CAMBRIDGE
UNIVERSITY PRESS & ASSESSMENT

A Level

Chemistry

Session: 1967 June
Type: Question paper
Code: 507/517

507/1 517/1

CHEMISTRY

(SYLLABUSES N AND T)

ADVANCED LEVEL

PAPER 1

(Two hours and a half)

Answer **five** *questions.*

Begin each answer on a fresh sheet of paper and write on **one** *side of the paper only.*

Mathematical tables are provided.

1 State Graham's *law of diffusion* and describe **one** method for comparing the rates of diffusion of gases.

A gaseous compound **X** contained 44·4 % of carbon, 51·9 % of nitrogen and 3·7 % of hydrogen. Under like conditions, 50 ml. of **X** diffused through a porous plug in 25 sec. and the same volume of hydrogen diffused in 6·8 sec. Deduce the molecular formula of **X**.

[C = 12; N = 14.]

2 Discuss the role played by (*a*) change of pressure, (*b*) change of temperature, in the methods employed for the liquefaction of gases. Illustrate your answer with reference to carbon dioxide and air.

Assuming that air consists of 79 % nitrogen, 20 % oxygen and 1 % argon, calculate the percentage by volume of each gas in the mixture of gases dissolved when water is saturated with air at N.T.P.

[Absorption coefficients (ml./100 ml.) for these gases at 0° C. are: N_2, 0·024; O_2, 0·049; Ar, 0·053.]

3 Outline the chemistry of the manufacture of pig-iron.

Starting from iron, how would you prepare specimens of (*a*) ferrous ammonium sulphate, (*b*) ferrous oxide, (*c*) anhydrous ferrous chloride?

4 Explain the following observations.

(*a*) A precipitate is obtained when hydrogen sulphide is passed through an aqueous solution of a zinc salt acidified with acetic acid but no precipitate is obtained when hydrochloric acid is present.

(*b*) Lead chloride is less soluble in dilute hydrochloric acid, but more soluble in concentrated hydrochloric acid, than it is in water.

(*c*) Calcium phosphate dissolves in dilute hydrochloric acid but calcium sulphate does not.

(*d*) The heat of neutralisation of acetic acid by sodium hydroxide is less than that of hydrochloric acid by the same base.

5 Describe how you would prepare (using sulphur as the only source of that element) specimens of (*a*) disulphur dichloride, S_2Cl_2; (*b*) sodium thiosulphate.

How, and under what conditions, does sulphuric acid react with (i) benzene, (ii) sulphur, (iii) iron?

6 State, and explain in detail, what happens when:

(*a*) an aqueous solution of ammonia is slowly added to an aqueous copper sulphate solution until present in excess;

(*b*) red phosphorus is heated and the vapour condensed;

(*c*) a solution of potassium dichromate acidified with dilute sulphuric acid is saturated with sulphur dioxide and the solution allowed to evaporate;

(*d*) powdered potassium chlorate is heated.

7 What do you understand by (*a*) *homologous series*, (*b*) *isomerism*?

Give the **full** structural formulae for (i) **all** compounds having the molecular formula $C_4H_{10}O$, (ii) **two** compounds having the molecular formula C_3H_6O. Name **four** of the compounds in (i) and describe **two** experimental methods by which you could distinguish between the two compounds in (ii).

8 Outline the laboratory preparation of a pure sample of ethylene dibromide starting from ethanol (ethyl alcohol).

Describe **one** chemical method in **each** case by which you could distinguish

(*a*) between ethylene and acetylene,

(*b*) between acetamide and ammonium acetate,

(*c*) between acetic acid and oxalic acid.

507/2

CHEMISTRY (Syllabus T)

ADVANCED LEVEL

PAPER 2

(*Two hours and a half*)

Answer **five** *questions, including* **one** *question from* **each** *of the Sections* **A**, **B** *and* **C**.

Begin each answer on a fresh sheet of paper and write on **one** *side of the paper only.*

Mathematical tables and squared paper are provided.

SECTION A

1 Explain the terms (i) *lattice energy*, and (ii) *latent heat of fusion*, illustrating your answer by reference to crystalline sodium chloride.

The heats of combustion of graphite, hydrogen, methane and ethane are 94·1, 68·3, 212·8 and 370·0 kcal./mole respectively. The heat of atomization of graphite and the heat of dissociation of molecular hydrogen are −171·7 and −104·2 kcal./mole respectively.

Calculate (i) the heats of formation of methane and ethane, and (ii) the bond energies of the C—H and C—C bonds.

2 The following data apply to the system tin–lead which forms a eutectic:

% tin	0	20	40	60	70	80	90	100
Melting-point (° C.)	327	280	234	187	193	206	219	232

Assuming that tin and lead are immiscible in the solid state, plot the phase diagram for the system and estimate the composition of the eutectic mixture.

Using a single diagram, sketch cooling curves (temperature against time) for mixtures containing respectively 10 % and 80 % tin, and for the eutectic mixture.

Describe the changes that take place when a mixture containing 40 % tin is cooled from 400° C. to 100° C.

3 Explain the formation of the line spectra of hydrogen and show how the line spectra are related to the electronic structure and ionization energy of the atom. What evidence concerning atomic structure is provided by X-ray spectra?

4 Outline a method for measuring the equilibrium constant of the reaction represented by the equation

$$CH_3.CO.OC_2H_5 + H_2O \rightleftharpoons CH_3.CO.OH + C_2H_5OH.$$

Indicate how you would calculate the equilibrium constant from the experimental results.

State and explain the effect on (i) the position of the equilibrium, (ii) the rate at which equilibrium is attained, of using the following as hydrolysing agents: (*a*) water, (*b*) hydrochloric acid.

Section B

5 Draw diagrams to show the bonding in aluminium chloride and sodium aluminium fluoride. Explain how the physical properties of these compounds are related to their structures.

Neutron irradiation of aluminium gives an isotope X, each aluminium atom, $^{27}_{13}Al$, absorbing one neutron and then emitting an α-particle in the process. Isotope X then decays by β emission to another element Y. Deduce the mass numbers and atomic numbers of X and Y.

If, when some of the aluminium had changed to Y, the product were dissolved in dilute hydrochloric acid, explain how you would show the presence in the solution of ions from both aluminium and Y.

6 Explain the following observations.

(i) Hydrogen fluoride is both less volatile and a weaker acid than hydrogen chloride.

(ii) Silver chloride dissolves in ammonia solution; silver iodide does not.

(iii) Chlorine and methane react rapidly when exposed to strong sunlight.

(iv) Pure hydrogen bromide is not readily obtained by the action of concentrated sulphuric acid on sodium bromide.

(v) Sulphuric acid and hydrochloric acid are equally strong, yet hydrogen chloride is evolved by the action of concentrated sulphuric acid on sodium chloride.

7 (i) Justify the classification of **either** manganese **or** chromium as a transition element, illustrating your answer by reference to suitable compounds of the element you choose.

(ii) Describe the preparation of a crystalline sample of **either** potassium permanganate from manganese dioxide **or** potassium dichromate from chromium sesquioxide (chromium III oxide).

Section C

8 The following mixtures are obtained in the usual preparation of the first-named compound in each pair:

(i) benzoic acid; hydrated manganese dioxide,

(ii) aniline; sodium stannate solution,

(iii) ethyl acetate; aqueous ethanol,

(iv) acetaldehyde; water.

Describe and explain the method you would use to obtain a pure sample of the compound from each of the mixtures.

9 Describe the preparation of a pure sample of nitrobenzene from benzene.

How would you distinguish between the members of the following pairs by **one** chemical test in **each** case:

(i) chlorobenzene and bromobenzene,

(ii) nitrobenzene and aniline,

(iii) monobromoethane and 1:1 dibromoethane?

10 Suggest the identity of compounds *A*, *B* and *C* from the following data, and explain the reactions which are described.

A is a crystalline solid. When a little water is added to *A* two liquid layers are formed; addition of more water gives a homogeneous aqueous solution. This liquid

(i) has no reaction with sodium carbonate solution but indicators show that it has a pH value of less than 7;

(ii) gives a purple coloration on the addition of a few drops of ferric chloride solution;

(iii) gives a white precipitate on the addition of bromine water.

B is a white crystalline solid which, on heating with an excess of soda lime, evolves a gas producing an alkaline solution in water. An aqueous solution of *B*

(i) deposits a white crystalline precipitate on the addition of concentrated nitric acid;

(ii) evolves carbon dioxide and nitrogen on the addition of sodium nitrite solution followed by dilute hydrochloric acid;

(iii) evolves nitrogen on the addition of alkaline sodium hypochlorite solution.

C is a gas which dissolves in water to give a strongly alkaline solution. This solution, when neutralized by hydrochloric acid, gives a white crystalline compound on evaporation.

When *C* is burnt it produces twice its own volume of carbon dioxide, the gas volumes being measured at the same temperature and pressure.

517/2

CHEMISTRY (Syllabus N)

ADVANCED LEVEL

PAPER 2

(Two hours and a half)

Answer **five** *questions.*

Begin each answer on a fresh sheet of paper and write on **one** *side of the paper only.*
Mathematical tables are provided.

1 State and discuss the factors which affect (*a*) the *velocity of reaction*, and (*b*) the *position of equilibrium* in the hydrolysis of ethyl acetate.

After 5 gm. of ethyl acetate had been heated at 60° C. for 5 min. with 100 ml. of a normal solution of sodium hydroxide, the mixture was cooled and diluted with water to stop further reaction. The mixture then required 88 ml. of normal hydrochloric acid for neutralisation. Calculate the fraction of ethyl acetate that had reacted.

[H = 1; C = 12; O = 16.]

2 Describe how you would determine by experiment:

(*a*) the equivalent weight of potassium permanganate as an oxidising agent;

(*b*) the basicity of a strong acid of known molecular weight;

(*c*) the volume composition of ammonia.

3 Describe how you would determine the molecular weight of a volatile compound by Victor Meyer's method.

The chloride of a non-metallic element *Y* contained 85·13 % of chlorine; and the specific heat of *Y* was 0·2. Calculate the atomic weight of the element.

When 0·1 gm. of the chloride of *Y* was volatilised in Victor Meyer's apparatus at 180° C., 16·6 ml. of air were displaced at 17° C. and a pressure of 742 mm.

Suggest (i) an explanation of the data gained from the vapour density experiment, (ii) how the true molecular weight of the chloride might be determined.

[Cl = 35·5; 1 mole (1 gm. molecule) of a gas occupies 22·4 litres at N.T.P.]

4 Compare and contrast the properties of the elements chlorine and iodine by reference to their reactions with the following:

(*a*) potassium iodide,

(*b*) hydrogen,

(*c*) sodium hydroxide,

(*d*) sodium thiosulphate,

(*e*) concentrated nitric acid.

How do these reactions bear upon the position of these elements in the periodic table?

5 Describe how carbon monoxide can be prepared and collected in the laboratory.

How, and under what conditions, does carbon monoxide react with (*a*) chlorine, (*b*) hydrogen, (*c*) sodium hydroxide, (*d*) nickel?

6 State and explain what happens in **four** of the following reactions:

(*a*) aluminium is heated with sulphur and the product added to water;

(*b*) lead monoxide is heated in air at 480° C. and the product treated with dilute nitric acid;

(*c*) tin is exposed to the action of chlorine and the product treated with excess aqueous sodium hydroxide;

(*d*) excess mercury is allowed to react with dilute nitric acid and the clear solution diluted with water;

(*e*) sodium is heated in dry air and the product heated with carbon monoxide.

7 Describe briefly how you would obtain **one** constituent in a pure condition from **each** of the following mixtures (a chemical method is required in **each** case):

(*a*) phenol and benzene sulphonic acid,

(*b*) ethanol (ethyl alcohol) and acetone,

(*c*) acetic acid and formic acid,

(*d*) aniline and chlorobenzene,

(*e*) benzene and toluene.

8 Outline the laboratory preparation of pure methyl cyanide (acetonitrile) from acetic acid.

How, and under what conditions, does methyl cyanide react with:

(*a*) hydrogen,

(*b*) a mixture of ethanol and sulphuric acid,

(*c*) sodium hydroxide?

What change takes place when the product from (*c*) is heated with solid sodium hydroxide?

507/0 517/0

CHEMISTRY

SPECIAL PAPER

(SYLLABUSES T AND N)

(*Two hours and a half*)

Answer **five** *questions, of which not more than* **two** *may be selected from one section.*

Begin each answer on a fresh sheet of paper and write on **one** *side of the paper only.*

The answers to questions in Sections A, B *and* C *are to be given up separately.*

Mathematical tables are provided.

Section A

1 Describe how the equivalent conductivities at infinite dilution of (*a*) strong, and (*b*) weak, electrolytes are determined, and explain the principles underlying the methods.

Using the same conductivity cell, the resistances of 0·1M solutions of potassium chloride and bromoacetic acid were 24·96 and 66·50 ohms respectively at 25° C. Calculate the pH of 0·1M bromoacetic acid, given that the specific conductivity of the potassium chloride solution is 0·01164 ohm^{-1} $cm.^{-1}$, and that the equivalent conductivity of bromoacetic acid at infinite dilution is 389·0 $cm.^2$ ohm^{-1} $equiv.^{-1}$ at 25° C.

2 What conditions must be fulfilled if a heat of reaction is to be measured directly in a calorimeter? How may the heat of reaction be found if a calorimeter cannot conveniently be used?

In aqueous acetaldehyde the following equilibrium is rapidly established:

$$CH_3CHO + H_2O \rightleftharpoons CH_3CH(OH)_2$$

and at 25° C. the equilibrium constant is 0·022 litre $mole^{-1}$. Use the data given below for two calorimetric experiments carried out at 25° C. in the same apparatus to determine the heat of hydration of acetaldehyde. (The thermal capacity of the apparatus and its contents was determined by means of experiment **B**, taking the heat of neutralisation of hydrochloric acid by sodium hydroxide to be 13·80 kcal. $mole^{-1}$ at 25° C.)

Exp.	Reactants	Final volume ($cm.^3$)	Temperature rise (° C.)
A	0·4 gm. acetaldehyde with water	100	0·193
B	50 $cm.^3$ of 0·05N HCl with 50 $cm.^3$ of 0·05N NaOH	100	0·262

[C = 12; O = 16.]

3 Suggest explanations for the following observations.

(*a*) At 1 atm. pressure, the density of gaseous tetrafluorohydrazine (N_2F_4) is 0·00425 gm. $cm.^{-3}$ at 25° C. and 0·00270 gm. $cm.^{-3}$ at 150° C.

[N = 14; F = 19; molar volume at N.T.P. = 22·4 litre.]

(*b*) The temperatures at which solid first appears on cooling solutions of 2 mole % of sodium chloride, lithium nitrate and calcium chloride in molten sodium nitrate are 302·2° C., 302·4° C. and 294·5° C. respectively. (The melting-point of sodium nitrate is 306·0° C.)

(*c*) At 320° C., the initial rate of reaction of mixtures of hydrogen and chlorine is increased by the addition of 0·25 % of nitric oxide, but is decreased by the addition of 0·25 % of nitrosyl chloride (NOCl).

Section B

4 Discuss concisely the factors that determine the position of an element (*a*) in the periodic system, and (*b*) in the electrochemical series.

Give **three** properties of an element that can be better predicted from a knowledge of its position in the periodic system and **three** properties that can be better predicted from its position in the electro-chemical series.

5 On shaking a strong aqueous solution of potassium hydrogen sulphite with disulphur dichloride and allowing the solution to evaporate, crystals of a salt **G** separate which, after drying, are found to contain only potassium, sulphur and oxygen.

An aqueous solution **H** containing 3·600 gm./litre of salt **G** was prepared. When 25 ml. of this solution were treated with an ion exchange resin so that the potassium ion was quantitatively replaced by the hydrogen ion, the latter required 13·3 ml. of 0·05M sodium hydroxide solution for neutralisation.

A portion of salt **G** weighing 0·1350 gm. was subjected to prolonged evaporation with nitric acid and barium nitrate and gave 0·3501 gm. of barium sulphate, $BaSO_4$.

When a 25 ml. portion of solution **H** was titrated with potassium iodate solution in the presence of concentrated hydrochloric acid, 26·6 ml. of 0·025M potassium iodate solution were required for equivalence. The reaction of iodate under these conditions follows the equation:

$$IO_3^- + 6H^+ + 4e = I^+ + 3H_2O.$$

Determine the formula of salt **G** and write an equation for its reaction with potassium iodate.

[O = 16·0; S = 32·1; K = 39·1; I = 126·9; Ba = 137·4.]

6 The following equations are written to represent the action of water on chromyl chloride, of heat on ammonium dichromate and on ferrous oxalate, and the reaction between an iodide and a nitrite in acid solution:

(*a*) $CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl$.

(*b*) $(NH_4)_2Cr_2O_7 = N_2 + 4H_2O + Cr_2O_3$.

(*c*) $FeC_2O_4.3H_2O = FeO + CO + CO_2 + 3H_2O$.

(*d*) $2NO_2^- + 2I^- + 4H^+ = I_2 + 2H_2O + 2NO$.

Select any **two** of these equations and outline experiments you would perform to show that reaction takes place quantitatively in accordance with them.

SECTION C

7 Three isomeric compounds, **A**, **B** and **C**, have the molecular formula $C_8H_8O_2$.

(*a*) When heated for a long time with soda-lime **A** gave benzene, while both **B** and **C** gave toluene.

(*b*) **A** was a neutral compound, whereas both **B** and **C** were monobasic acids.

(*c*) **B** and **C** were both readily chlorinated in sunlight; **B** gave a compound containing three chlorine atoms per molecule which was easily hydrolysed to a dibasic acid **D** which in turn gave an anhydride on heating. When **D** was heated with soda-lime it gave benzene. The chlorinated product from **C** contained two chlorine atoms per molecule and was a strong monobasic acid.

Identify **A**, **B**, **C** and **D**, write equations for the reactions, and indicate how you would prepare **A** from benzoic acid.

8 Explain the following observations and identify any unnamed compounds.

(*a*) A volatile compound **P**, C_3H_5N, reacts with hydrogen in the presence of a catalyst to give **Q** which in turn reacts with nitrous acid to give a neutral yellow oil **R**.

(*b*) The apparent molecular weight of acetic acid calculated from physical measurements was found to be 55 using a solution of the acid in water and 120 using a solution of the same concentration in benzene.

(*c*) A solution of lactic acid isolated from a natural source rotated polarised light to the right, whereas a solution of lactic acid synthesised from acetaldehyde did not rotate polarised light.

(*d*) Styrene, $C_6H_5.CH{:}CH_2$, changed into a hard, transparent solid on standing in air.

9 A compound **X** is believed to have the structure

$$H_2N.CH_2.CONH.CH_3.$$

How would you:

(*a*) show that **X** contains nitrogen;

(*b*) show that **X** contains an amine group?

How would **X** react with:

(i) soda-lime;

(ii) sulphuric acid;

(iii) acetyl chloride?

Suggest a series of reactions by which **X** could be prepared from acetic acid.