AN ROINN OIDEACHAIS

LEAVING CERTIFICATE EXAMINATION, 1975

CHEMISTRY—HIGHER LEVEL

WEDNESDAY, 18 JUNE—AFTERNOON, 2 to 4.45

Six questions to be answered.

All questions carry the same number of marks.

Relative atomic masses: H = 1, C = 12, N = 14, O = 16, Mg = 24, S = 32, I = 127, Pb = 207.
Molar volume at S.T.P. = 22·4 litres.
Avogadro constant = 6×10^{23}.

1. Answer *eleven* of the following items, (*a*), (*b*), (*c*), etc. All the items carry the same marks. *Keep your answers short.*

   (*a*) How many atoms are there in 0·36 g magnesium?

   (*b*) Define the electronegativity of an element.

   (*c*) Which one of the following is the least accurate for use in volumetric analysis:
   pipette, graduated cylinder, burette, volumetric flask, analytical balance?

   (*d*) How can acetylene be converted into acetaldehyde?

   (*e*) What do you understand by the activation energy of a reaction?

   (*f*) Define reduction in terms of electron transfer.

   (*g*) Distinguish between homogeneous and heterogeneous catalysis.

   (*h*) What volume of carbon monoxide at S.T.P. is needed to reduce completely 5·575 g of lead monoxide according to the equation $PbO + CO \rightarrow Pb + CO_2$?

   (*i*) In which of the following is the bond angle 180°?

   $$NH_3, \quad H_2O, \quad BeH_2, \quad H_2S$$

   (*j*) Why do most transition metals have variable valencies?

   (*k*) What is the oxidation number of nitrogen in NH_2OH?

   (*l*) What have the ions O^{2-}, F^-, Na^+ and Mg^{2+} got in common?

   (*m*) Which is the principal species being reduced during the electrolysis of dilute sulphuric acid?

   (*n*) Vinyl chloride ($CH_2 = CHCl$) polymerises in the same way as ethene (ethylene). Draw a section of the polymer molecule showing two repeating units.

2. Give a brief account of the electronic structure of atoms under the following headings:—

   (i) the spectroscopic evidence for the existence of energy levels,

   (ii) s and p orbitals.

   State Hund's rule and show how it is illustrated by the s, p configurations of aluminium, silicon, phosphorus and sulphur.

3. When 1·65 g of ethyl benzoate ($C_6H_5COOC_2H_5$) were dissolved in 125 g benzene the freezing point was lowered by 0·44 K. In a second experiment 0·936 g of an organic liquid "*X*" were dissolved in 200 g benzene. The freezing point was lowered by 0·15 K.

   (i) Define "freezing point constant."

   (ii) Find the freezing point constant for 1000 g benzene.

   (iii) Depression of freezing point and elevation of boiling point are two colligative properties of a solution. How are they connected?

   (iv) Find the relative molecular mass of *X*.

   (v) If *X* is an iodoalkane (alkyl iodide) what is its formula?

   (vi) Explain why the relative molecular mass (molecular weight) of acetic acid dissolved in benzene is found to be 120.

4. Outline the characteristics of a homologous series of organic compounds.
Write the structural formula for the *second* member of each of the following series:— (i) alkanes, (ii) alkenes, (iii) primary aliphatic amines.
Point out the functional group in each of the above series.
Show by an equation in each case how (i) an alkane, (ii) an alkene, reacts with chlorine. Under what conditions will each of these reactions occur? Discuss briefly a mechanism for one of them.
Explain why methylamine should be regarded as a base and give one example to show how it reacts as such.
Complete the following equation and name the products:

$$CH_3NH_2 + (CH_3CO)_2O \rightarrow$$

5. Define (i) heat of formation, (ii) heat of combustion, of a compound.
Calculate the heat of formation of ammonia given the following bond energies in kJ per mole:—

$$E(N \equiv N) = 944, \quad E(H - H) = 436, \quad E(N - H) = 388.$$

The combustion of ammonia in oxygen can be represented by the equation

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O.$$

If the heat of combustion of ammonia is – 380 kJ per mole and the heat of formation of water is – 286 kJ per mole, calculate again the heat of formation of ammonia.
Suggest one reason, other than experimental error, for the difference between the two values obtained.

6. What is meant by stereoisomerism?
What type of stereoisomerism is shown by
(i) maleic and fumaric acids, (ii) lactic acid?
In *each* case show clearly, using structural formulae, the difference between the two isomers and comment briefly on the similarity or otherwise of their properties.
In the case of each of the following compounds state whether or not stereoisomerism can exist and, if so, show how it arises:

(i) $CH_3\,CHCl\,COOH$, (ii) $(CH_3)_2\,CH\,COOH$,

(iii) $CH_3\,CH = CH\,COOH$, (iv) $CH_2 = CH\,COOH$,

(v) $NH_2\,CH\,(CH_3)\,COOH$.

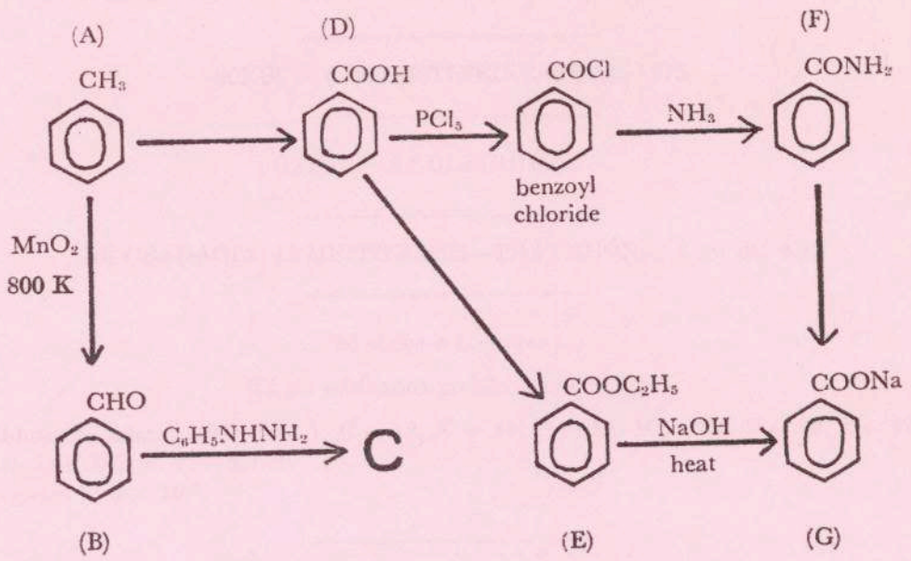
7. Give the name *or* the formula of
(*a*) one oxide in each case which reacts with water to give (i) an alkaline solution, (ii) an acidic solution;
(*b*) one hydride in each case which reacts with water to give (i) an alkaline solution, (ii) an acidic solution.
In each case describe (i) the appearance of the compound you select, (ii) the type of bonding, (iii) the reaction with water, giving an equation.
The hydrolysis of PCl_3 by water can be represented as follows:

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3H^+ + 3Cl^-.$$

The solution is found to be acidic. Describe one further test to confirm that this reaction had taken place.

8. The molecular formula of a certain strong acid is H_3SO_3N. In an experiment 2·91 g of this acid were dissolved in water and the solution made up to 250 cm³. It required 22·5 cm³ of this solution to neutralise 25 cm³ of 0·108 M sodium hydroxide solution.
(i) What is meant by a strong acid?
(ii) Calculate the molarity of the strong acid solution, assuming it is monobasic.
(iii) What would be the molarity of the solution if the acid were (*a*) dibasic, (*b*) tribasic?
(iv) Determine whether the strong acid is in fact monobasic, dibasic or tribasic.
(v) Define pH of a solution.
(vi) When a strong acid is being titrated against a strong base what is the pH of the solution when it is 0·00005 M with respect to (*a*) the strong acid, (*b*) the strong base?
(vii) Comment briefly on the indicators suitable for such a titration.

9. Study the following reaction scheme and then answer the questions which follow.



(i) Name compounds *A*, *B*, *D*, *E*, *F* and *G*.
(ii) Name the reagent used to convert *B* to *C*.
(iii) Give the name and structural formula for compound C.
(iv) How would you convert *A* to *D*?
(v) What type of reaction is represented by the change *A* to *D*?
(vi) How would you convert *D* to *E*?
(vii) What type of reaction is represented by the change *E* to *G*?
(viii) Write the equation for a reaction by which *F* is converted to *G*.
(ix) Suggest how *D* could be obtained from *G*.

10. Write an equilibrium constant expression for each of the following reactions:—
(i) $H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$,
(ii) $4HCl_{(g)} + O_{2(g)} \rightleftharpoons 2Cl_{2(g)} + 2H_2O_{(g)}$.

The equilibrium constant for the reaction $H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$ is 1·60 at 1250 K. Starting with equal volumes of H_2 and CO_2 what is the partial pressure of each of the four gases at equilibrium if the total pressure in the reaction vessel at this temperature is 4 atmospheres?

Why is it unnecessary to know the volume of the vessel in this case?

The following reaction occurs in a closed vessel at a certain temperature. The forward reaction is exothermic.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5.$$

What would be the effect on the concentration of PCl_5 in the equilibrium mixture of
(i) introducing more PCl_3 into the vessel,
(ii) increasing the pressure,
(iii) increasing the temperature?

11. Answer any *three* of the following:

(*a*) Explain what you mean by (i) a Brønsted-Lowry acid, (ii) a conjugate acid-base pair.
List the four species which can be described as acids in the following reactions and after each acid write its conjugate base:

$$H_2SO_4 + HF \rightleftharpoons H_2F^+ + HSO_4^-$$
$$NaNH_2 + H_2O \rightleftharpoons NH_3 + NaOH.$$

(*b*) How does sp^2 hybridisation arise in molecules? Discuss, giving one example, the shape you associate with it.

(*c*) Why do gases diffuse? State Graham's Law of diffusion.
One litre of fluorine gas weighs 1·69 g and one litre of hydrogen gas weighs 0·09 g. If fluorine diffuses through a porous plug at the rate of 6 cm^3 per second, at what rate will hydrogen diffuse through the same plug?

(*d*) What do you mean by the "first ionisation energy" of an element?
Suggest reasons for the general increase in first ionisation energies across a period. Why is the increase not uniform? (Refer to the table of first ionisation energies, Mathematics Tables, p. 45.)
If the twelve successive ionisation energies of magnesium were known, what evidence for the existence of energy levels would you expect to find?