AN ROINN OIDEACHAIS

LEAVING CERTIFICATE EXAMINATION. 1984

CHEMISTRY—HIGHER LEVEL

FRIDAY, 22 JUNE—AFTERNOON, 2.00 to 5.00

Six questions to be answered.

All questions carry the same number of marks.

Relative atomic masses: H = 1, C = 12, N = 14, O = 16, S = 32, Ca = 40
Molar volume at S.T.P. = 22·4 litres (dm^3)

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

(*a*) How many (i) neutrons, (ii) electrons are there in the ion $^{52}_{24}Cr^{3+}$?

(*b*) What is (i) the conjugate base of the acid HCOOH, (ii) the conjugate acid of the base NH_2^-?

(*c*) What is the oxidation number of (i) nitrogen in NH_4^+, (ii) phosphorus in $H_2PO_2^-$?

(*d*) What mass of calcium carbonate will remove 3·2 g of sulphur dioxide gas from the air in the reaction.

$$2CaCO_3 + 2SO_2 + O_2 \rightarrow 2CaSO_4 + 2CO_2\,?$$

(*e*) Write the structural formula for acetaldehyde (ethanal) phenylhydrazone.

(*f*) Name the two reagents you would use to confirm the presence of the carbonate ion in an insoluble metal carbonate.

(*g*) Calculate the approximate relative atomic mass of Gallium (Ga) given that it contains 60% of the isotope $^{69}_{31}Ga$ and 40% of the isotope $^{71}_{31}Ga$?

(*h*) Write the electronic configuration (*s*, *p*) for (i) the fluorine atom, (ii) the calcium ion.

(*i*) What type of binding force holds together in each case

(i) carbon atoms in a crystal of diamond, (ii) water molecules in a crystal of ice?

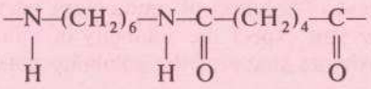
(*j*) Which of the following ions, which have similar electronic configurations, has (i) the smallest, (ii) the largest radius?

$$Na^+ \quad Mg^{2+} \quad Al^{3+} \quad O^{2-} \quad F^-$$

(*k*) Classify each of the following oxides as acidic, basic, amphoteric or neutral: (i) K_2O, (ii) Al_2O_3

(*l*) Balance the equation: $IO_3^- + I^- + H^+ \rightarrow I_2 + H_2O$

(*m*) Write the formulae of the two different monomer units which polymerise to give the structure shown in the following section:



(*n*) How many litres (dm^3) of oxygen would be needed to oxidise 112 litres (dm^3) of ammonia in the reaction:

$$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)},$$

all volumes being measured under the same conditions?

2. (*a*) Give one example in each case of (i) a linear triatomic molecule, (ii) a planar molecule, (iii) a tetrahedral molecule.
In the case of (ii) above describe how the bonding of the planar molecule you have selected can be explained in terms of hybrid orbitals.
What factors result in the water molecule being V-shaped with a bond angle of approximately 105°?

(*b*) Define (i) electronegativity, (ii) electron affinity.
Explain how polarity in a covalent bond can arise and distinguish it from ionic bonding.
What type of bonding would you expect in (i) CS_2, (ii) KBr, (iii) ZnI_2?
(Refer to the Table of Electronegativities, Mathematics Tables, p. 46.)
Suggest reasons for the trends in electronegativity values across a typical period (e.g. Na to Cl).
Give one major respect in which electronegativity differs from electron affinity.

3. The general gas equation for an ideal gas is given as $PV = nRT$.

(i) What do you understand by an ideal gas?

(ii) Write equations for two of the gas laws on which the general gas equation is based.

(iii) Explain the meaning of the terms R and n in the equation.

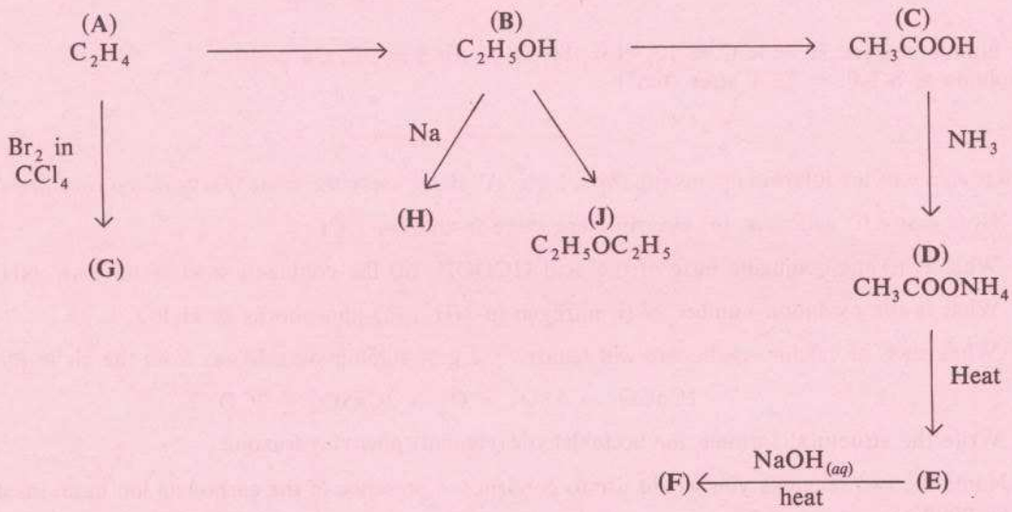
(iv) Express n in terms of actual mass (m) and relative molecular mass (M) of the gas.

(v) Suggest *two* reasons why real gases differ from ideal behaviour. Under what conditions of temperature and pressure would a real gas come nearest to being ideal?

(vi) 0·3 g of a gas occupied 168 cm^3 at 300 K and a pressure of $1{\cdot}0 \times 10^5$ $N\,m^{-2}$. Calculate the relative molecular mass (molecular weight) of the gas. ($R = 8{\cdot}4$ N m mol^{-1} K^{-1})

(vii) The gas in (vi) is an organic compound containing nitrogen and is soluble in water giving a solution with a pH greater than 7. Suggest a possible structure for a molecule of the gas and name the gas you have chosen.

4. Study the following reaction scheme and answer the questions which follow.



(i) Name the compounds **B, C, D** and **J**.

(ii) Give the name and structural formula for compound **G**.

(iii) Write a balanced equation for the change **B** to **H**.

(iv) What type of reaction is the change **B** to **C**?
Name the reagent or reagents you would use and state how you would use them to bring about this change.

(v) What type of reaction is the change **C** to **D**?

(vi) Give the name and structural formula for compound **E**.

(vii) Write an equation for the reaction which **E** would undergo to give **F**.

(viii) State briefly, mentioning reagent and conditions, how you would convert **B** to **J**.

(ix) Outline briefly any one method by which **A** could be converted to **B**.

5. Define (i) heat of solution, (ii) lattice energy of an ionic solid, (iii) hydration energy of an ion.
When 2 g ammonium nitrate (NH_4NO_3) was dissolved in a large excess of water it was found that 630 J of heat was absorbed. Calculate the heat of solution of ammonium nitrate.
State, giving your reason, how you expect the solubility of ammonium nitrate in water to vary with rise in temperature. Sketch the approximate shape of the solubility curve and label the axes.

Given the following data,

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)} \qquad \Delta H = -566 \text{ kJ}$$
$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \qquad \Delta H = -572 \text{ kJ}$$
$$2CH_3OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(l)} \qquad \Delta H = -1430 \text{ kJ}$$

calculate the heat change for the reaction

$$CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(l)}.$$

The hydration energies of some ions, in kJ mol^{-1}, are shown in the table.

Ion	Ag^+	Mg^{2+}	F^-	Cl^-
Hydration Energy (kJ mol^{-1})	−464	−1920	−496	−364

Why is the hydration energy of the Mg^{2+} ion much higher than that of the Ag^+ ion?
Calculate the heat of solution in a large excess of water of (i) $MgCl_2$, (ii) AgCl, (iii) AgF, given that the lattice energies of these salts are respectively 2493, 905 and 936 kJ mol^{-1} and assuming that no other energy factors are involved.

6. (i) Distinguish between empirical, molecular and structural formulae.

(ii) A weak organic acid was found to contain 41·39% carbon, 3·45% hydrogen and 55·16% oxygen by mass. Find its empirical formula.

(iii) 0·29 g of this acid, which was found to be dibasic (diprotic), required 40 cm^3 of a 0·125 moles per litre (mol dm^{-3}) solution of potassium hydroxide for neutralisation. Find its relative molecular mass (molecular weight) and hence its molecular formula.

(iv) Suggest a suitable indicator for this titration and explain briefly how it acts as an indicator.

(v) The acid can exist in two stereoisomeric forms. Write the structural formulae of the two stereoisomers, name them and explain how the stereoisomerism arises.

7. Here are the formulae of some inorganic compounds:

$$Na_2O,\ CO,\ LiH,\ NH_3,\ HBr,\ MgCl_2,\ PCl_5$$

From this list identify the compounds **P, Q, R** and **S** below and explain, using balanced equations, the reactions described.

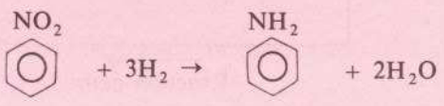
(i) **P** is a colourless poisonous gas which burns with a blue flame forming a product which is also a colourless gas and which turns lime water milky.

(ii) **Q** is a colourless gas with a characteristic smell. It forms dense white fumes when brought into contact with hydrogen chloride gas. A solution of **Q** in water causes the formation of a white precipitate when added to a solution of aluminium chloride.

(iii) **R** is a colourless gas which fumes in moist air. It is very soluble in water giving a solution which dissolves magnesium releasing another colourless gas which can reduce heated copper(II) oxide to copper.

(iv) **S** is a white solid which reacts with excess water to form a colourless solution which turns pH paper red. This solution gives a white precipitate when dilute nitric acid and silver nitrate solution are added. When **S** is heated in a closed vessel a greenish-yellow colour is seen.

8. A sample of aniline (phenylamine) was prepared as follows: 100 g granulated tin were added to 61·5 g nitrobenzene in a flask. 10 cm^3 concentrated hydrochloric acid were then added with shaking every three minutes until a total of 200 cm^3 of the acid had been added. The flask was heated on a water-bath for half an hour and then cooled. A 6 moles per litre (mol dm^{-3}) solution of sodium hydroxide was then added gradually with shaking until the mixture was alkaline. The mixture was now steam distilled and the aniline (phenylamine) extracted from the distillate with ether (ethoxyethane). The ether (ethoxyethane) was distilled off and the aniline (phenylamine) was dried overnight with sodium hydroxide pellets. Pure aniline (phenylamine) (b.p. 183°C) was distilled using an air condenser. 27·9 g of aniline (phenylamine) were obtained. The overall reaction can be represented



(i) What type of reaction does the nitrobenzene undergo?

(ii) In the course of the reaction tin undergoes the following changes: $Sn \rightarrow SnCl_2 \rightarrow SnCl_4 \rightarrow SnCl_6^{2-}$. Write down the oxidation number of tin at each of the four stages.

(iii) The aniline (phenylamine) reacts with excess hydrochloric acid as it is formed. What ions are formed in the mixture as a result of this?

(iv) What is the purpose of adding excess sodium hydroxide solution? Write an equation for the reaction which results.

(v) Mention one precaution you would take in distilling off the ether (ethoxyethane).

(vi) Why is an air condenser rather than a water-cooled condenser used in distilling the aniline (phenylamine) at the end?

(vii) Calculate the percentage yield of aniline (phenylamine). Suggest two reasons why the yield is less than 100%.

(viii) Write an equation for the reaction of acetic (ethanoic) anhydride with aniline (phenylamine).

9. State Le Chatelier's Principle.
Write the equilibrium constant expression for the reaction,

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \quad \Delta H = -115 \text{ kJ}.$$

What would be the effect on the amount of nitrogen dioxide (nitrogen (IV) oxide) formed of

(i) increasing the pressure,

(ii) increasing the temperature?

The salt, sodium acetate (ethanoate), hydrolyses in aqueous solution. Explain, indicating the equilibria involved, the effect of this hydrolysis on the pH of the solution.
Acetic (ethanoic) acid and ethanol react together as follows:

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

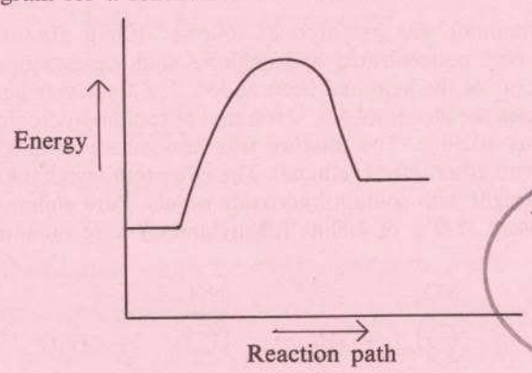
A mixture of 27·6 g ethanol and 36 g acetic (ethanoic) acid was allowed to reach equilibrium at a certain temperature. It was found that 12 g acetic (ethanoic) acid remained unchanged. Find the equilibrium constant for the reaction at this temperature.
How many grams of ethanol must be mixed with 60 g acetic (ethanoic) acid so that 70·4 g ethyl acetate (ethanoate) are present in the equilibrium mixture at the same temperature?

10. Answer any *two* of the following.

(*a*) Explain what is meant by the ionic product of water. Define the pH of a solution.
If the ionic product of water (Kw) at room temperature is $1{\cdot}0 \times 10^{-14}$, what is the hydrogen ion concentration in pure water at this temperature?
What is the hydrogen ion concentration in a solution which has a pH value of 5 at room temperature?
The dissociation constant (Ka) of a monobasic (monoprotic) acid at room temperature is $5{\cdot}5 \times 10^{-5}$. Find the pH of a solution of this acid containing $5{\cdot}0 \times 10^{-2}$ mol in 100 cm^3 of the solution.

(*b*) Describe with the aid of a diagram the procedure you would follow in the laboratory to find the lowering of freezing-point of a pure solvent by a dissolved solute. The description should include the precautions you would take to ensure accuracy and should indicate the readings taken.
The freezing-point of pure benzene is 6°C (279K). The freezing-point constant for benzene is 5·12 K mol^{-1} kg. What mass of naphthalene ($C_{10}H_8$) dissolved in 250 g benzene would give a solution with a freezing-point of 5°C (278 K)?

(*c*) An energy profile diagram for a reaction is shown below:



Copy this diagram and indicate on it

(i) the activation energy for the forward reaction (E_1),

(ii) the heat of reaction (E_2),

(iii) the activation energy for the reverse reaction (E_3).

Is the forward reaction which is illustrated exothermic or endothermic? Explain your reasoning.
Using an energy profile diagram similar to the above explain in general terms the effect of a catalyst on the rate of a chemical reaction.
Comment on the mechanism of the following reactions in which platinum and nitrogen monoxide (nitrogen (II) oxide) respectively are used as catalysts:

(i) $2H_{2(g)} + O_{2(g)} \xrightarrow{Pt} 2H_2O_{(l)}$

(ii) $NO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow NO_{2(g)}$
$NO_{2(g)} + SO_{2(g)} \longrightarrow SO_{3(g)} + NO_{(g)}$

(*d*) State Faraday's Laws of Electrolysis.
Sketch and label the apparatus you would use to carry out the electrolysis of water to which dilute sulphuric acid had been added (acidified water).
Explain how a solution of an electrolyte conducts electricity.
Give equations to show the electron changes occurring and the products formed (i) at the cathode, (ii) at the anode, during the electrolysis of acidified water.