PROBLEMS IN PHYSICAL CHEMISTRY

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Preface

The study of physical chemistry is one of great importance and relevance since its principles govern both the operations of the chemical industry and the workings of biological systems. However, the reputation of many a newly-minted graduate chemist has been tarnished by his inability to apply his knowledge of the principles to a practical situation. A reason for this state of affairs is not hard to find. Student chemists are seldom called upon to apply their learning to situations outside the classroom, chemical problems being often little more than an exercise in number substitution. This book of problems is designed to give students practice in the application of the principles usually taught in first year courses in physical chemistry at Australian universities. It is hoped the book will fill a gap in the training of graduates from universities and institutes of technology.

The book is in two parts. The first, Part A, is essentially a selection of standard problems which have been grouped into categories according to the area of chemistry involved. The purpose of this section is to allow students to gain familiarity with the equations of physical chemistry. Since the problems are of a relatively straightforward nature, answers, but not worked solutions, are given at the end of the section.

Part B is a selection of applied problems on subjects ranging from the utilisation of surplus grape juice during the period of liquor prohibition in the U.S.A. to the dangers of smoking for swimming pool attendants. In these problems, students are asked to apply chemical reasoning to something approaching a real life situation. Since the problems are not arranged in any special order, the student's first step, when faced with a problem, must be to decide which piece of chemical knowledge is appropriate to it and how this knowledge can be formulated in order to achieve a numerical solution. In some cases, it is necessary to draw on knowledge of more than one area of chemistry. At the end of the book, the problems are grouped under the various headings of Part A. While grouping the problems in this way is an oversimplification,

it is hoped that the list may be of some use to those who wish to
try a problem relevant to a particular area of chemistry.   A
further feature of these problems is the need in many cases to make
judicious approximations.   To know when approximations are necess-
ary and justified is of prime importance to the applied chemist.
Because of these difficulties, worked solutions together with
comments have been given for all the problems in Part B.   One
assumption that has been used throughout our solutions is that ionic
concentrations can be used in place of activities.   We are aware
that this approximation is a very poor one unless the solutions are
dilute.   However, without this assumption, the chemical principles
involved in many of the problems would be obscured by intractable
mathematics.

Because we believe that it is vitally important for students to
get into the habit of looking up facts and figures for themselves,
very little information of the standard type (e.g. free energies,
solubility products, conductivities) has been written into
any of the problems.   Students are expected to decide what
information is required and then consult an appropriate data book.
The answers given here have been worked out using *S I Chemical Data*,
2nd ed., by G.H. Aylward and T.J.V. Findlay (John Wiley and Sons
Australasia, Pty Ltd, Sydney, 1971).   Data taken from other sources
such as the S I Edition of the *Chemistry Data Book* by J.G. Stark and
H.G. Wallace (John Murray, London, 1974) may give slightly different
values.   In this connection it should be remembered that all
scientific facts are the result of experimental work, and are there-
fore subject to some error in determination and to constant revision.
Moreover, the numerical value of some physical quantities, such as
a solubility product, may vary according to the method of their
measurement.   Before embarking on precise chemical calculations, a
chemist will normally make a careful review of the data available
to ascertain the most reliable figure for his particular purpose.

S I units and symbols have been used throughout the book, but
not exclusively so, since some familiarity with the other units in
which so many important scientific papers have been written seems
desirable.   The only consistent exception to S I nomenclature is

our use of the symbol M, which, in conformity with time-hallowed tradition, we have taken to mean the concentration in mol dm^{-3}. Square brackets denote concentrations.

It is not possible to write a book of this type without help from a large number of people. We are very grateful to those of our colleagues who have suggested ideas for problems and criticised the format of others. The bulk of the problems in Part A have been in use at Melbourne for a number of years and, to the best of our knowledge, are not reproduced elsewhere. However, such standard problems cannot be unique as are those in Part B.

We hope that students will find the solving of these problems not only interesting and instructive, but also on occasions fun.

October, 1974

Contents

Introductory Problems

PART A

Suppose that the gas pressure in the mercury reservoir R is initially very small.   If it is increased above the unknown pressure P, which is also small, mercury will be forced up the tube A until the height of the mercury in the apparatus is sufficient to balance the gas pressure in R.   Since this latter quantity can be fixed by admitting air or pumping it out through the two way tap T, the height of the mercury in the gauge can be fixed at any desired level.

(a)   Let the mercury level be slowly raised until the meniscus in the capillary tube B is just opposite the top of the closed capillary tube C.   As the mercury level is raised to this point, gas at the unknown pressure P is trapped in the vessel V when the mercury closes the open end D, and is compressed into the closed capillary tube C.   If the cross-sectional area of C is a cm^2, the column of gas h mm long and the volume of V together with the capillary tube is v cm^3, show that

$$P \approx \frac{a\,h^2}{10\,v} \text{ mm Hg.}$$

(b)   Let the mercury level be slowly raised until the length of gas trapped in C is 10 cm.   Let the level of the meniscus in B be 5 cm above that in C.   Calculate the unknown pressure P given that the diameter of the capillary tubes is 1 mm and that the combined volume of V and C is 250 cm^3.

3.   A sample of the gas butane (C_4H_{10}) was exploded with an excess of oxygen.   The sample measured 150 cm^3 at 1 atm and 273 K.

(a)   What volume of oxygen at 1 atm and 273 K was used in the combustion?

(b)   What weight of carbon monoxide could be made from the carbon dioxide by reduction with carbon?

4.   Sulphides of arsenic contain 29.99%, 39.05% and 51.70% by weight of sulphur respectively.   Deduce empirical formulae for these compounds.

1.
Introductory Problems

1. Air consists of 21% oxygen, 78% nitrogen and 1% argon by volume. Calculate

   (a) the partial pressures in Pa

   (b) the concentration in mol m^{-3}

   of each of the three gases in air at 273 K.

2. A McLeod gauge is a device for measuring low gas pressures between 10^{-2} and 10^{-6} mm mercury. A schematic drawing of a McLeod gauge, whose mode of operation will now be described is given in the accompanying figure.
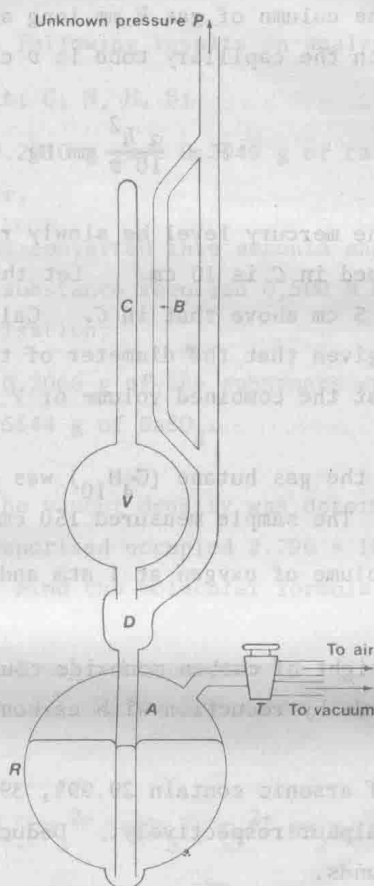

Fig. 1: Schematic diagram of a McLeod gauge.

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4. Sulphides of arsenic contain 29.99%, 39.05% and 51.70% by weight of sulphur respectively.   Deduce empirical formulae for these compounds.
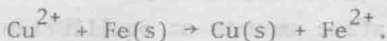
5. A mixture of anhydrous barium and magnesium carbonates weighed
    0.850 g and, when treated with an excess of hydrochloric acid,
    yielded 203.0 cm^3 of carbon dioxide at 13°C and 9.60×10^4 Pa.
    What was the proportion of the two carbonates in the mixture?

6. In order to standardise a sample of approximately M/4 hydro-
    chloric acid, 25.00 cm^3 of the acid was added to 0.2492 g pure
    anhydrous calcium carbonate. When the reaction was complete,
    the excess acid was determined by titration with a sodium
    hydroxide solution using methyl orange as an indicator; 5.87 cm^3
    of the alkali was required. The concentration of the acid and
    alkali were compared, 25.00 cm^3 hydrochloric acid being
    equivalent to 31.78 cm^3 sodium hydroxide. Calculate the
    molarity of the acid.

7. A liquid yielded the following results on analysis:

    (a) elements present; C, N, H, S;

    (b) on combustion 0.2010 g gave 0.3049 g of carbon dioxide
    and 0.1040 g of water;

    (c) the nitrogen was converted into ammonia and that obtained
    from 1.010 g of the substance required 0.500 M of hydrochloric
    acid for its neutralisation;

    (d) the sulphur in 0.2066 g of the substance was converted to
    sulphate yielding 0.5544 g of $BaSO_4$.

        In addition the vapour density was determined: 0.1015 g
    of the liquid when vaporised occupied 2.796×10^{-5} m^3 at 288 K
    and 1.00×10^5 Pa. Find the molecular formula of the substance.

8. (a) Using the Lowry-Bronsted concept as a criterion, comment
    on whether the following species are acids, bases or ampholytes
    in aqueous solutions.

        HCl, NH_3, NH_4^+, SO_3^{2-}, HSO_3^-, $Fe^{2+}.6H_2O$, H_2O, O_2^{2-}.
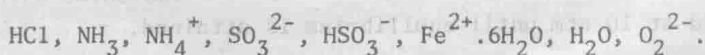
    (b) What are the principal ionic and/or molecular entities

$$Cu^{2+} + Fe(s) \rightarrow Cu(s) + Fe^{2+}.$$

In one study of the kinetics of the reaction, an iron plate was immersed in 1 dm^3 of an acidified 0.02 M copper sulphate solution. One hour after the reaction was started, a sample was withdrawn from the solution, filtered to remove any copper powder and analysed for copper and iron. 10.00 cm^3 of the sample was found to contain 1.0×10^{-4} mol of copper. Another 10.00 cm^3 of the sample was treated with lead metal, which selectively reduces any iron(III) to iron(II), and titrated with standard dichromate solution to determine the amount of iron(II) present. 9.83 cm^3 of a 0.00191 M solution of potassium dichromate was required.

Calculate the concentration of copper and iron in solution after one hour of reaction. Suggest reasons why the reaction does not conform to the stoicheiometry of the above equation.

14. When copper is heated in air at 800°C, a black oxide is formed which, on cooling to room temperature, readily flakes from the metal surface. In one experiment, 254 mg of the oxide was dissolved in nitric acid, and diluted to 100 cm^3. To a 20 cm^3 aliquot of this copper(II) solution, an excess of potassium iodide was added, liberating iodine according to the equation

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2.$$

The iodine was then titrated against a 0.01056 M solution of sodium thiosulphate using starch as an indicator; 33.62 cm^3 of thiosulphate were required. Determine whether the black oxide was Cu_2O or CuO or a mixture of these oxides.

15. Copper(II) oxide and aluminium are to be used as the basic reactants in a new design of battery for portable calculators. Suggest equations for likely reactions at the electrodes and for the total cell reaction if auxiliary chemicals used are sodium hydroxide and water.

16. Outline and explain the reactions which occur at the electrodes in each of the following cases:

(a) a solution of sodium sulphate, to which litmus has been added, is electrolysed using platinum electrodes;

(b) a solution of sodium sulphate, acidified with sulphuric acid, is electrolysed using copper electrodes.

2.

Acid-Base Equilibria

1. Calculate the pH of the following solutions at 298 K:

(a) 0.05 M $Ba(OH)_2$;
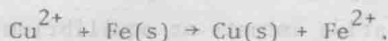
(b) 0.01 M CH_3COOH;

(c) 0.03 M NH_4Br;

(d) 1×10^{-5} M CH_3COOH;

(e) 1.0 M $NaHSO_3$.

2. A saturated aqueous solution of phenol at 25°C has a pH of 5.01. Estimate the weight of phenol that can be dissolved in a cubic meter of water at this temperature.

3. Prove that at equilibrium, in a solution made by adding CH_3COONa to water, the concentration of undissociated CH_3COOH is exactly equal to the difference in the concentrations of OH^- and H_3O^+ ions.

4. In dilute aqueous H_2SO_4 solutions, $K_a(H_2SO_4)$ is infinite and $K_a(HSO_4^-)$ is 0.010. Calculate the pH of an exactly 0.1 M solution of H_2SO_4. Compare the value obtained with that for a strong monoprotic acid ($K_a(HSO_4^-) = 0.0$) and for a strong diprotic acid ($K_a(HSO_4^-)$ is infinite) and comment on the results.

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5. Calculate the concentration of a solution of HCN which is 0.1% ionized. Is it possible for a solution of this acid to be 1% ionized? Give reasons.

6. Prove that the acidity constant (K_a) of a weak acid is related to its concentration (c) and its degree of dissociation (α) by

$$K_a = \alpha^2 c/(1-\alpha)$$

provided the self dissociation of the solvent is ignored. If the latter is taken into account, show that

$$K_a = \tfrac{1}{2}\alpha^2 c \left[1 + (1+4K_w\alpha^{-2}c^{-2})^{\tfrac{1}{2}} \right]/(1-\alpha).$$

7. The pH of 0.100 M sodium acrylate (C_2H_3COONa) at 25°C is 8.63. Calculate:

(a) the acidity constant of acrylic acid at this temperature;

(b) the concentration of the acid necessary in a solution which is 0.100 M in sodium acrylate to give a pH of 4.00.

8. Either acetic acid or chloracetic acid could be used to prepare a buffer solution of pH 4.50. How much 0.100 M NaOH would need to be added to 200 cm^3 of a 0.100 M acid solution in each case? Explain why one of the acids is to be preferred.

9. (a) What would be the pH of:

(i) 0.5 M NH_3 solution;

(ii) 0.5 M NH_3 solution which is also 1.0 M with respect to NH_4Cl?

(b) Calculate the change in pH when 0.1 cm^3 of 2.0 M HCl is added to 2.0 cm^3 of each of the solutions (i) and (ii).

10. Find the concentration of *all* species present in a solution which is 0.10 M in HCN and 0.25 M in KCN. What is the pH of the solution? Is this solution a buffer? Give reasons.

11. Discuss whether a 0.1 M solution of acetic acid:

(a) has the same pH as a 0.1 M solution of HCl;

(b) requires the same amount of standard base for neutralisation as a 0.1 M solution of HCl;

(c) should be titrated against NaOH in the presence of an indicator which changes colour at a pH above 7;

(d) will liberate the same amount of hydrogen upon reaction with excess zinc as will a 0.1 M HCl solution.

12. Calculate the pH of a mixture of 100 cm^3 of a 0.1 M solution of NH_3 and

(a) 20 cm^3

(b) 50 cm^3

(c) 90 cm^3

(d) 99.9 cm^3

(e) 100 cm^3

(f) 150 cm^3

of a 0.1 M solution of HCl. From these figures construct a titration curve. Suggest at least two indicators which would give the correct value for the equivalence point.

13. 1 mmol of HCOOH is to be titrated against NaOH solution using a suitable indicator. The final volume will be about 100 cm^3.

For the greatest possible accuracy a buffer solution is required which, on addition of an acid-base indicator, will give exactly the same colour at the equivalence point as will the titration mixture. Indicators available are bromo-cresol purple, phenol red and phenolphthalein. Buffer solutions available are $H_2PO_4^-/HPO_4^{2-}$ and $H_3BO_3/H_2BO_3^-$.

(a) What will be the pH at the equivalence point?

(b) Which indicator would be the most suitable and why?