PRACTICE PAPER 2*

Time allowed : 2 hours **Maximum marks : 35**

General Instructions : Read the following instructions carefully.

(a) There are 16 questions in this question paper. All questions are compulsory.
(b) Section A : Q. No. 1 to 8 are objective type questions. Q. No. 1 is passage based question carrying 4 marks while Q. No. 2 to 8 carry 1 mark each.
(c) Section B : Q. No. 9 to 12 are short answer questions and carry 2 marks each.
(d) Section C : Q. No. 13 and 14 are short answer questions and carry 3 marks each.
(e) Section D : Q. No. 15 and 16 are long answer questions carrying 5 marks each.
(f) There is no overall choice. However, internal choices have been provided.
(g) Use of calculators and log tables is not permitted.

SECTION - A (OBJECTIVE TYPE)

1. Read the passage given below and answer the following questions :

In the presence of Lewis acid catalysts such as aluminium chloride or ferric chloride ($FeCl_3$), alkyl halides were found to alkylate benzene to give alkyl benzenes. The reaction is called Friedel-Crafts alkylation. It involves

(A) formation of carbocation.
(B) attack of electrophile (carbocation) over ring to form arenium ion.
(C) abstraction of hydrogen.

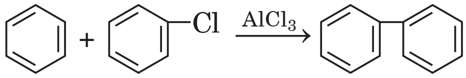
- When $R - X$ is a primary halide, a simple carbocation probably doesn't form. Instead, the aluminium chloride forms a complex with the alkyl halide, and this complex acts as electrophile.
- FC alkylation is not restricted to the use of alkyl halides and aluminium chloride. Many other pairs of reagents that form carbocations (or carbocation like species) may be used as well.
- Polyalkylation and rearrangement of carbocation are necessary evils of FC alkylation.
- Highly activating and highly deactivating groups, usually don't give good yield.

The following questions are multiple choice questions. Choose the most appropriate answer.

(i)  + $CH_3CH_2-Cl \xrightarrow{AlCl_3}$ Product

Which of the following is actual electrophile involved in the reaction ?

(a) $CH_3CH_2^{\oplus}$
(b) $CH_3-CH_2-\overset{\delta+}{Cl}\cdots\overset{\delta-}{AlCl_3}$
(c) $CH_3-\overset{\delta+}{CH_2}\cdots\overset{\delta+}{Cl}\cdots AlCl_3$
(d) $CH_3-\overset{\delta+}{CH_2}\cdots Cl\cdots\overset{\delta-}{AlCl_3}$

(ii) I. 

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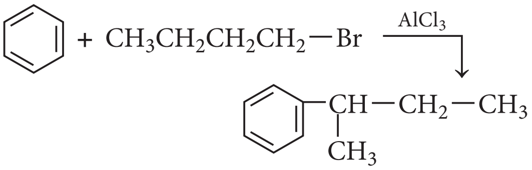

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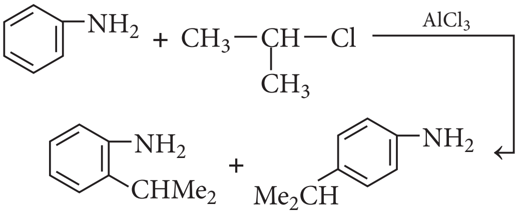

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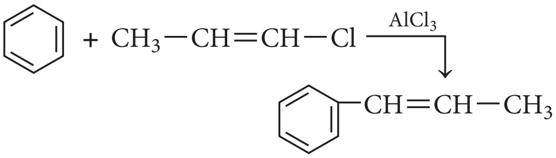
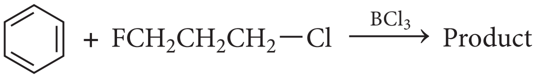


Which of the above mentioned Friedel-Crafts reactions is/are not feasible?

(a) II and IV only (b) II and III only

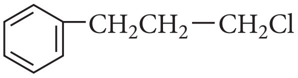
(c) I, II and IV only (d) I, III and IV only

(iii)

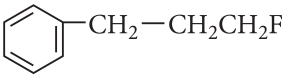


The main product is

(a)



(b)



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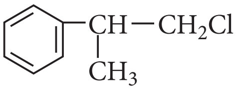
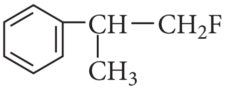


(d)



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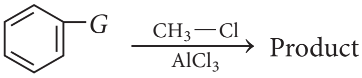


Friedel-Crafts reaction proceeds most efficiently when G is

(a) — NHR (b) — CH_3 (c) — CHO (d) — NO_2

OR

Among the following statements on the nitration of aromatic compounds, the false one is

(a) the rate of nitration of benzene is almost the same as that of hexadeuterobenzene

(b) the rate of nitration of toluene is greater than that of benzene

(c) the rate of nitration of benzene is greater than that of hexadeuterobenzene

(d) nitration is an electrophilic substitution reaction.

Following questions (Q. No. 2-6) are multiple choice questions carrying 1 mark each :

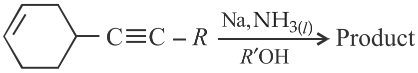
2. When Friedel-Crafts alkylation of benzene is carried out with *n*-propyl bromide, the major product is

(a) *n*-propyl benzene (b) isopropyl benzene

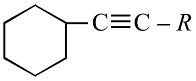
(c) 2-ethyl benzene (d) none of the above.

OR

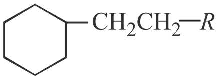
The main product of the reaction is



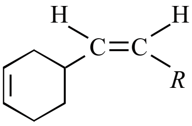
(a)



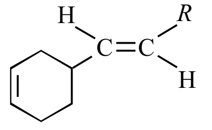
(b)



(c)



(d)



3. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is

(a) London force　　(b) hydrogen bond

(c) ion - ion interaction　　(d) ion-dipole interaction.

4. Both lithium and magnesium display several similar properties due to the diagonal relationship, however, the one which is incorrect, is

(a) both form nitrides

(b) nitrates of both Li and Mg yield NO_2 and O_2 on heating

(c) both form basic carbonates

(d) both form soluble bicarbonates.

OR

Among LiCl, RbCl, $BeCl_2$, $MgCl_2$ the compounds with greatest and least ionic character respectively are

(a) LiCl and RbCl　　(b) RbCl and $BeCl_2$

(c) RbCl and $MgCl_2$　　(d) $MgCl_2$ and $BeCl_2$

5. An organic compound with molecular formula C_6H_{12} upon ozonolysis gave only acetone as the product. The compound is

(a) 2,3-dimethyl-1-butene　　(b) 3-hexene

(c) 2-hexene　　(d) 2,3-dimethyl-2-butene

6. A reaction is spontaneous at high temperatures if

(a) ΔH and ΔS both are negative　　(b) ΔH and ΔS both are positive

(c) ΔH is positive and ΔS is negative　　(d) none of these.

In the following questions (Q. No. 7 and 8), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

7. **Assertion :** K_p can be less than, greater than or equal to K_c.

Reason : Relation between K_p and K_c depends on the change in number of moles of gaseous reactants and products (Δn).

8. **Assertion :** Although aluminium is above hydrogen in electrochemical series, it is stable in air and water.

Reason : The thin protective layer of oxide (Al_2O_3) on aluminium is stable in air and water.

OR

Assertion : Carbon atom is tetravalent though it has two unpaired electrons.

Reason : Carbon has unique ability to form $p\pi - p\pi$ multiple bonds like $C{=}C$, $C{\equiv}C$.

SECTION - B

The following questions, Q. No. 9 - 12 are short answer type and carry 2 marks each.

9. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27° C from 10 litre to 5 litre. Calculates q, W and ΔU for this process. ($R = 2.0$ cal K^{-1} mol^{-1}, atomic weight of Argon = 40)

OR

The molar heat of formation of $NH_4NO_{3(s)}$ is – 367.54 kJ and those of $N_2O_{(g)}$ and $H_2O_{(l)}$ are +81.46 kJ and –285.78 kJ respectively at 25° C and 1.0 atmospheric pressure. Calculate ΔH and ΔU for the reaction,

$NH_4NO_{3(s)} \rightarrow N_2O_{(g)} + 2H_2O_{(l)}$

10. BCl_3 exists as monomer whereas $AlCl_3$ is dimerised through chlorine bridging. Give reason. Also explain the structure of the dimer of $AlCl_3$.

OR

Discuss the Lewis acid nature of boron halides.

11. An iron cylinder contains helium at a pressure of 250 kPa at 300 K. The cylinder can withstand a pressure of 1×10^6 Pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not (melting point of the cylinder = 1800 K).

12. (i) Name the chief factors responsible for the anomalous behaviour of lithium.

(ii) Complete the following reactions :

(a) $4LiNO_3 \xrightarrow{\Delta}$ (b) $2NaNO_3 \xrightarrow{\Delta}$

SECTION - C

Q. No. 13 and 14 are short answer type II carrying 3 marks each.

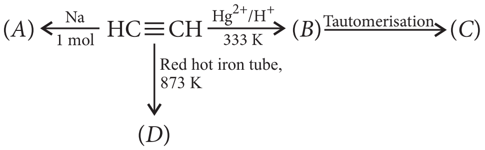
13. At 300 K, the standard enthalpies of formation of $C_6H_5COOH_{(s)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ are – 408, – 393 and – 286 kJ mol^{-1}, respectively. Calculate the heat of combustion of benzoic acid at (i) constant pressure and (ii) constant volume. ($R = 8.314$ J mol^{-1} K^{-1})

14. (a) Benzene is highly unsaturated compound but behaves like a saturated compound. Why?

(b) Out of benzene, *m*-dinitrobenzene and toluene which will undergo nitration most easily and why?

OR

(a) Identify '*A*', '*B*', '*C*' and '*D*' in the following sequence of reactions :



(b) Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

SECTION - D

Q. No. 15 and 16 are long answer type carrying 5 marks each.

15. (a) Classify the following as acid or base and also mention the concept on the basis of which these are so.

(i) $HCl_{(aq)}$ (ii) $Na_2CO_{3(aq)}$ (iii) H_2O (iv) NH_4^+

(b) Predict whether a precipitate will be formed or not on mixing equal volumes of 2×10^{-4} M $BaCl_2$ solution and 2×10^{-5} M Na_2SO_4 solution if solubility product of $BaSO_4$ is 1×10^{-10}.

OR

(a) For the exothermic formation of sulphur trioxide from sulphur dioxide and oxygen in the gas phase :

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

$K_p = 40.5$ atm^{-1} at 900 K and $\Delta_r H = -198$ kJ mol^{-1}

(i) Write the expression for the equilibrium constant for the reaction.

(ii) At room temperature (≈ 300 K) will K_p be greater than, less than or equal to K_p at 900 K?

(iii) How will the equilibrium be affected if the volume of the vessel containing the three gases is reduced, keeping the temperature constant. What happens?

(iv) What is the effect of adding 1 mole of $He_{(g)}$ to a flask containing SO_2, O_2 and SO_3 at equilibrium at constant volume?

(b) A vessel at 1000 K contains carbon dioxide at a pressure of 0.5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of *K*, if the total pressure at equilibrium is 0.8 atm.

16. (a) Explain the difference in properties of diamond and graphite on the basis of their structures.

(b) Rationalise the given statements and give chemical reactions :

(i) Lead (II) chloride reacts with Cl_2 to give $PbCl_4$.

(ii) Lead (IV) chloride is highly unstable towards heat.

(iii) Lead is known not to form an iodide, PbI_4.

OR

(a) How can the fullerenes be prepared?

(b) Account for the following : $PbCl_4$ is a powerful oxidising agent.

(c) Account for the following :

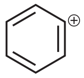
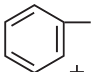
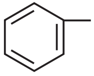
(i) $PbCl_2$ is more stable than $PbCl_4$.

(ii) $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ not.

(d) Why carbon shows anomalous behaviour?

ANSWERS

1. **(i) (d) :** Complex electrophile

(ii) (d) :  and $CH_3 — CH = CH^+$ are not possible.,  NH_2 coordinates with $AlCl_3$, first giving,  $\overset{+}{N}H_2\overset{-}{Al}Cl_3$, ring becomes deactivated, thus alkylation is not possible.

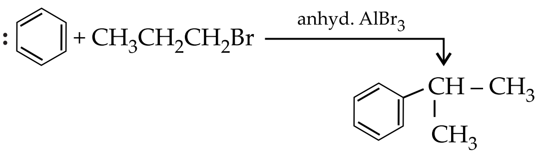
(iii) (a) : $R — F$ is more reactive than $R — Cl$.

(iv) (b) : Highly activating and deactivating groups are not favourable for Friedel-Craft reaction.

OR

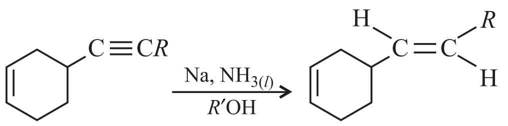
(a) : Hexadeuterobenzene, C_6D_6 is less reactive than benzene C_6H_6 due to isotopic effect.

2. **(b) :**



OR

(d) : An isolated olefinic bond is not affected by the Birch reagent except in an end methylene ($= CH_2$) or in strained system like cyclobutenes or cyclopropenes. Acetylenes readily give olefinic compounds with alkali metal in liq. NH_3 and gives *trans* product.



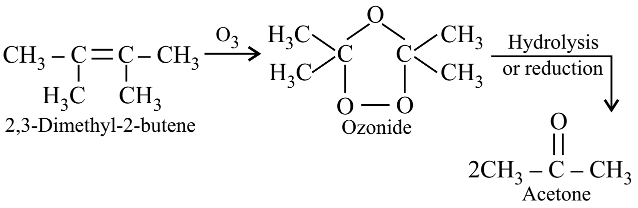
3. **(b) :** Dipole-dipole interaction (hydrogen bonding) is proportional to $1/r^3$, where r is the distance between the polar molecules.

4. **(c) :** Due to diagonal relationship, both Li and Mg display some similar properties, but in the case of carbonates, Mg can form basic carbonates such as $MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$. In contrast, Li only form typical carbonate Li_2CO_3 as other alkali metals. It does not form any basic carbonate having both carbonate and hydroxide ions.

OR

(b) : The larger the size of cation, the greater is the ease with which the valence electrons can be removed from it and hence more will be the ionic character.

5. **(d) :** The reaction sequence is as follows :



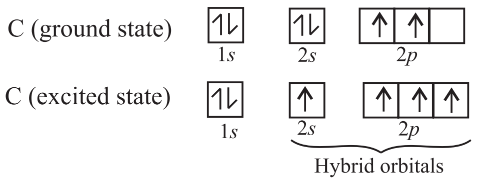
6. **(b) :** A reaction is spontaneous at high temperature, if ΔH and ΔS are positive and it is an entropy driven process.

7. **(a) :** $K_p = K_c (RT)^{\Delta n}$

8. **(a) :** Due to Al_2O_3 layer, the metal is protected from further attack of air and water.

OR

(b) : Carbon is tetravalent due to empty p-orbitals which hybridise in excited state to give sp^3 hybridisation with one electron each in $2s$ and $2p$-orbitals showing tetravalency.



9. $$W_{\text{iso, rev}} = -2.303nRT\log\frac{V_2}{V_1} = -2.303nRT\log\frac{5}{10}$$

$$= -2.303\times\frac{10}{40}\times 2\times 300\log\frac{5}{10} = 103.9\text{ cal}$$

For isothermal process $\Delta U = 0$

From 1st law of thermodynamics, $\Delta U = q + W$

$\therefore\quad q = -W = -103.9$ cal

OR

$$\begin{array}{lccc} & NH_4NO_{3(s)} \rightarrow & N_2O_{(g)}\ + & 2H_2O_{(l)} \\ \Delta H_f\ \text{(kJ)} & -367.54 & 81.46 & 2\times -285.78 \end{array}$$

$\Delta H = \Delta H_{f\text{ (Products)}} - \Delta H_{f\text{ (Reactants)}}$

$= [2\times(-285.78) + 81.46] - (-367.54)$

$= -122.56\text{ kJ} = -122.56\times 10^3\text{ J}$

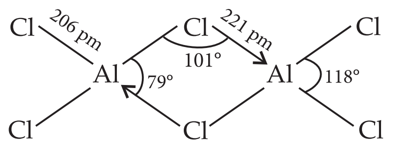
$\Delta n_g = n_p - n_r = 1 - 0 = 1$

$\Delta H = \Delta U + \Delta n_g RT \Rightarrow \Delta U = \Delta H - \Delta n_g RT$

$\Delta U = -122.56\times 10^3 - 1\times 8.314\times 298 = -125.04\times 10^3\text{J}$

$= -125.04$ kJ

10. Due to absence of *d*-orbitals in boron, BCl_3 exists as an electron deficient monomer and achieves stability through accepting electrons from a base like NH_3. BCl_3 cannot exist as dimer due to small size of B which cannot accommodate four bigger size Cl-atoms around it. $AlCl_3$ achieves stability by forming a dimer as shown :

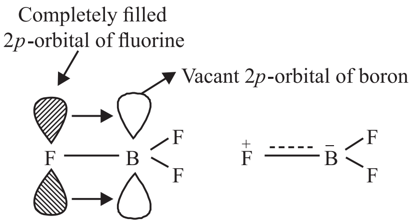


OR

The Lewis acid character of boron trihalides follows the order :

$BI_3 > BBr_3 > BCl_3 > BF_3$.

The above order is just the reverse of the expected order on the basis of relative electronegativities of the halogens. This can be explained on the basis of the tendency of the halogen atom to back-donate its electrons to the boron atoms resulting in the formation of an additional $p\pi-p\pi$ bond. This type of bond formation is known as dative or back bonding.



Formation of back bonding between boron and fluorine in BF_3 molecule.

As a result of back donation of electrons from fluorine to boron, the electron deficiency of boron atom gets compensated and therefore, the Lewis acid character of BF_3 decreases.

The tendency to form $p\pi-p\pi$ bond is maximum in the case of BF_3 and falls rapidly as we move to BCl_3 and BBr_3.

11. According to Gay-Lussac's law, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$\frac{250}{300} = \frac{P_2}{1800} \Rightarrow P_2 = 1500$ kPa

As the cylinder can withstand a pressure of 10^6 Pa $= 10^3$ kPa $= 1000$ kPa, hence, it will blow up.

12. (i) Chief factors responsible for the anomalous behaviour of lithium are :

- its very small size
- high electronegativity
- high ionization enthalpy and
- absence of vacant *d*-atomic orbital in the valence shell.

(ii) (a) $4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$

(b) $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$

13. $C_6H_5COOH + \frac{15}{2}O_2 \rightarrow 7CO_2 + 3H_2O$ ...(i)

Given,

$7C_{(s)} + 3H_{2(g)} + O_{2(g)} \rightarrow C_6H_5COOH_{(s)}$;

$\Delta H^\circ = -408\text{ kJ mol}^{-1}$ ...(ii)

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H^\circ = -393\text{ kJ mol}^{-1}$ ...(iii)

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$; $\Delta H^\circ = -286\text{ kJ mol}^{-1}$ ...(iv)

In order to obtain eqn (i) operate 7 × (iii) + 3 × (iv) – (ii)

$\Delta H^\circ = [-393\times 7 - 286\times 3 + 408]$

$\therefore\quad \Delta H^\circ = -3201\text{ kJ mol}^{-1}$

Also $\Delta H_P = \Delta H_V + \Delta nRT$

$\therefore\quad -3201 = \Delta H_V + (-1/2)\times 8.314\times 10^{-3}\times 300$

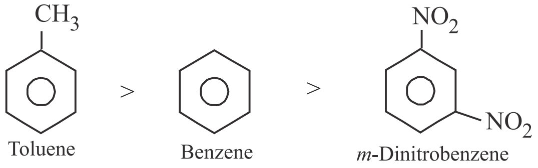
($\because \Delta n = -1/2$ and $R = 8.314\times 10^{-3}\text{ kJ mol}^{-1}\text{ K}^{-1}$)

$\therefore\quad \Delta H_V = -3201 + 1.2471 = -3199.7529\text{ kJ mol}^{-1}$

14. (a) The benzene molecule is unsaturated but the double bonds present inside the benzene ring are delocalized due to bond resonance (π-structure). This makes the double bonds of benzene much less reactive than more discrete double bonds. This makes it behave more like a saturated compound.

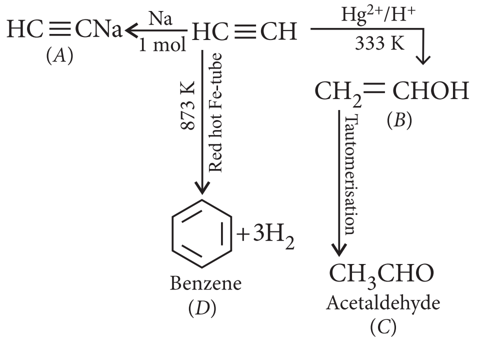
(b) During nitration, the electrophile NO_2^+ attacks the benzene ring. Nitration will be easier if the benzene ring shows increased electron density. This happens when electron releasing groups such as $-R$, $-NH_2$, $-NHCOCH_3$, $-OH$, $-OMe$ etc. are attached to the ring whereas, the attachment of electron withdrawing groups such as $-NO_2$, $-CHO$, $-COR$, $-COOH$ reduces the electron availability for NO_2^+ and nitration becomes difficult.

Therefore, relative ease of nitration of given molecules may be arranged as :



OR

(a)



(b) Due to the presence of an electron cloud containing 6 π-electrons above and below the plane of the ring, benzene is a rich source of electrons. Consequently, it attracts the electrophiles (electron-deficient reagents) towards it and repels nucleophiles (electron-rich reagents). As a result, benzene undergoes electrophilic substitution reactions easily and nucleophilic substitutions with difficulty.

15. (a) (i) $HCl_{(aq)}$: Acid, according to Arrhenius concept and Bronsted–Lowry concept,

$HCl \rightarrow H^+ + Cl^-$ (proton donor)

(ii) $Na_2CO_{3(aq)}$: Base, according to Bronsted–Lowry concept,

$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$

$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$ (proton acceptor)

(iii) H_2O : Both acid and base *i.e.*, amphoteric according to Arrhenius concept and Bronsted–Lowry concept

$$H_3O^+ \xrightleftharpoons{\text{Proton acceptor}} H_2O \xrightleftharpoons{\text{Proton donor}} H^+ + OH^-$$

(iv) NH_4^+: Acid, according to Arrhenius, Bronsted–Lowry concept.

$NH_4^+ \rightleftharpoons NH_3 + H^+$ (proton donor and electron deficient)

(b) $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$, $BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$

$\therefore$ $Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$

Since equal volumes of $BaCl_2$ and Na_2SO_4 are mixed, concentration of Ba^{2+} and SO_4^{2-} after mixing would be

$$[Ba^{2+}] = \frac{[BaCl_2]}{2} = \frac{2\times10^{-4}}{2} = 10^{-4}\text{ M}$$

$$[SO_4^{2-}] = \frac{[Na_2SO_4]}{2} = \frac{2\times10^{-5}}{2} = 10^{-5}\text{ M}$$

Ionic product of $BaSO_4$

$= [Ba^{2+}][SO_4^{2-}] = [10^{-4}][10^{-5}] = 10^{-9}$ M

Ionic product (10^{-9} M) > K_{sp} (1×10^{-10})

Hence, precipitation will take place.

OR

(a) (i) The equilibrium constant for this reaction is written in terms of the partial pressure of the reactants and products. So,

$$K_p = \frac{p^2_{SO_3(g)}}{p^2_{SO_2(g)} \times p_{O_2(g)}}$$

(ii) This reaction is exothermic. So, its equilibrium constant should increase with the lowering of temperature ($d\ \ln K/dT = \Delta_r H°/RT^2$). Therefore, the value of K_p at 300 K will be greater than the value at 900 K.

(iii) When the volume of the vessel is reduced, the volume of the reaction mixture will decrease. As a result, pressure of the gaseous mixture will increase. According to the Le Chatelier's principle, the system will move in a direction to undo the effect of the pressure increase. The system therefore will move in a direction so as to decrease the number of moles of the gaseous substances in the system. The number of moles decrease in going from reactants to the product side. Therefore, a decrease in the volume of the reacting system will shift the equilibrium to the right. That is, more $SO_{3(g)}$ will be formed from the reactants.

(iv) Addition of helium to the reaction mixture at equilibrium under constant volume has no effect on the equilibrium.

(b) $CO_2 + C_{(graphite)} \rightleftharpoons 2CO$

Let the decrease in pressure of CO_2 after reaction $= p$ atm

Then, increase in pressure due to CO after reaction $= 2p$ atm

Final total pressure = $(0.5 - p) + 2p = 0.8$ atm

$\Rightarrow \quad p = 0.3$ atm

Thus after reaction, $p_{CO_2} = 0.5 - 0.3 = 0.2$ atm

$p_{CO} = 2p = 2 \times 0.3 = 0.6$ atm

$$\Rightarrow \quad K = \frac{p_{CO}^2}{p_{CO_2}} = \frac{(0.6)^2}{(0.2)} = 1.8 \text{ atm}$$

16. (a)

Criterion	**Diamond**	**Graphite**
Hybridisation	sp^3	sp^2
Structure of C	Tetrahedral carbon which gives rise to a 3-dimensional structure.	Planar trigonal which gives rise to a 2-dimensional sheet like structure of carbon.
C — C	154 pm	141.5 pm
Hardness	Due to 3-D structure, diamond is the hardest natural element on the earth.	It is made up of 2-D sheets of carbon which slip over each other. This gives graphite a slippery surface.
Electrical Conductivity	Diamond is an insulator.	Graphite is a good conductor of electricity due to presence of delocalised π-electrons.

(b) (i) $PbCl_2 + Cl_2 \nrightarrow PbCl_4$

Lead is more stable in +2 oxidation state than in +4 state due to inert pair effect. Thus, the reaction is not feasible.

(ii) $PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2$

Pb is more stable in its +2 oxidation state due to inert pair effect. As a result, when subjected to heat, Pb (IV) goes to Pb (II) state.

(iii) $Pb + 2I_2 \nrightarrow PbI_4$

I^- is a good reducing agent and therefore, reduces Pb (IV) to Pb (II) easily. That is why, PbI_4 does not exist.

OR

(a) Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon.

(b) In $PbCl_4$, the oxidation state of Pb is +4. Due of inert pair effect, Pb^{2+} is more stable than Pb^{4+}. Hence, Pb^{4+} is easily reduced to Pb^{2+}, thereby acting as a good oxidising agent.

(c) (i) +2 oxidation state of Pb is more stable due to inert pair effect. Thus, lead (IV) chloride readily decomposes to lead(II) chloride.

$PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2$

(ii) Due to small size of F, six fluorine atoms can be accommodated around silicon but six chlorine atoms cannot due to large size of Cl-atoms.

(d) Due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of *d*-orbitals.

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