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2002

02/6

PART A — STRUCTURED ESSAY

*Answer **all four** questions. Each question carries **10** marks.*

Do not write anything in this column

1. (*a*) Identify the elements discribed in (i) - (iv) below and write down their chemical symbols. Also write down these chemical symbols in the appropriate cages in the skeletal periodic table given in page 3.

(i) The element which is a liquid at room temperature and shows the maximum oxidation state of +7.

.....

(ii) The element which forms a stable dichloride without completing the octet of electrons.

.....

(iii) The non-metallic element of which an allotropic form is a good conductor of electricity.

.....

(iv) The first row (3d) transition element forming a highly stable white coloured dioxide.

.....

(4·0 marks) .....

(*b*) **A** is a non-transition element. It forms an oxide with molecular formula A_2O_5. The highest chloride formed by **A** is ACl_3. Identify **A**.

A = ...

Write down the chemical symbol of **A** in the appropriate cage of the skeletal periodic table given in page 3.

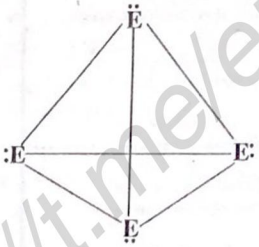
Write below the **balanced chemical equations** for reactions between water and (i) A_2O_5 (ii) ACl_3. **(Use only chemical symbols.)**

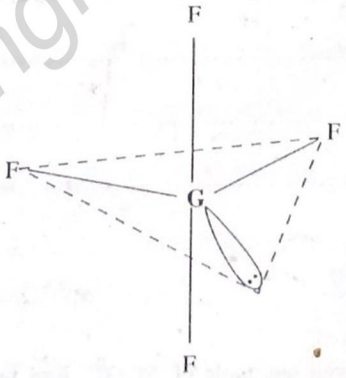
(i) .....

(ii) .....

(3·0 marks) .....

(*c*) Identify the elements **E**, **G** and **J** in the structures for molecules E_4, GF_4 and J_3 given below.







E = ... **G** = ... **J** = ...

Write down the chemical symbols of **E**, **G** and **J** in the appropriate cages in the skeletal periodic table given in page 3.

(3·0 marks) .....

[see page three

Skeletal Periodic Table

1																	2
3	4											5	6	7	8	9	10
11	12											13	14	15	16	17	18
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36

Do not write anything in this column

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100

2. (*a*) A piece of pure magnesium was completely burnt in a mixture of N_2 and O_2 and the mixture of MgO and Mg_3N_2 so obtained had a mass of 1·8 g. When this mixture was heated with excess water and the product obtained ignited, only MgO was formed. The mass of this MgO was 2·0 g.

Write **balanced chemical equations** for all the relevant reactions (Ignore the reaction between MgO and H_2O).

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Calculate the mole ratio MgO : Mg_3N_2 in the mixture formed by burning the piece of magnesium. (Mg = 24; O = 16; N = 14)

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MgO : Mg_3N_2 = ... : ..... *(3.5 marks)*

.....

35

(*b*) 6 moles of I^- ions react completely with one mole of $M_2O_5^{2-}$ ions in acidic medium, forming I_2 and M^{n+} ions.

What is the value of n in M^{n+} ? .....

Write down the **balanced equation** representing the half reaction for the conversion of $M_2O_5^{2-}$ to M^{n+}.

.....

(1.5 marks)

.....

15

[see page four

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(c) (i) What are the basic requirements that must be satisfied by the reactant molecules for any chemical reaction to occur?

(Kinetics)

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Sketch the Boltzmann distribution for the molecules of a given gas at temperatures T_1 and T_2, where $T_2 > T_1$. Label your diagram/graph fully.



(ii) Consider the reaction,

$$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g)\ ; \qquad \Delta H = -490\ kJ$$

and explain the following parts (A) and (B).

(A) A mixture of $H_2(g)$ and $O_2(g)$ is stable at room temperature. However the mixture reacts rapidly when a small amount of platinum powder is added to it.

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(B) This reaction is often accompanied by an explosion.

.....

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..... 30

(3·0 marks)

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(*d*) This part is related to the experiment for the determination of the order of the reaction between thiosulphate ions and hydrochloric acid.

(i) Write down the **balanced chemical equation** for the reaction studied in this experiment.

.....

(ii) Describe how a measure of the rate of the reaction is obtained in this experiment.

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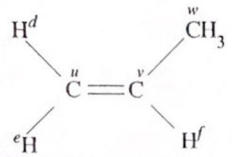
.....

(2.0 marks)

.....
20

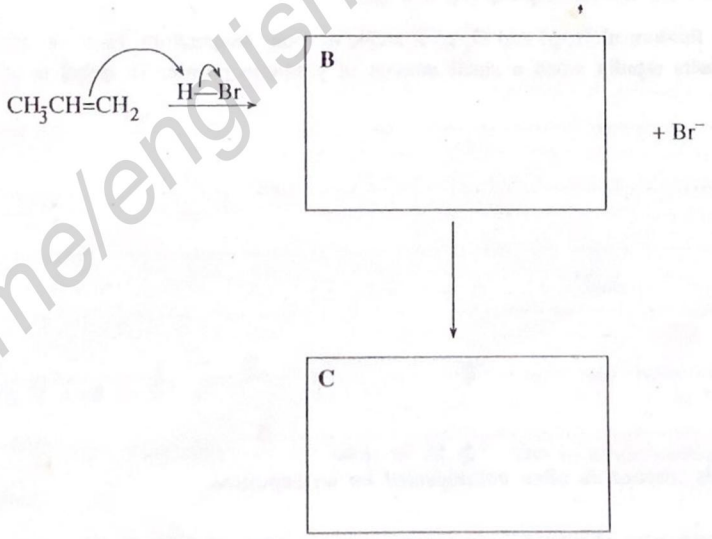
100

3. (*a*) Consider the molecule **A** given below. (Superscripts *d*, *e*, *f*, *u*, *v* and *w* are used to label the H and C atoms).



A

(i) A part of the mechanism of the reaction of **A** with HBr is depicted below. Writing the structures corresponding to **B** and **C** in the boxes below, complete the mechanism using curved arrows where appropriate.



(1.5 marks)

.....
15

[see page six

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(ii) The following statements refer to **A** and its reaction with HBr. Indicate whether each of these statements is correct (✓) or wrong (×) in the appropriate box. If you are unable to evaluate any of these statements keep the box vacant.

N. B: For each correct answer 0.5 marks will be awarded.
For each incorrect answer 0.2 marks will be deducted.
If a box is kept vacant, no marks will be awarded or deducted.
However the minimum marks for this part [(a) (ii)] will be zero(0).

(1) Carbon atom denoted by *u* is sp^2 hybridised. (1) ☐

(2) Carbon atom denoted by *w* is sp^2 hybridised. (2) ☐

(3) The double bond between C atoms denoted by *u* and *v* consists of a σ bond and a π bond. (3) ☐

(4) A π bond is formed by the lateral overlap of two sp^2 orbitals. (4) ☐

(5) The bond between C atoms denoted by *v* and *w* is formed by the linear overlap of two hybridised orbitals. (5) ☐

(6) All the atoms in **A** lie in the same plane. (6) ☐

(7) In this reaction bonds undergo heterolytic cleavage. (7) ☐

(8) A curved arrow (↷) indicates the movement of an atom or a group of atoms, from one position to another. (8) ☐

(9) This reaction is a nucleophilic reaction. (9) ☐

(4.5 marks)

(*b*) (i) Write down in the box below, the structure of the acyclic hydrocarbon **D** (C_6H_{12}) which is optically active.

N. B: It is not necessary to draw the three dimensional structure.

D

(1.5 marks)

(ii) Does this compound show geometrical isomerism? .....

(0.5 marks)

(iii) Write down the structure of the product **E** formed when **D** is treated with H_2/Pt.

(0.5 marks)

E

(iv) Giving a reason state whether **E** could exist in optically active forms.

.....

.....

(0.5 marks)

[see page seven

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(v) Write down the structure of the product **F** formed when **D** is reacted with Br_2/CCl_4.

F

(0.5 marks)

(vi) How many asymmetric carbon atoms are there in the molecule **F**? .....

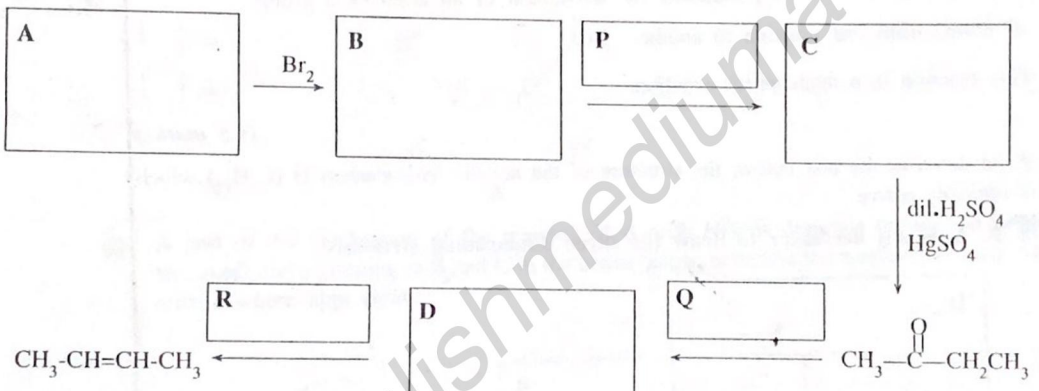
(0.5 marks)

4. (*a*) Consider the following reaction schemes.

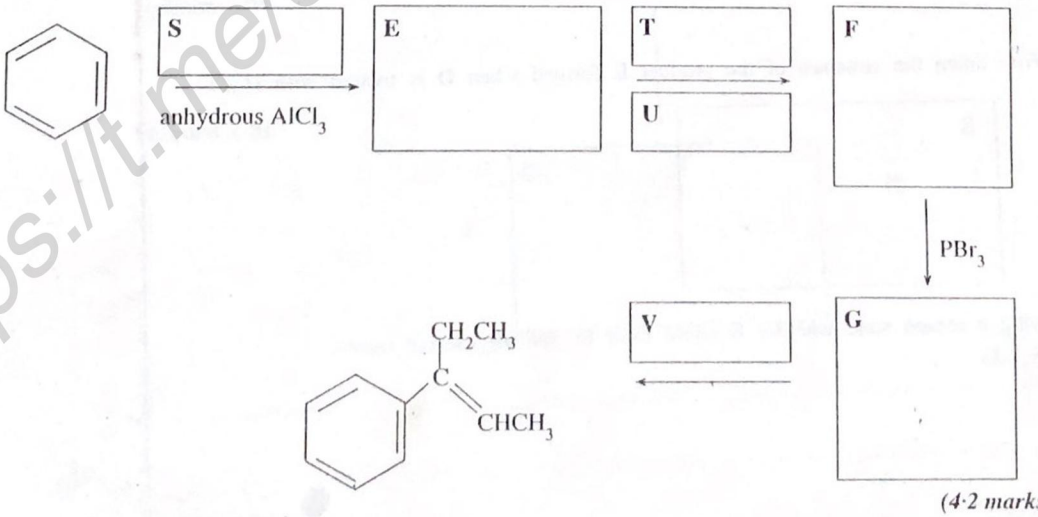
Write down in the appropriate boxes the structures corresponding to compounds, **A, B, C, D, E, F** and **G**.

Also indicate in the appropriate boxes the reagents corresponding to **P, Q, R, S, T, U** and **V**.

(i)



(ii)



(4·2 marks)

[see page eight

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40

100

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(*b*) Show how you would carry out the following conversion.

$$C_6H_5COOH \longrightarrow C_6H_5CH{=}N\text{-}CH_2C_6H_5$$

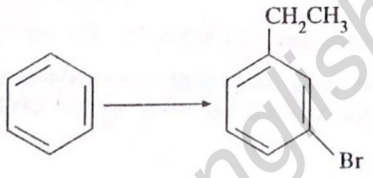
(The only organic compound which could be used as a reagent is C_6H_5CHO)

N.B: This conversion can be carried out in four steps.
Marks will not be awarded to answers containing more than six steps.

.....
36

(3.6 marks)

(*c*) Show how you would carry out the following conversion.



N.B: This conversion can be carried out in three steps.
Marks will not be awarded to answers containing more than five steps.

.....
22

(2.2 marks)

100

[see page nine

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National Evaluation & Testing Service
Department of Examinations, Sri Lanka
இலங்கைப் பரீட்சைத் திணைக்களம்
02 E II

අධ්‍යයන පොදු සහතික පත්‍ර (උසස් පෙළ) විභාගය, 2002 අප්‍රේල්
கல்விப் பொதுத் தராதரப்பத்திர(உயர் தர)ப் பரீட்சை, 2002 ஏப்பிரல்
General Certificate of Education (Advanced Level) Examination, April 2002

රසායන විද්‍යාව II
இரசாயனவியல் II
Chemistry II

PART B — ESSAY

*Answer **two** questions only. Each question carries **15** marks.*

5. (*a*) Read the following passage and answer the questions given below.

"A gas molecule has a mass **a.** Its relative molecular mass is **W**. **X** molecules (**y** mol) of this gas occupy a vessel of volume **G** at a temperature **T**. At this temperature **T**, the mean speed of the gas molecules is **b** while the root mean square speed is **d**. There are no intermolecular forces between the gas molecules. Volumes of the gas molecules can be considered to be negligible."

Using **some or all** the symbols given in the above passage, **write down** (no proof is required) in respect of the gas in the vessel, expressions for

(i) the gas pressure p.

(ii) the product ZR (Z is the compressibility factor of the gas and R is the gas constant.)

[N.B : If any symbol other than those given in the passage above appears in your expressions, no marks will be given for the relevant expressions.]

(3.0 marks)

(*b*) (i) Estimate the standard enthalpy change for the reaction

$$C_2H_5OH\ (l) + CH_3CO_2H\ (l) \rightleftharpoons CH_3CO_2C_2H_5\ (l) + H_2O\ (l)$$

Standard bond enthalpies (kJ mol^{-1})

C—H	: 414	C=O	: 724
C—C	: 347	O—H	: 464
C—O	: 360		

(ii) Explain why your estimated value found above is different from the experimental value (6 kJ mol^{-1}) obtained for this reaction.

(3.0 marks)

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(c) Steam reacts with carbon at high pressures and temperatures above 450°C to produce an equimolar mixture of H_2 and CO, known as "syn gas". This equilibrium reaction takes place in accordance with the following equation.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

A rigid vessel whose volume remains constant at 5·0 dm^3, contains N_2 gas and 0·843 dm^3 of powdered carbon at a pressure of 10^5 Pa and at a temperature of 127°C. 0·5 mol of steam is then introduced into the vessel and the temperature of the vessel is increased to 527°C. At this temperature, only the above reaction takes place. When equilibrium is attained, the pressure inside the vessel is found to be $13·2 \times 10^5$ Pa.

Assuming that the change in volume of the carbon powder due to the reaction is negligible and **stating any other assumptions you make**, answer the following :

(i) Calculate the number of moles of N_2 gas present in the vessel.

(ii) After equilibrium is attained at 527°C, calculate
(A) the total number of moles of gas,
(B) the number of moles each of steam, H_2 and CO, and
(C) the partial pressures of steam, H_2, CO and N_2,
present inside the vessel.

(iii) Calculate the equilibrium constant, K_p, for the above reaction at 527°C.

(iv) If the above reaction is repeated in a similar manner, but in the absence of N_2 gas, deduce
(A) the partial pressure of steam
(B) the partial pressure of CO
(C) the partial pressure of H_2
(D) the total pressure
inside the vessel.

(v) Suggest **one** possible industrial use for "syn gas".

(9.0 marks)

6. (a) Two liquids **L** and **M** are fully miscible and form ideal solutions with one another. The standard boiling point of **L** is higher than the standard boiling point of **M**.

(i) Draw the temperature - composition phase diagram of the above **L** - **M** system at one standard atmosphere pressure.
Label your diagram fully.

(ii) Clearly mark the following on this diagram, using the relevant symbols given within brackets.
(A) the composition of the liquid (X_1) with mole fraction of **L** = 0·8.
(B) the standard boiling point (T_1) of the liquid with composition X_1.
(C) the composition (Y_1) of the vapour in equilibrium with the liquid boiling at T_1.
(D) the composition (X_2) of the liquid obtained by condensing vapour of composition Y_1.
(E) the standard boiling point (T_2) of the liquid with composition X_2.
(F) the composition (Y_2) of the vapour in equilibrium with the liquid boiling at T_2.

(iii) Answer the following questions.
(A) When a mixture of **L** and **M** is boiling, the vapour obtained is condensed and the solution obtained from the condensation is boiled again. If this process is repeated many times, what will be the final composition of the vapour that will be obtained?
(B) State **one** industrial process in Sri Lanka that uses a technique based on the above procedure.
(C) What is the name of the technique used in the above mentioned industrial process?
(D) What is the name of the apparatus that is used in this industrial process?

(6.0 marks)

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(b) (i) Inside an unopened bottle of soda water there exists the following equilibrium between $CO_2(g)$ and $CO_2(aq)$

$$CO_2(g) \rightleftharpoons CO_2(aq) \quad ; \quad \text{(Equilibrium constant, } K_C \text{, at 27°C = 0·9)}$$

as well as the following equilibrium among $CO_2(aq)$, $H^+(aq)$ and $HCO_3^-(aq)$

$$CO_2(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \quad ; \quad \text{(Equilibrium constant, at 27°C = } K_C'\text{)}.$$

Here, CO_2 (g) can be assumed to behave as an ideal gas; further dissociation of $HCO_3^-(aq)$ can be neglected.

Write down expressions for K_C and K_C'.

(ii) Inside the unopened bottle of soda water at 27 °C, the pressure of $CO_2(g)$ is 498 840 Pa and pH of the soda water is 4·0. Calculate and express the following to the **first decimal place**.

(A) the concentration of CO_2 (g) in mol dm^{-3}

(B) the concentration of CO_2 (aq) in mol dm^{-3}

(C) the value of K_C'.

(iii) The bottle of soda water was opened and its contents poured into a beaker. The soda water was then allowed to reach equilibrium in air at 27°C. Under these conditions, the partial pressure of CO_2 in air is 30 Pa. Calculate the pH value of the soda water in equilibrium with atmospheric CO_2 at 27°C.

(9.0 marks)

7. *(a)* (i) **Write down** an expression for the dissociation constant, K_a, of a **very weak** monobasic acid HA in an aqueous solution in terms of the concentrations of H^+ (aq), A^- (aq) and HA (aq) in the solution.

(1.0 marks)

(ii) Hence, show that

$$pK_a = pH - \log_{10} \frac{[A^-(aq)]}{[HA(aq)]} \quad \text{where } pK_a = -\log_{10} K_a$$

(1.5 marks)

(iii) At a particular temperature, $2{\cdot}00 \times 10^{-3}$ mol of the acid HA was dissolved in water and the solution diluted until the volume was 75·00 cm^3. When 25·00 cm^3 of a 0·04 mol dm^{-3} NaOH solution was added to that acid solution, the pH of the resulting solution was found to be 6·0. Calculate the dissociation constant, K_a, of the acid HA at that temperature.

(3·5 marks)

(b) (i) **Write down** the expression for the solubility product of Bi_2S_3 in aqueous solution.

(1.0 marks)

(ii) In a qualitative analytical experiment, Cu^{2+} ions were planned to be precipitated as CuS by saturating a solution containing Cu^{2+} and Ni^{2+} ions with gaseous H_2S. If the initial concentrations of Cu^{2+} and Ni^{2+} ions in the solution are 0·01 mol dm^{-3} and 0·10 mol dm^{-3} respectively, calculate the minimum H^+ ion concentration that should be present in the solution to prevent precipitation of NiS.

The solubility products of CuS and NiS at the relevant temperature are $8{\cdot}0 \times 10^{-45}$ mol^2 dm^{-6} and $1{\cdot}0 \times 10^{-19}$ mol^2 dm^{-6} respectively. At the same temperature,

$$[H^+(aq)]^2 [S^{2-}(aq)] = 1{\cdot}0 \times 10^{-24} \text{ mol}^3 \text{ dm}^{-9}$$

(4·0 marks)

[see page twelve

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(c) Two half reactions related to the corrosion of iron are given below with the relevant standard electrode potentials :

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e \; ; \quad E^\circ = -0{\cdot}44 \text{ V}$$

$$2H_2O + O_2(g) + 4e \longrightarrow 4\,OH^-(aq) \; ; \quad E^\circ = +0{\cdot}40 \text{ V}$$

(i) Write the **balanced chemical equation** for the overall reaction that occurs during the corrosion of iron considering only the half reactions given above. *(1.5 marks)*

(ii) Using your knowledge of electro-chemical cells, calculate the standard e.m.f. of the electro-chemical cell in which the above mentioned overall reaction occurs during the discharge of the cell. *(1.5 marks)*

(iii) An iron tank is to be protected against corrosion by the cathodic protection method. Stating briefly the relevant principle, deduce which of the two metals, **Q** and **R** described below would be suitable for this purpose.

$$Q^{2+}(aq) + 2e \longrightarrow Q(s) \; ; \quad E^\circ = -0{\cdot}60 \text{ V}$$

$$R^{2+}(aq) + 2e \longrightarrow R(s) \; ; \quad E^\circ = -0{\cdot}13 \text{ V}$$

(1.0 marks)

6.

[see page thirteen

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PART C — ESSAY

*Answer **two** questions only. Each question carries **15 marks**.*

8. *(a)* Explain the following statements involved with the industrial manufacture of sulphuric acid.

(i) The conversion of $SO_2(g)$ to $SO_3(g)$ is favoured at high pressures and at low temperatures.

(ii) Temperatures lower than 450°C and pressures higher than 250 atmospheres are not used for the conversion of $SO_2(g)$ to $SO_3(g)$.

(iii) V_2O_5 is generally used in this process.

(6·0 marks)

(b) The mixtures **A** and **B** are identical in colour and colour intensity.

Mixture **A**	5 cm^3 of tube-well water	5 cm^3 of distilled water	5 cm^3 of 0·001 mol dm^{-3} salicylic acid
Mixture **B**	1·5 cm^3 of 0·002 mol dm^{-3} Fe^{3+} ion solution	8·5 cm^3 of distilled water	5 cm^3 of 0·001 mol dm^{-3} salicylic acid

(i) Calculate the concentration of Fe^{3+} in the tube-well water sample and give it in mg dm^{-3} (Fe = 55).

(ii) What is the colour of the complex formed between Fe^{3+} ions and salicylic acid?

(iii) What is the stoichiometric ratio between Fe^{3+} ions and salicylate ions in the above mentioned complex?

(iv) State an appropriate method for the removal of Fe^{2+} and Fe^{3+} ions in water.

(5·0 marks)

(c) (i) Give names of **three** plants from which essential oils are extracted in Sri Lanka.

(ii) Write down the name of **one** major constituent present in the essential oils extracted from each of the plants you mentioned in (i) above.

(iii) Steam distillation is generally used to extract essential oils. Give **two** advantages of using this method. *(4·0 marks)*

9. *(a)* Motor vehicle emissions, constitute a major source of air pollution. Considering these emissions **only**, answer the following :

(i) Name **five** major gaseous pollutants.

(ii) Name **two** elemental pollutants released.

(iii) Name **two** pollutants that form stable complexes with haemoglobin.

(iv) Name **two** pollutants responsible for acid rain.

(v) Name **three** pollutants causing the greenhouse effect.

(vi) State **one** method that can be used to minimise the pollutants in motor vehicle emissions. (No description of the method is required.)

(4·5 marks)

(b) A large quantity of dolomite containing silica (SiO_2) as the only impurity is available. Using this dolomite, water and dilute HCl only, outline a method to prepare a sample of pure MgO.

(4·5 marks)

(c) Write down the relevant **balanced chemical equations** and necessary conditions for all the steps involved in the following processes.

(i) Industrial manufacture of $NH_4NO_3(s)$, starting with N_2 and H_2.

(ii) Synthesis of $Na_2CO_3(s)$ by the Solvay process.

What are the sources of the starting materials used in the above processes?

State the methods for regeneration of raw materials used in the Solvay process.

(6·0 marks)

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10. *(a)* **M** is a first row (3d) transition element. The atoms of this element have six unpaired electrons each.

(i) Identify **M**.

(ii) Write down the complete electronic configuration of **M**.

(iii) Write down the **balanced chemical equation** for the reaction that occurs when an aqueous solution containing M^{3+} is warmed with NaOH and H_2O_2. (The accepted chemical symbol should be used for **M**.)

(iv) What is the colour of the solution obtained after carrying out the reaction mentioned in (iii) above?

(v) Give **two** other compounds of **M** where **M** is in the same oxidation state as in the product obtained in (iii) above.

(vi) Write down **one** important industrial use of **M**.

(5·2 marks)

(b) Write down **balanced chemical equations** for the following.

(i) The thermal decomposition of $NaNO_3$

(ii) The thermal decomposition of $Mg(NO_3)_2$

(iii) The thermal decomposition of $AgNO_3$

(iv) The thermal decomposition of NH_4NO_3

(v) The oxidising action of SO_2

(vi) The reducing action of SO_2

(vii) The oxidising action of H_2S

(viii) The reducing action of H_2S

(4.8 marks)

(c) Labels of bottles containing aqueous solutions of KI, H_2O_2, $FeCl_3$ and $K_3[Fe(CN)_6]$ have fallen off. In an attempt to identify these solutions, the bottles were labelled **A**, **B**, **C** and **D**. The solutions were mixed in pairs in separate test tubes as indicated below. Each of the mixtures so obtained was then acidified and shaken with $CHCl_3$. The colours of the $CHCl_3$ layers are given below.

Experiment	(i)	(ii)	(iii)	(iv)
Solutions mixed	**A + C**	**B + C**	**C + D**	**B + D**
Colour of $CHCl_3$ layer	Colourless	Colourless	Purple	Purple

Addition of **A** to the mixture obtained in experiment (iv) above, produced a deep blue precipitate in the aqueous layer.

Identify, giving reasons, the solutions in bottles **A**, **B**, **C** and **D**.

(5·0 marks)

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