms or molecules, namely, the "mole" was developed. A mole of atoms is the mass in grams equal to the atomic weight. The mole is defined as the number of carbon atoms in 12.00 grams of the isotope $^{12}C_6$. This number is known as Avogadro's number and has a value 6.023×10^{23}. This is a huge number!

The atomic weights listed in periodic table, gives the mass of an atom of an element, as it occurs in nature relative to that of ^{12}C atom, which is taken to be exactly 12. Atomic weights are average values. Often they are not whole numbers because most natural elements consist of more than one isotope. Carbon for example, is mostly $^{12}C_6$ but contains small amounts of $^{13}C_6$ and $^{14}C_6$, so the average atomic weight of carbon is 12.0115. The atomic weight of hydrogen is 1.00797; of cobalt 58.9332, and so on. The gram atomic weight is the mass of an element in grams, which is numerically equal to its atomic weight.

Molecular weight may be determined by summing atomic weights when the formula of a molecular substance is known. For instance, we know that the formula of water is H_2O. This tells us that each water molecule contains two hydrogen atoms and one oxygen atom.

One mole of water molecules would, therefore, contain two moles of hydrogen atoms and one mole of oxygen atom. Therefore, the molecular weight of water is $(2\times 1.009)+(1\times 16.00) = 18.02$ g. The gram molecular weight of water is 18.02 g. Formula weight is a widely used term as it can be employed both for molecular and ionic substances.

Empirical formula is the relative number of each kind of atom in a molecule.

Molecular formula is the total number of each kind of atom in a molecule.

A chemical equation represents a chemical reaction. The reactants are written on the left side and the products on the right side of the equation. A balanced equation gives (*i*) reactants and products in a chemical reaction, (*ii*) relationship between moles and masses of products and reactants in a chemical reaction. For balancing more complicated equations, the concept of oxidation numbers of the elements must be understood. Oxidation numbers are assigned according to following arbitrary rules:

(*a*) All the elements in their elemental state are assigned zero oxidation number.

(*b*) Oxygen in compounds is assigned an oxidation number of —2.

(*c*) Hydrogen in compounds is assigned an oxidation number of +1.

(*d*) The sum of the oxidation numbers for a molecule must equal zero.

(*e*) The sum of the oxidation numbers for an ionic species is equal to the charge on the ion.

Problem 1.1. Using the modern experimental techniques, the mass of one atom can be determined. If the mass of one sodium atom has been found to be 3.82×10^{-23}g, how many sodium atoms are contained in one mole of sodium?

Solution. The atomic weight of sodium = 22.9 g, and 3.82×10^{-23} g is weight of one atom of sodium. 22.9 g will be the weight of $=\dfrac{22.9}{3.82\times 10^{23}}$ or the number of sodium atoms in one gram-atom $= 6.02\times 10^{23}$. A mole of atoms is the mass in grams equal to the atomic weight. A mole of atoms contains Avogadro's number of atoms (6.02×10^{23}).

Problem 1.2. In a specific compound, the per cent of oxygen is 18.6. There is one mole of oxygen atom (a gram-atom) in each mole of the compound. What is the molecular weight of the compound?

Solution. 100 grams of compound contains 18.6 g oxygen and

81.4 g other atoms.

18.6 g oxygen corresponds to 81.4 g of other atoms

16 g oxygen will correspond to $\frac{81.4}{18.6} \times 16.0$

$= 70$ g of other atoms

$\therefore$ Molecular weight $= 70+16 = 86$.

or

18.6 g of oxygen corresponds to 100 g of compound

16.0 g of oxygen will correspond to $\frac{100}{18.6} \times 16.0 = 86$.

Problem 1.3. A sample of sodium chloride, NaCl contaminated with KBr weighs 0.225 gram. It was found to contain 0.0840 gram of sodium.

(*i*) How many moles of Na did the sample contain?
(*ii*) How many moles of NaCl did the sample contain?
(*iii*) How many moles of Cl did the sample contain?
(*iv*) How many grams of NaCl did the sample contain?
(*v*) What was the purity of the sample?

Solution. (*i*) $\frac{0.0840}{23.0 \text{ g/mole}} = 3.65 \times 10^{-3}$ mole Na

(*ii*) $\frac{3.65 \times 10^{-3} \text{ mole Na}}{1 \text{ mole Na}} = 3.65 \times 10^{-3}$ mole NaCl

(*iii*) $\frac{3.65 \times 10^{-3} \text{ NaCl}}{1 \text{ mole Na} \times 1 \text{ mole NaCl}} = 3.65 \times 10^{-3}$ mole Cl

(*iv*) $\frac{3.65 \times 10^{-3} \text{ mole NaCl}}{58.5 \text{g NaCl}} = 0.214$ g NaCl

(*v*) $\frac{0.214 \text{ g NaCl} \times 100}{0.225} = 95.1$ per cent.

Problem 1.4. Morphine contains 67.3% carbon, 4.6% nitrogen and remaining are other constituents. Calculate the relative number of carbon and nitrogen atoms in morphine.

Solution. 100 grams of morphine contains 67.3 g carbon and 4.6 g nitrogen. The atomic weight of carbon is 12.011 g/gram-atom and that of nitrogen is 14.006 g/gram-atom.

67.3 g of carbon $= \frac{67.3}{12.011} = 5.60$ gram-atoms

4.3 g of nitrogen $= \frac{4.3}{14.006} = 0.33$ gram-atom.

5.60 gram-atoms of carbon per 0.33 gram-atom of nitrogen is the same as 5.60 atoms of carbon per 0.33 atom of nitrogen or C = 17 atoms N = 1 atom.

Problem 1.5. Natural oxygen consists 99.759% of ^{16}O with mass 15.9949 amu, 0.037% of ^{17}O with mass 16.991 amu and 0.204% of ^{18}O with mass 17.9991 amu. With this distribution, calculate the chemical atomic weight of natural oxygen.

Solution. Let the total number of atoms = 100,000 of these

99,759 will have mass 15.9949 amu =	1,595,635
37 will have mass 16.9991 amu =	630
204 will have mass 17.9991 amu =	3,670
100,000 atoms will weigh =	1,599,935

The average atomic weight of natural oxygen will be 15.999.

Problem 1.6. A drop of water is about 0.05 ml. The density of water at room temperature is about 1.0 g/ml. How many H_2O molecules are present in a drop of water?

Solution. Volume of 1 drop of H_2O = 0.05 ml

$$\text{Weight of 1 drop of } H_2O = 0.05\times(1.0\text{ g/ml}) = 0.05\text{ g}$$

The molecular weight of $H_2O = 2\times1+1\times16 = 18.0$ amu.

Since one gram mole of water at NTP contains 6.02×10^{23}

$$18\text{ g } H_2O \text{ contains} = 6.02\times10^{23}\text{ molecules}$$

$$0.05\text{ g } H_2O \text{ contains} = \frac{6.02\times10^{23}\times0.05}{18} = 2\times10^{21}\text{ molecules.}$$

∴ Number of water molecules in a drop of water $= 2\times10^{21}$.

Problem 1.7. Green plants produce glucose ($C_6H_{12}O_6$) and molecular oxygen by "photosynthesis" of carbon dioxide and water. How many grams of CO_2 are required to produce one mole of glucose?

Solution. The chemical reaction in photosynthesis can be symbolized as,

$$6CO_2+6H_2O\rightarrow C_6H_{12}O_6+6O_2$$

$$\text{Number of gram of } CO_2 = 1\text{ mol } C_6H_{12}O_6\times\frac{6\text{ moles } CO_2}{1\text{ mole } C_6H_{12}O_6}\times\frac{44.0\text{ g } CO_2}{1\text{ mole } CO_2}$$

$$= 264\text{ g } CO_2$$

$$= 264\text{ g } CO_2.$$

Problem 1.8. The percentage composition of a compound was found to be 65.8% Pb, 16.5% Cr and 17.7% O. What is the empirical formula of the compound? (Atomic weights of Pb = 207.2, Cr = 52.0, O = 16)

Solution. Let us consider 100 grams of compound.

$$\text{Number of moles of Pb} = \frac{65.8}{207.2}$$
$$= 0.318 \text{ mole.}$$
$$\text{Number of moles of Cr} = \frac{16.5}{52.0}$$
$$= 0.317 \text{ mole}$$
$$\text{Number of moles of O} = \frac{17.7}{16.0} = 1.11 \text{ moles}$$
$$\frac{0.317 \text{ mole Cr}}{0.318 \text{ mole Pb}} = 1 \text{ (2 Cr for 2 Pb)}$$
$$\frac{1.11 \text{ mole O}}{0.318 \text{ mole Pb}} = 3.5 \text{ (7.0 for 2 Pb)}$$

The empirical formula is $Pb_2Cr_2O_7$.

Problem 1.9. Calculate the oxidation number of the italicized element in the following compounds.

(*a*) $H_2\mathit{SO}_4$ (*b*) SO_2 (*c*) $\mathit{Mn}O_2$ (*d*) $K_2\mathit{Cr}_2O_7$ (*e*) $\mathit{Mn}O_4^-$ (*f*) $K_4\mathit{Fe}(CN)_6$

Solution. Let x be the oxidation number of the italicized element.

(*a*) $H\ SO_4$
$$1 \times 2 + x + (-2) \times 4 = 0$$
$$2 + x - 8 = 0$$
$$x = +6$$

(*b*) SO_2
$$x + (-2) \times 2 = 0$$
$$x = +4$$

(*c*) MnO_2
$$x + (-2) \times 2 = 0$$
$$x = 4$$

(*d*) $K_2CT_2O_7$
$$(+1) \times 2 + 2x + (-2) \times 7 = 0$$
$$2 + 2x - 14 = 0$$
$$x = +6$$

(*e*) MnO_4^-
$$x + (-2) \times 4 = -1$$
$$x - 8 = -1$$
$$x = +7$$

(*f*) $K_4Fe(CN)_6$
$$(+1) \times 4 + x + (-1) \times 6 = 0$$
$$x = +2$$

Problem 1.10. Balance the following equations:

(*a*) $H_3AsO_4 + H_2S \rightarrow H_3AsO_3 + S + H_2O$

(*b*) $KMnO_4 + FeCl_2 + HCl \rightarrow KCl + H_2O + MnCl_2 + FeCl_3$

(*c*) $Sn + HNO_3 + H_2O \rightarrow H_{10}Sn_5O_{15} + NO$

Solution. (*a*) In this reaction the oxidation number of As changes from +5 to +3. The net change is 2. The oxidation number of S in H_2S is − 2 and it becomes zero in element S. The net change is again 2. The equation is thus balanced.

(*b*) The oxidation number of Mn changes from +7 to +2 a change of 5. The oxidation number of Fe changes from +2 to +3 a change of 1. The balanced equation will be

$$KMnO_4 + 5\,FeCl_2 + 8HCl \rightarrow KCl + 4H_2O + MnCl_2 + 5FeCl_3$$

(*c*) The oxidation number of Sn changes from 0 to +4 change of 4, i.e., change of 20 per molecule of $H_{10}Sn_5O_{15}$. The oxidation number of nitrogen changes from +5 to +2 a change of 3. The balanced equation will be

$$15Sn + 20HNO_3 + 5H_2O \rightarrow 3H_{10}Sn_5O_{15} + 20NO$$

EXERCISES

1.1. How many moles are there in

(*a*) 17.5 g of Sn (*c*) 7.20 g of H_2O

(*b*) 50.0 g of NaCl (*d*) 160.0 g of CCl_4

[**Ans**. (*a*) 0.147, (*b*) 0.855, (*c*) 0.40, (*d*) 1.05.]

1.2. How many molecules are there in

(*a*) 6.0 moles of benzene (*c*) 6.0 g of NaCl

(*b*) 6.0 g of benzene (*d*) 6.0 g of XeF_4

[**Ans**. (*a*) 3.61×10^{24}, (*b*) 4.62×10^{22}, (*c*) There are no molecules of NaCl, (*d*) 1.74×10^{22}.]

1.3. Analysis of chlorophyll shows that it contains 2 68% magnesium. How many atoms of magnesium does 1.00 g of chlorophyll contain?

[**Ans**. 6.62×10^{20} atoms.]

1.4. Natural brominei s compcsed only of $^{79}_{35}Br$ and $^{81}_{35}Br$. The first of these isotopes has a mass of 78.9183 amu and the second 80.9163 amu. Calculate the relative abundance of the two isotopes.

[**Ans**. 50.65% $^{79}_{35}Br$ and 49.35%.]

1.5. How many atoms of copper are there in a piece of copper that weighs the same as a piece of aluminium that contains 4.86×10^{21} aluminium atoms.

[**Ans**. 2.08×10^{21}.]

1.6. In making transistors one needs to control the concentration of impurity very carefully. Suppose you wanted to make a germanium transistor containing 1.0×10^{18} boron atoms per cubic centimetre as impurity. If the density of germanium is 5.35 g/cm^3, what relative weights of germanium need to be mixed. [**Ans**. 5.35 g of germanium and 1.8×10^{-5} g of boron.]

1.7. LSD is a complex compound whose mass is made up of 74.27% carbon, 7.79% hydrogen, 12.99% nitrogen and 4.95% oxygen. What per cent of the atoms in LSD are carbon atoms? [**Ans**. 40.8%.]

1.8. Calculate the weight of one molecule of quinine, $C_{20}H_{24}N_2O_2$.

[**Ans**. 5.39×10^{-22} g.]

1.9. A material X was found to contain 8.62×10^{21} molecules of X in 3.39 g of X. Calculate the molecular weight of X.

1.10. A drug marijuana owes its activity to tetrahydrocannabinol, which contains 70% as many carbon atoms as hydrogen atoms and 15 times as many hydrogen atoms as oxygen atoms. The number of moles in a gram of tetrahydrocannabinol is 0.00318. Determine its molecular formula.

[**Ans.** $C_{21}H_{30}O_2$.]

1.11. An impure sample of aluminium sulphate weighs 2.732 grams. It was found to contain 7.75×10^{-3} moles of $Al_2(SO_4)_3$. What is the purity of the sample expressed in terms of percentage of aluminium sulphate? [**Ans.** 97.1%.]

1.12. How many grams of hydrogen sulphide contain one half as many molecules of H_2S as there are in 100 grams of iron? [**Ans.** 30.6 g.]

1.13. What is the empirical formula of a compound for which an analysis gave 0.653 mole of K, 0.653 mole of Cl, and 1.305 mole of O. [**Ans.** $KClO_2$.]

1.14. The per cent of nitrogen in a compound is 20.0% and there are 2.00 moles of nitrogen atoms per mole of compound. What is the molecular weight of the compound? [**Ans.** 140 g/mole.]

1.15. An unknown oxide of manganese is reacted with carbon to form manganese metal and carbon dioxide. Exactly 31.6 g of the oxide Mn_xO_y, yield 13.2 g of CO_2. Find the simplest formula of the unknown oxide.

[**Ans.** Mn_2O_3.]

1.16. Nitromethane, (CH_3NO_2) is used as a fuel in aircraft and racing car engines. When burned the products are CO_2, H_2O and NO. How many grams of oxygen are required to completely burn 122 grams of CH_3NO_2?

[**Ans.** 80.0 g.]

1.17. Reaction of xenon with excess fluorine, produced a mixture of three products, each containing Xe and F and weighing a total of 2.073 grams by weight. The mixture contained 20% XeF_2, 60% A and 20% B. Product B contained 0.193 gram of fluorine. Identify A and B (Total Xe=1.331 g),

[**Ans.** $A=XeF_4$; $B=XeF_6$]

1.18. Ethyl alcohol reacts with phosphorous tribromide according to the following equation,

$$3C_2H_5OH + PBr_3 \rightarrow 3C_2H_5Br + H_3PO_3$$

How many grams of C_2H_5Br could be produced from 5.42 grams of PBr_3?

[**Ans.** 6.54 g.]

1.19. Calculate the number of moles of oxalic acid ($H_2C_2O_4$) present in a solution, 10.00 ml of which requires 18.35 ml of a 0.04982 M solution of NaOH for neutralisation, What is the molarity of the acid?

[**Ans.** Moles of oxalic acid in the sample$=4.57 \times 10^{-4}$, molarity of oxalic acid$=4.57 \times 10^{-2}$.]

1.20. The equation

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

represents the thermal decomposition of calcium carbonate in which carbon dioxide is driven off. According to this reaction, how many grams of $CaCO_3$ must be decomposed to yield (*a*) 3.00 moles of CO_2 (*b*) 4.0 g of CO_2 (*c*) 1.00 moles of CaO.

[**Ans.** (*a*) 300 g $CaCO_3$ (*b*) 9.1 g $CaCO_3$ (*c*) 100 g $CaCO_3$.]

1.21. A 7,00 g sample containing a mixture of $CaCO_3$ and $NaHCO_3$ is heated causing the two compounds to decompose according to the following equations:

$$2NaHCO_3\ (s) \rightarrow Na_2CO_3\ (s) + H_2O\ (g) + CO_2\ (g)$$
$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g).$$

If, after decomposition is complete, there remains 4.00 g of solid residue, how much of the original sample was $NaHCO_3$? [**Ans.** 1.04 g.]

1.22. Write the balanced redox equation for the following half reactions:

(*a*) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
$2Cl^- \rightarrow Cl_2 + 2e^-$

(*b*) $H^+ + e^- + HNO_2 \rightarrow NO + H_2$
$2HI \rightarrow I_2 + 2H^+ + 2e^-$

(*c*) $F_2 + 2e^- \rightarrow 2F^-$
$Al \rightarrow Al^{3+} + 3e^-$

[**Ans.** (*a*) $2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$
(*b*) $2HNO_2 + 2HI \rightarrow 2NO + 2H_2O + I_2$
(*c*) $3\ F_2 + 2Al \rightarrow 6F^- + 2Al^{3+}$.]

2

GASEOUS STATE

Matter may exist in any of three states of aggregation, solid, liquid and gas. The gaseous state is characterized by the fact that the density of matter in this state is lowest *i.e.* the molecules in a gas are separated by a large distance.

Gas Laws

A gas that obeys Boyle's law and Charles' law is said to be ideal.

Boyle's law. Boyle found that at constant temperature the volume of gas appeared to vary inversely with pressure. Mathematically

$$V \propto \frac{1}{P}$$

or

$$V = k\left(\frac{1}{P}\right) \quad \ldots (1)$$

where k is a proportionality constant.

Charles' law. It states that volume for any definite quantity of a gas at constant pressure is directly proportional to the absolute temperature. Mathematically,

$$V = K_pT \quad \ldots (2)$$

where K_p is a constant of proportionality, depends upon the pressure mass and nature of the gas and the units in which volume is expressed.

The combined gas law. If a quantity is independently proportional to two other quantities, a rule of proportionality states that the first quantity is also proportional to the product of the other two, *i.e.*

$$V \propto \frac{1}{P} \quad \ldots (3)$$

$$V \propto T \quad \ldots (4)$$

$\therefore$

$$V \propto \frac{T}{P}$$

or

$$PV = KT \quad \ldots (5)$$

where K is constant of proportionality. This is known as the combined gas law. Since volume of a gas is an extensive property, at constant temperature and pressure, the volume of an ideal gas is proportional to the number of moles of the gas. Since pressure and temperature are intensive properties, i.e., they do not depend on the number of moles of the gas, K must also be proportional to the number of moles of the gas. That is

$$K \propto n$$

or

$$K = Rn \qquad \ldots (6)$$

where R is a constant known as ideal gas constant.

Equation (5) can be written as,

$$PV = nRT \qquad \ldots (7)$$

Values for Ideal Gas Constant R

8.31431	$JK^{-1}\ mol^{-1}$
1.98717	cal $K^{-1}\ mol^{-1}$
0.0820575	l-atm.K^{-1} .mol^{-1}
8.31431×10^7	erg. K^{-1} .mol^{-1}

Graham's law. The rate of diffusion of a gas is inversely proportional to the square root of the molecular weight of the gas

$$\text{Rate} \propto 1/\sqrt{\text{Molecular weight}} \qquad \ldots (8)$$

Kinetic Theory of Gases

The kinetic theory of gases assumes model gas and we can postulate certain properties characteristic of a model gas.

First postulate. The gaseous substances consist of molecules that are far apart in comparison with their own diameters.

Second postulate. The gas molecules are in a state of constant random motion interrupted only by collisions with each other and with the walls of the container.

Third postulate. The gas molecules are perfectly elastic and the walls of the container are perfectly elastic.

Fourth postulate. The average kinetic energy of molecules is proportional to temperature.

From the kinetic theory of gases the pressure p exerted by an ideal gas can be calculated from the expression,

$$p = \frac{1}{3}\frac{mn\overline{C}^2}{V} \qquad \ldots (9)$$

where m is the mass of one molecule, n is the number of molecules and $\overline{C}$ is the root mean square velocity. V is the volume occupied by the gas.

Average velocity. The average velocity C_{av} of the molecules may be defined as

$$C_{av} = \sqrt{\frac{8RT}{\pi M}} \qquad \ldots (10)$$