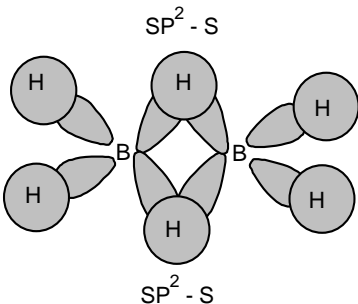
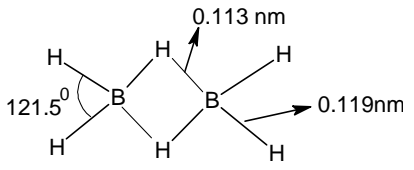


SCHEME OF VALUATION

PART – A

Answer any **eight** of the following questions. Each question carries two marks.

(8 x 2 = 16)

Qtn Nos	Model answers	Marks
1. Ans	<p>Derive an expression of half-life period of second order reaction when a = b.</p> <p>Consider rate constant equation of a second order reaction $K = \frac{1}{t} \left[\frac{x}{a(a-x)} \right]$</p> <p>For half-life period, $t = \frac{t_1}{2}$, $x = \frac{1}{2} a = 0.5a$</p> <p>$\therefore a - x = a - 0.5a = 0.5a$</p> <p>Substitute these values in above equation we get $K = \frac{1}{t_1(1/2)} \left[\frac{0.5a}{a(0.5a)} \right] = K = \frac{1}{t_1(1/2)} \left[\frac{1}{a} \right]$</p> <p>$\therefore \frac{t_1}{2} = \frac{1}{k \cdot a}$, i.e. $\frac{t_1}{2} \propto \frac{1}{a}$ Where K is proportional constant</p>	1 1
2. Ans	<p>State third law of thermodynamics.</p> <p>"A perfect crystalline substance at absolute zero temperature has a zero entropy"</p> <p style="text-align: center;">OR</p> <p>"Every substance has a finite positive entropy but at the absolute zero temperature, the entropy may become zero and does so in the case of pure crystalline substances."</p>	2
3. Ans	<p>Write the expression for weight average molecular weights of polymers.</p> $\overline{M}_w = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 + \dots + n_i M_i^2}{n_1 m_1 + n_2 m_2 + n_3 m_3 + \dots + n_i m_i}$ <p style="text-align: right;">OR $\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i m_i}$</p>	2
4. Ans	<p>What is an adsorption indicator? Give an example.</p> <p>An indicator used in solutions to detect slight excess of a substance or ion, precipitate becomes coloured when the indicator is adsorbed. Example: fluorescein</p>	2
5. Ans	<p>Write the structure of diborane.</p> <div style="display: flex; align-items: center;"><div style="text-align: center;"><p style="margin-left: 50px;">SP² - S</p><p style="margin-right: 50px;">SP² - S</p></div><div style="margin: 0 20px;">OR</div><div style="text-align: center;"><p style="margin-top: 10px;">Diborane</p></div></div>	2

<p>6 Ans</p>	<p>How are silicones prepared?</p> <p>i) Reaction between silicon and alkyl halides</p> $ \begin{array}{c} \text{Si} \\ \text{Silicon} \end{array} + 2\text{CH}_3\text{Cl} \xrightarrow[\Delta]{\text{Cu}} (\text{CH}_3)_2\text{SiCl}_2 \xrightarrow{\text{Hydrolysis}} \begin{array}{c} \text{CH}_3 \\ \\ \text{HO}-\text{Si}-\text{OH} \\ \\ \text{CH}_3 \\ \text{Monomer} \end{array} $ <p style="text-align: center;">methyl chloride Dimethyl dichloro silane</p> <p>Polymerisation</p> $ \longrightarrow \text{HO} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} \\ \\ \text{CH}_3 \end{array} - \text{O} - \begin{array}{c} \text{CH}_3 \\ \\ \text{Si} \\ \\ \text{CH}_3 \end{array} - \text{O} \right]_n $ <p style="text-align: center;">Silicones</p> <p>ii) Reaction between silicon halides and Grignard reagent</p> $ \begin{array}{c} \text{SiCl}_4 \\ \text{Silicon} \\ \text{(IV) chloride} \end{array} + 2\text{CH}_3\text{MgCl} \xrightarrow{\text{Ether}} (\text{CH}_3)_2\text{SiCl}_2 \xrightarrow{\text{Hydrolysis}} \begin{array}{c} \text{CH}_3 \\ \\ \text{HO}-\text{Si}-\text{OH} \\ \\ \text{CH}_3 \\ \text{Monomer} \end{array} $ <p style="text-align: center;">methyl magnesium chloride Dimethyl dichloro silane</p> <p>Polymerisation</p> $ \longrightarrow \text{HO} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} \\ \\ \text{CH}_3 \end{array} - \text{O} - \begin{array}{c} \text{CH}_3 \\ \\ \text{Si} \\ \\ \text{CH}_3 \end{array} - \text{O} \right]_n $ <p style="text-align: center;">Silicones</p>	<p>2</p>
<p>7 Ans</p>	<p>Write any two applications of bleaching powder.</p> <ol style="list-style-type: none"> 1) It is used in the textile industry 2) It is used in the paper and pulp industry 3) It is used in the purification of water 	<p>2</p>
<p>8 Ans</p>	<p>How monohydric alcohols are prepared from alkenes?</p> $ \begin{array}{c} \text{R-CH=CH}_2 \\ \text{Alkenes} \end{array} \xrightarrow[2) \text{H}_2\text{O, Distill}]{1) \text{H}_2\text{SO}_4, 0^\circ\text{C}} \begin{array}{c} \text{R-CH}_2\text{-CH}_2\text{-OH} \\ \text{Monohydric} \\ \text{Alcohol} \end{array} + \text{H}_2\text{SO}_4 $	<p>2</p>
<p>9 Ans</p>	<p>Write a reaction to show that ethers act as Lewis bases.</p> <p>The two lone pairs of electrons present on oxygen atom of ether can readily donated to proton to form co-ordinate bond. This indicates ethers act as Lewis bases.</p> $ \begin{array}{c} \text{R}-\ddot{\text{O}}-\text{R}_1 \\ \text{Ether} \end{array} + \text{H}^+ \longrightarrow \begin{array}{c} \text{H} \\ \\ \text{R}-\overset{+}{\text{O}}-\text{R}_1 \\ \text{Oxonium salt} \end{array} $ <p style="text-align: center;">Proton from acid</p>	<p>1</p>
<p>10 Ans</p>	<p>Write any two functions of nitrogen as essential plant nutrient.</p> <p>a) Nitrogen is a special constituent of chlorophyll pigment without which photosynthesis is not possible.</p> <p>b) Nitrogen in plant tissues is very essential for the synthesis of amino acids, proteins and</p>	<p>1</p> <p>1</p>

	enzymes. c) The proteins thus synthesized from a part of protoplasm & enzymes are needed for biochemical reactions in plant cells.	
11 Ans	How is methyl lithium converted into ethanoic acid? Carbonation of methyl lithium leads to ethanoic acid. $\text{H}_3\text{C}-\text{Li} + \text{CO}_2 \longrightarrow \text{CH}_3\text{COOLi} \xrightarrow{\text{H}^+/\text{H}_2\text{O}} \text{CH}_3\text{COOH}$ Methyl lithium Carbon dioxide Lithium acetate Ethanoic acid	2
12 Ans	What are Grignard reagents? Give an example Alkyl magnesium halides (R – Mg – X) are called Grignard reagent. Example: Ethyl magnesium bromide (C ₂ H ₅ MgBr), Phenyl magnesium chloride (C ₆ H ₅ MgCl)	1 1

PART – B

Answer any NINE of the following questions. Each question carries six marks (9 x 6 = 54)

13(a) Ans	<p>Derive an expression for velocity constant of second order reaction with a ≠ b.</p> <p>Consider a second order reaction</p> $\text{A} + \text{B} \longrightarrow \text{Products}$ <p>The rate of the above reaction is determined by change in concentration of reactants A and B.</p> <p>i.e. $\frac{dx}{dt} = K[A][B]$ ----- (1)</p> <p>Let 'a' mole dm⁻³ be the initial concentration of the reactant 'A' and 'b' mole dm⁻³ be the initial concentration of the reactant 'B'. After an interval of time 't', let 'x' mole dm⁻³ of each reactant A and B be the consumed to form the products. i.e. [A] = a-x, [B] = b-x. The rate of formation of products is given by the concentration of the reactant at that instant is</p> $\frac{dx}{dt} = K(a-x)(b-x) \quad \text{i.e.} \quad \frac{dx}{(a-x)(b-x)} = Kdt \quad \text{-----}(2)$ <p>Let $\frac{1}{(a-x)(b-x)} = \frac{P}{(a-x)} + \frac{Q}{(b-x)}$</p> <p>Taking LCM $(a-x)(b-x)$ on both side</p> $\frac{1}{(a-x)(b-x)} = \frac{P(b-x) + Q(a-x)}{(a-x)(b-x)}$ $P(b-x) + Q(a-x) = 1$ <p>Put $(b-x) = 0 \Rightarrow b = x$ then $Q = \frac{1}{(a-b)}$</p> <p>And put $(a-x) = 0 \Rightarrow a = x$ then $P = -\frac{1}{(a-b)}$</p> $\therefore \frac{1}{(a-x)(b-x)} = -\left(\frac{1}{(a-b)}\right)(b-x) + \frac{1}{(a-b)}(a-x)$ $\frac{1}{(a-x)(b-x)} = \frac{1}{(a-b)} \left[\frac{(a-x) - (b-x)}{(a-x)(b-x)} \right]$ $= \frac{1}{(a-b)} \left[\frac{1}{(b-x)} - \frac{1}{(a-x)} \right]$ <p>Substitute this value in equation (2)</p>	1 1 2
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	$\frac{1}{(a-b)} \left[\frac{1}{(b-x)} - \frac{1}{(a-x)} \right] dx = K dt$ <p>Integrating both sides</p> $\int \frac{1}{(a-b)} \left[\frac{1}{(b-x)} - \frac{1}{(a-x)} \right] dx = K \int dt$ $\frac{1}{(a-b)} \int \frac{1}{(b-x)} dx - \int \frac{1}{(a-x)} dx = K \int dt$ $\frac{1}{(a-b)} [-\ln(b-x) - (-)\ln(a-x)] = kt + c$ <p>where 'c' is constant called integrating constant.</p> $\frac{1}{(a-b)} [-\ln(b-x) + \ln(a-x)] = kt + c$ $\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = kt + c \text{ -----(3) by logarithm property}$ <p>At start of the reaction, time t = 0 and x = 0</p> <p>Then, the equation (3) becomes</p> $\frac{1}{(a-b)} \ln \frac{a}{b} = c$ <p>substitutes this value in equation (3) we get</p> $\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = kt + \frac{1}{(a-b)} \ln \frac{a}{b}$ $kt = \frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} - \frac{1}{(a-b)} \ln \frac{a}{b} =$ $\frac{1}{(a-b)} \left[\ln \left[\frac{(a-x)}{(b-x)} \right] - \ln \left[\frac{a}{b} \right] \right] \text{ by logarithm property}$ $kt = \frac{1}{(a-b)} \left[\ln \left[\frac{(b(a-x))}{a(b-x)} \right] \right] \text{ or } k =$ $\frac{1}{(a-b)t} \ln \left[\frac{(b(a-x))}{a(b-x)} \right]$ $\therefore k = \frac{2.303}{(a-b)t} \log \left[\frac{(b(a-x))}{a(b-x)} \right]$ <p>This equation is the expression for rate (velocity) constant of a second order reaction with $a \neq b$</p>	
<p>13(b) Ans</p>	<p>Write any two limitations of collision theory</p> <ol style="list-style-type: none"> 1) This theory fails to explain the low value of steric factor P 2) It is applicable to gaseous reactions only. 3) This theory fails to explain the contributions of rotational energy and vibrational energy. 4) This theory fails to explain K value for complex reactions. 	2
<p>14(a) Ans</p>	<p>Explain the experimental determination for velocity constant of a reaction between potassium persulphate and potassium iodide by spectrophotometric method.</p> <p>Consider a reaction</p> $K_2S_2O_8 + KI \longrightarrow K_2SO_4 + I_2$ <p>This reaction is a second order reaction (first order w. r. t. each reactant). The reaction can be made to follow first order kinetics by maintaining the concentration of KI in large excess.</p> <p>In this experiment the rate of $K_2S_2O_8$ and KI reaction is followed spectrophotometrically under first order kinetic conditions.</p> <p>Procedure: The Spectrophotometer is set with distilled water to read 0.00 absorbance at 350nm. 0.002M solution of $K_2S_2O_8$ (100 cm^3) and 0.02M KI (100 cm^3) are prepared and equal volumes of $K_2S_2O_8$ and KI ($10 \text{ cm}^3 + 10 \text{ cm}^3$) are mixed. The stop clock is started. The reaction mixture is immediately transferred into a cuvette. The absorbance (A) of I_2 liberated after mixing is measured as a function of time up to 45 minutes at 5 min intervals at wavelength 350 nm. Let 'A₀' represent the absorbance at zero time and A_t after a time interval 't'.</p>	2

The absorbance of the solution after the reaction is completed (A_{∞}) is measured. This is done carefully heating the mixture over water both kept 60°C for 10 min and cooling the reaction mixture to room temperature before absorbance (A_{∞}) is measured.

From the absorbance, ($A_1(t) - A_1(0)$), $[(A)_{1(t)} - A_1(t)]$, $\log\left(\frac{A_{\infty} - A_0}{A_{\infty} - A_t}\right)$ calculated. Finally, rate constant (K) is calculated by using the formula $K = \frac{2.303}{t} \log\left[\frac{A - A_0}{A - A_t}\right] \text{ min}^{-1}$

A graph is plotted with $\log\left(\frac{A_{\infty} - A_0}{A_{\infty} - A_t}\right)$ against time, which is a straight line. This indicates that the reaction between potassium persulphate and potassium iodide is a pseudo first order reaction. From the graph, rate constant is calculated.

Observation and Calculation:

- 1) Absorbance (O.D.) at time 0 minute (A_0) = -----
 - 2) Absorbance (O.D.) at time ∞ minute after heating the mixture ($A_1(\infty)$) = -----
- $\therefore A_1(\infty) - A_0 = \text{-----}$

Time in min, 't'	Absorbance(O.D) at 350 nm, A_t	$A_1(\infty) - A_0$	$\log\left[\frac{A - A_0}{A - A_t}\right]$	$K = \frac{2.303}{t} \log\left[\frac{A - A_0}{A - A_t}\right] \text{ min}^{-1}$
5				
10				

45				

Plot a graph of $\log\left(\frac{A_{\infty} - A_0}{A_{\infty} - A_t}\right)$ versus time. The slope of the linear plot gives $\frac{K}{2.303}$. Then k is calculated.

	<p>Slope = BC/AB $k = \text{slope} \times 2.303$</p> <p>Result: The rate constant of reaction was found to be a) Experimentally _____ b) Graphically _____</p>
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14(b)
Ans

For a reaction, the values of the rate constants at 298 K and 338K were 3.46×10^{-3} and 4.81×10^{-3} respectively. Calculate the energy of activation. $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$.

Given that $K_1 = 3.46 \times 10^{-3}$, $K_2 = 4.81 \times 10^{-3}$, $T_1 = 298 \text{ K}$, $T_2 = 338 \text{ K}$

$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$

$$E_a = 2.303R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \log \frac{K_2}{K_1}$$

$$E_a = 2.303 \times 8.314 \left(\frac{298 \times 338}{338 - 298} \right) \log \frac{4.81 \times 10^{-3}}{3.46 \times 10^{-3}}$$

$$E_a = 103.327 \text{ kJ mol}^{-1}$$

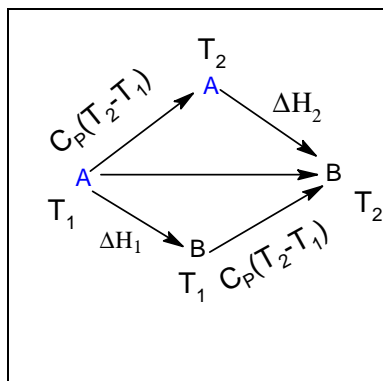
15(a) **Derive Kirchoff's equation.**

Ans

Making use of first law of thermodynamics, Kirchoff in 1858 deduced mathematical expressions to define the variation of heat of reaction with temperature. The enthalpies of reaction i.e. dH , generally vary with temperature. The exact influence of temperature can be worked out as follows

2

Consider a simple reaction, $A \longrightarrow B$



Let the above reaction proceed at temperature T_1 accompanied by heat change dH_1 . The product B at temperature T_1 be brought to temperature T_2 which involves absorption of heat $C'_p(T_2 - T_1)$ where C'_p is mean molar heat capacity of the products. The total heat change accompanying the above process is $dH_1 + C'_p(T_2 - T_1)$. The same reaction may be carried out by initially raising the temperature of the reactants to T_2 from T_1 .

The reaction is then allowed to proceed at temperature T_2 .

In this case, heat absorbed in the first step $C_p(T_2 - T_1)$ where C_p is the mean molar heat capacity of the reactants, and heat change accompanying the reaction at T_2 is dH_2 . The total heat change accompanying the above process is

$$dH_2 + C_p(T_2 - T_1)$$

In both the cases, the reactant A at temperature T_1 is changed to product B at temperature T_2 . Obviously the two energy changes must be equal.

$$dH_1 + C'_p(T_2 - T_1) = dH_2 + C_p(T_2 - T_1) \quad \text{or} \quad dH_2 - dH_1 = C'_p(T_2 - T_1) - C_p(T_2 - T_1)$$

$$= (C'_p - C_p)(T_2 - T_1)$$

$$\frac{dH_2 - dH_1}{T_2 - T_1} = C'_p - C_p$$

$$= dC_p$$

dC_p is the difference in the molar heat capacities of the products and reactants at constant pressure.

dH_2 and dH_1 are the changes in enthalpies of the reaction at temperatures T_2 and T_1 respectively.

$$dH_2 - dH_1 = dC_p(T_2 - T_1)$$

The above equation is known as Kirchoff's equation.

Similarly, at constant volume,

$$dU_2 - dU_1 = dC_v(T_2 - T_1)$$

OR

Consider a simple reaction, $A \longrightarrow B$

Where A is the reactant giving the product B.

The enthalpy change of the reaction, $\Delta H = H_p - H_r = H_A - H_B$

Differentiating the above equation with respect to temperature, keeping pressure constant we have,

$$\left(\frac{\partial(\Delta H)}{\partial T} \right)_p = \left(\frac{\partial(H_B)}{\partial T} \right)_p - \left(\frac{\partial(H_A)}{\partial T} \right)_p$$

2

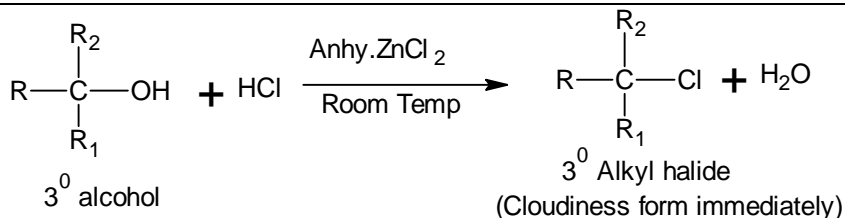
	<p>Since $\left(\frac{\partial(H)}{\partial T}\right)_P = C_P$ = Molar heat capacity at constant pressure</p> $\therefore \left(\frac{\partial(\Delta H)}{\partial T}\right)_P = (C_P)_B - (C_P)_A = \Delta C_P$ $\partial(\Delta H) = \Delta C_P \partial T$ <p>Integrating both side with limits of enthalpy H_1 to H_2 and temperature T_1 to T_2</p> $\int_{H_1}^{H_2} \partial(\Delta H) = \int_{T_1}^{T_2} \Delta C_P \partial T$ $\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1) \text{ ----(1)}$ <p>Assuming ΔC_P to be constant over this range of temperature</p> <p>Similarly, the internal energy change of the reaction,</p> $\Delta U = U_P - U_R = U_A - U_B$ <p>Differentiating the above equation with respect to temperature, keeping volume constant we have,</p> $\left(\frac{\partial(\Delta U)}{\partial T}\right)_V = \left(\frac{\partial(U_B)}{\partial T}\right)_V - \left(\frac{\partial(U_A)}{\partial T}\right)_V$ <p>Since $\left(\frac{\partial(U)}{\partial T}\right)_V = C_V$ = Molar heat capacity at constant volume</p> $\therefore \left(\frac{\partial(\Delta U)}{\partial T}\right)_V = (C_V)_B - (C_V)_A = \Delta C_V$ $\partial(\Delta U) = \Delta C_V \partial T$ <p>Integrating both side with limits of enthalpy U_1 to U_2 and temperature T_1 to T_2</p> $\int_{U_1}^{U_2} \partial(\Delta U) = \int_{T_1}^{T_2} \Delta C_V \partial T$ $\Delta U_2 - \Delta U_1 = \Delta C_V (T_2 - T_1) \text{ -----(2)}$ <p>Assuming ΔC_V to be constant over this range of temperature</p> <p>Equations (1) and (2) are called Kirchhoff's equations.</p>	
<p>15(b) Ans.</p>	<p>What are spontaneous processes? Give an example.</p> <p>Those processes which take place on their own without any external help or assistance are called spontaneous processes.</p> <p>Example, flowing of water from higher level to lower level, burning of candle, ice melting into water, radio isotope decay, rusting of iron etc.</p>	2
<p>16(a) Ans</p>	<p>Derive an expression of work done in the reversible isothermal expansion of an ideal gas.</p> <p>In isothermal process, the temperature remains constant during the entire operation. Consider an ideal gas contained in a cylinder fitted with a frictionless weightless piston placed in a thermostat. Let the pressure of the gas be P. During expansion let the external pressure be reduced by a very small quantity dp and let the volume change during reversible expansion be dv. The work done, W by the gas in the reversible expansion is given by</p> $W = - (P - dP)dV = - PdV + dP.dV$ <p>dP.dV being the product of two very small quantities, is extremely small and can be neglected. Thus $W = - PdV$</p> <p>Total work done W by the gas, when the volume changes from V_1 to V_2 is then given by</p> $\int_{V_1}^{V_2} W, \text{ Then } \int_{V_1}^{V_2} W = - \int_{V_1}^{V_2} PdV$ <p>For one mole of ideal gas $PV = RT$ under reversible conditions so that</p> $P = \frac{RT}{V}$	2

	<p>Now $-\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} \frac{RT}{V} dV = -RT \int_{V_1}^{V_2} \frac{1}{V} dV$</p> <p>i.e. $W = -RT \ln \frac{V_2}{V_1} = -2.203RT \log \frac{V_2}{V_1}$</p> <p>For n moles of an ideal gas : $W = -2.203nRT \log \frac{V_2}{V_1}$</p> <p>At constant temperature $P_1V_1 = P_2V_2$ from Boyle's law</p> <p>$\therefore \frac{V_2}{V_1} = \frac{P_1}{P_2}$</p> <p>$\therefore W = -2.203nRT \log \frac{P_1}{P_2} \text{ Or } W = -2.203nRT \log \frac{P_2}{P_1}$</p> <p>This expression is called expression for work done in reversible isothermal expansion.</p>	
<p>16(b) Ans</p>	<p>Explain the change in entropy during fusion of solid.</p> <p>The ratio of change in enthalpy of fusion to the melting point of the solid in a solid liquid equilibrium reaction is called "The change in entropy during fusion of solid"</p> <p>i.e. $\Delta S = \frac{\Delta H_f}{T_f}$</p>	<p>2</p>
<p>17(a) Ans</p>	<p>Derive Van't Hoff's reaction isochore.</p> <p>Expression for variation of equilibrium constant with temperature can be derived from Gibbs –Helmholtz equation.</p> <p>$\Delta G^0 = \Delta H^0 - T\Delta S^0$ And also $\Delta G^0 = -RT \ln K_P/P_0$</p> <p>$\therefore \frac{-RT \ln K_P}{P_0} = \Delta H^0 - T\Delta S^0$</p> <p>$\frac{\ln K_P}{P_0} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$</p> <p>$P_0$ is standard pressure which is 1 atmosphere</p> <p>At temperature T_1 and T_2 if the equilibrium constants for the reaction be K_1 and K_2 then</p> <p>$\ln K_1 = -\frac{\Delta H^0}{RT_1} + \frac{\Delta S^0}{R} \quad \text{and} \quad \ln K_2 = -\frac{\Delta H^0}{RT_2} + \frac{\Delta S^0}{R}$</p> <p>$\Delta H$ and ΔS are assumed to remain essentially constant over the given temperature range and values of ΔH^0 and ΔS^0 may be used</p> <p>$\ln K_2 - \ln K_1 = -\frac{\Delta H^0}{RT_2} + \frac{\Delta S^0}{R} - \left(-\frac{\Delta H^0}{RT_1} + \frac{\Delta S^0}{R} \right)$</p> <p>$\ln [K_2/K_1] = [\Delta H^0/R(1/T_1 - 1/T_2)]$</p> <p>$[\log] [K_2/K_1] = [\Delta H^0/2.303R((T_2 - T_1)/(T_1 T_2))] \text{ ----- This equation is called Van't Hoff isochore}$</p> <p>OR</p> <p>The relation $\left(\frac{\partial \ln K}{\partial T} \right)_V = \frac{\Delta E^0}{RT^2}$</p>	<p>2</p>

	<p>It is called Van't Hoff isochore. It is used to calculate energies of reactions ΔE by measuring the variation of equilibrium constant K of a reversible reaction at absolute zero temperature. R is gas constant.</p> <p>Derivation : K_c and K_p are related to each other as follows</p> $K_p = K_c (RT)^{\Delta n} \text{ -----(1)}$ <p>Taking logarithm on both sides of eqn (1), we get</p> $\ln K_p = \ln K_c + \Delta n \ln RT \text{ ----- (2)}$ <p>Differentiating eqn (2) w.r.t. temperature, we get</p> $\left(\frac{d \ln K_p}{dT}\right) = \left(\frac{d \ln K_c}{dT}\right) + \frac{\Delta n}{T} = \frac{d \ln K_p}{dT} - \frac{\Delta n}{RT}$ $\frac{\Delta H^0}{RT^2} - \frac{\Delta n}{RT} = \frac{\Delta H^0 - \Delta n RT}{RT^2}$ <p>But, $\Delta H^0 - \Delta n RT = \Delta E$</p> $\frac{d \ln K_c}{dT} = \frac{\Delta E^0}{RT^2}$	2
<p>17(b) Ans</p>	<p>The value of equilibrium constant for a reaction is 1.06×10^{-5} at 298 K. Calculate the standard free energy change for the reaction at 298 K. $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$.</p> <p>Given that $K_p = 1.06 \times 10^{-5}$, $T = 298\text{K}$, $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$</p> $\Delta G^0 = -2.303RT \log K_p$ $= -2.303 \times 8.314 \times 298 \log 1.06 \times 10^{-5}$ $= -28673.6\text{J}$	2
<p>18(a) Ans</p>	<p>Derive Langmuir Adsorption isotherm.</p> <p>Langmuir Equation depicts a relationship between the number of active sites of the surface undergoing adsorption (i.e. extent of adsorption) and pressure.</p> <p>If P be the pressure of the gas and θ is the surface coverage i.e. the fraction of the surface covered by the gas molecules. Then,</p> <p>(1 - θ) is the fraction of the total number of sites vacant and available for adsorption.</p> <p>∴ Rate of adsorption $\propto (1 - \theta) \times P$ i.e. $R_a = K_a (1 - \theta) P$ -----(1)</p> <p>Where K_a is proportionality constant called adsorption constant</p> <p>And rate of desorption $\propto \theta$ i.e. $R_d = K_d (\theta)$ -----(2) for desorption</p> <p>From the assumption, at equilibrium $R_a = R_d$,</p> <p>Equating equation 1 and 2, we get</p> $K_a (1 - \theta) P = K_d \theta$ $K_d \theta = K_a P - K_a P \theta$ $(K_d + K_a P) \theta = K_a P$ $\theta = \frac{K_a P}{K_d + K_a P} \quad \text{Divide this equation by } K_d$ $\theta = \frac{\frac{K_a P}{K_d}}{\frac{K_d}{K_d} + \frac{K_a P}{K_d}}$	4

	$\theta = \frac{bP}{1 + bP}$ <p>This equation is called Langmuir adsorption of isotherm</p> <p>Where $b = \frac{K_a}{K_d}$ is called langumuir's constant or adsorption co-efficient</p>											
18(b) Ans	<p>What is heterogeneous catalysis? Give an example.</p> <p>In heterogeneous catalysis, the reactants and the catalysis are in different phases.</p> <p>Examples:</p> $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \xrightarrow{\text{Pt}(\text{s})} \text{C}_2\text{H}_6(\text{g})$ $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \xrightarrow{\text{Fe}(\text{s})/\text{Mo}(\text{s})} 2\text{NH}_3(\text{g})$ $\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \xrightarrow{\text{V}_2\text{O}_5(\text{s})} 2\text{SO}_3(\text{g})$	2										
19(a) Ans	<p>Describe the extraction of nickel metal from sulphide ore.</p> <p>Pentlandite is the sulphide ore of Ni,Cu and Fe.</p> <p>Nickel is extracted from pentlandite as follows:</p> <p>i) Concentration of the ore: By froth flotation process, the heavier gangue particles are removed.</p> <p>ii) Roasting: The concentrated ore is roasted in a current of air when iron sulphide is converted into itsoxide but sulphides of nickel and copper are not affected.</p> <p>iii) Smelting: The roasted ore is mixed with coke and quartz and smelted in a blast furnace. Most of the iron is removed as iron silicate as slag. The heavier lower layer contains sulphides of Ni, Cu with alittle of Co and Fe. This is called matte.</p> <p>iv) Bessemerization: The matte is heated in a Bessemer converter where the matte is heated in a blast of air, any un-oxidized FeS is converted into Fe which forms a slag with SiO₂. $\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3$</p> <p>The molten slag is skimmed off. The bessemerized matte contains 56% Ni.</p> <p>The bessemerized matte is roasted to get Nickel oxide.</p> <p>v) Reduction: NiO is separated and reduced by passing a current of water gas(CO+H₂)</p> $2\text{NiO} + (\text{H}_2 + \text{CO}) \rightarrow 2\text{Ni} + \text{H}_2\text{O} + \text{CO}_2.$ <p>The crude nickel is further refined by Mond's process.</p>	4										
19(b) Ans	<p>Write two differences between organic and inorganic polymers.</p> <table border="1"> <thead> <tr> <th>Organic Polymers</th> <th>Inorganic Polymers</th> </tr> </thead> <tbody> <tr> <td>1)They have C-C linkage in their backbone-generally homopolymer net work</td> <td>1. They are having generally hetero type that is metal as the back bone-heteropolymer network.</td> </tr> <tr> <td>2)They are having high degree of Polymerization.</td> <td>2)They are having low degree of Polymerization.</td> </tr> <tr> <td>3) These are three dimensional polymer may lose their structure on heating.</td> <td>3) They exit in highly stable Crystalline form & maintain regularity even on heating.</td> </tr> <tr> <td>4) They are less resistant to acid, Alkalies</td> <td>4) They are comparatively more Stable & other organic solvents.</td> </tr> </tbody> </table>	Organic Polymers	Inorganic Polymers	1)They have C-C linkage in their backbone-generally homopolymer net work	1. They are having generally hetero type that is metal as the back bone-heteropolymer network.	2)They are having high degree of Polymerization.	2)They are having low degree of Polymerization.	3) These are three dimensional polymer may lose their structure on heating.	3) They exit in highly stable Crystalline form & maintain regularity even on heating.	4) They are less resistant to acid, Alkalies	4) They are comparatively more Stable & other organic solvents.	2
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20(a) Ans	<p>What are Ellingham's diagrams? Give two applications.</p> <p>The series of curves obtained by plotting change in standard free energy against temperature for the formation of oxides of elements called Ellingham diagram</p> <p>It is used in</p> <p>a) selection of suitable reducing agent for the reduction of metal oxide in metallurgical operations, and for the</p> <p>b) Selection of optimum temperature for the effective reduction of the metal oxide</p>											
20(b)	Aluminium is used as reducing agent for reduction of chromium oxide. Give											

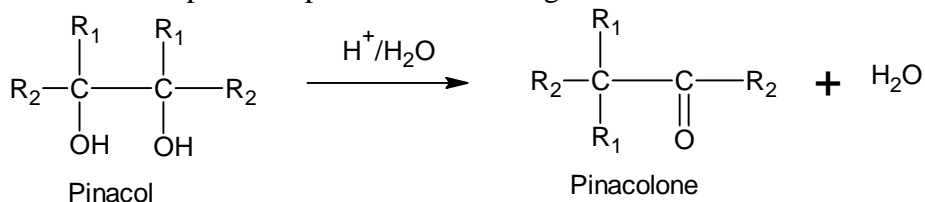
Ans	reasons? Aluminium can reduce chromic oxide. This is because free energy of formation of Al_2O_3 is more negative than that of Cr_2O_3 , therefore Al_2O_3 is a stable oxide than Cr_2O_3 . The plot of Al lies below Cr in the Ellingham diagram, indicating that Al can act as a good reducing agent for Chromic oxide.	
21(a) Ans	Explain the classification of monohydric alcohols with an example. Based on the hydroxyl group attached to the different types of carbon atom, monohydric alcohols are classified into following types <ol style="list-style-type: none"> Primary (1^0) alcohols: Those monohydric alcohols in which hydroxyl group attached to the primary carbon atom (carbon atom attached to one alkyl group, two hydrogen atoms and one hydroxyl group or three hydrogen atoms and one hydroxyl group) called primary (1^0) alcohol. Example: $\text{CH}_3\text{-OH}$, $\text{C}_2\text{H}_5\text{-OH}$ Secondary (2^0) alcohols: Those monohydric alcohols in which hydroxyl group attached to the secondary carbon atom (carbon atom attached to two alkyl groups, one hydrogen atom and one hydroxyl group) called secondary (2^0) alcohol. Example: $(\text{CH}_3)_2\text{CH-OH}$, $(\text{CH}_3\text{CH}_2)_2\text{CH-OH}$ Tertiary (3^0) alcohols: Those monohydric alcohols in which hydroxyl group attached to the tertiary carbon atom (carbon atom attached to three alkyl groups and one hydroxyl group) called tertiary (3^0) alcohol. Example: $(\text{CH}_3)_3\text{C-OH}$, $(\text{CH}_3\text{CH}_2)_3\text{C-OH}$ 	2 2
21(b) Ans	How does periodic acid react with methane thiol? Give equation. Methane thiol undergo oxidation using strong oxidizing agent like periodic acid to form methane sulphonic acid. $\text{H}_3\text{C-SH} + 3[\text{O}] \xrightarrow{\text{HIO}_4} \text{CH}_3\text{SO}_3\text{H}$ <p style="text-align: center;">Methane thiol Methane sulphonic acid</p>	2
22(a) Ans.	What is Lucas reagent? How it is used to distinguish between 1^0, 2^0 and 3^0 alcohols? Give equations. A solution of anhydrous zinc chloride and concentrated hydrochloric acid is called Lucas reagent. It is used to distinguish between 1^0 , 2^0 and 3^0 alcohols <ol style="list-style-type: none"> Primary 1^0 alcohol: When alcohol is treated with Lucas reagent no cloudiness is form at room temperature. This indicates the given alcohol is primary alcohol. $\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \end{array} + \text{HCl} \xrightarrow[\text{Room Temp}]{\text{Anhy. ZnCl}_2} \text{No reaction} \\ \text{1}^0 \text{ alcohol} \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \text{(No cloudiness)}$ Secondary 2^0 alcohol: When alcohol is treated with Lucas reagent cloudiness is form in 5 - 10 minutes at room temperature. This indicates the given alcohol is secondary alcohol. $\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{R}_1 \end{array} + \text{HCl} \xrightarrow[\text{Room Temp}]{\text{Anhy. ZnCl}_2} \begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{Cl} \\ \\ \text{R}_1 \end{array} + \text{H}_2\text{O}$ <p style="text-align: center;">2^0 alcohol 2^0 Alkyl halide (Cloudiness form in 5 -10 minutes)</p> Tertiary 3^0 alcohol: When alcohol is treated with Lucas reagent cloudiness is form immediately room temperature. This indicates the given alcohol is tertiary alcohol. 	1 1 1 1



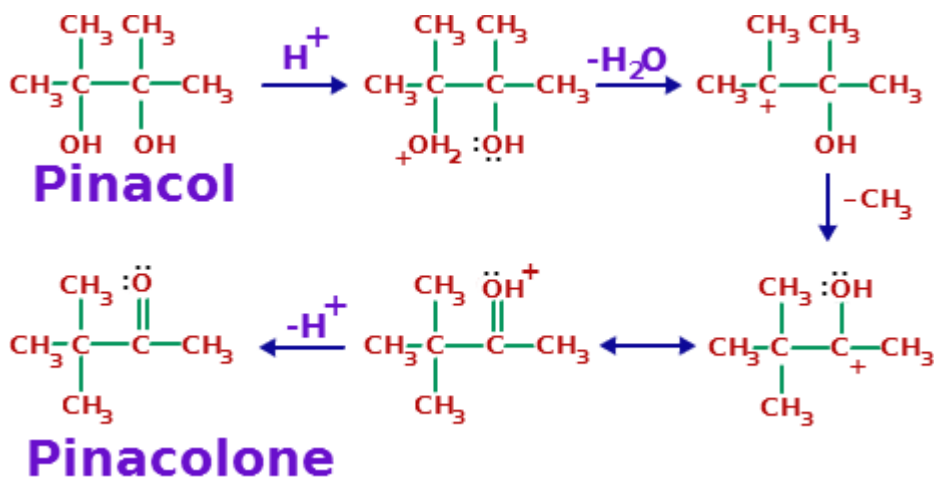
22(b)
Ans

Explain Pinacol - pinacolone rearrangement with an example.

When vicinol diol undergo rearrangement in presence acid hydrolyzed catalyst to form ketone called pinacol –pinacolone rearrangement.



Example.

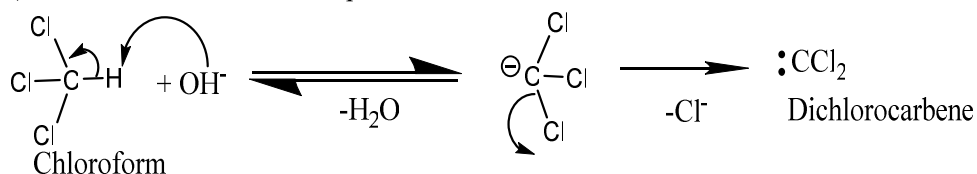


23(a)

Explain the mechanism of Reimer-Tiemann reaction.

Mechanism of Reimer - Tiemann reaction involved following steps

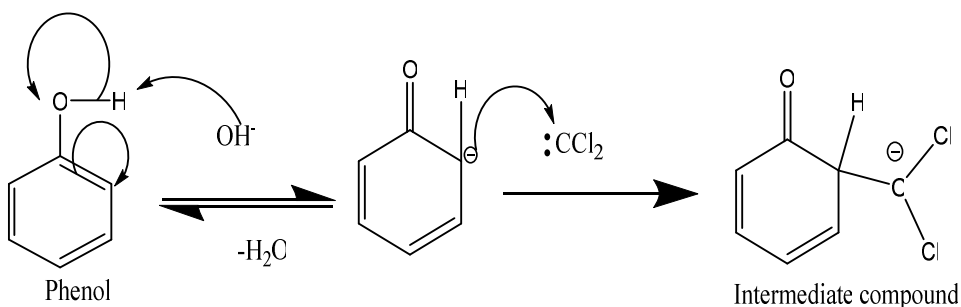
a) Formation of neutral electrophile:



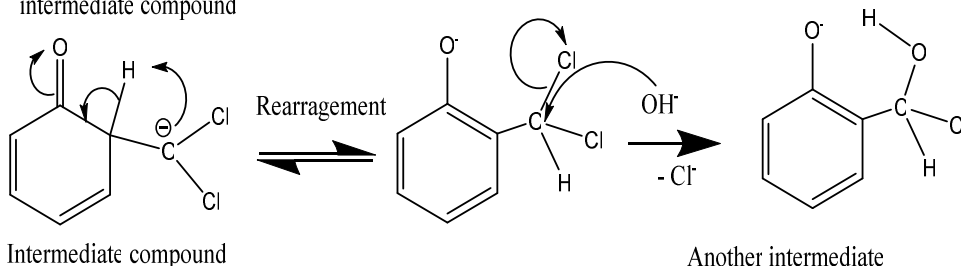
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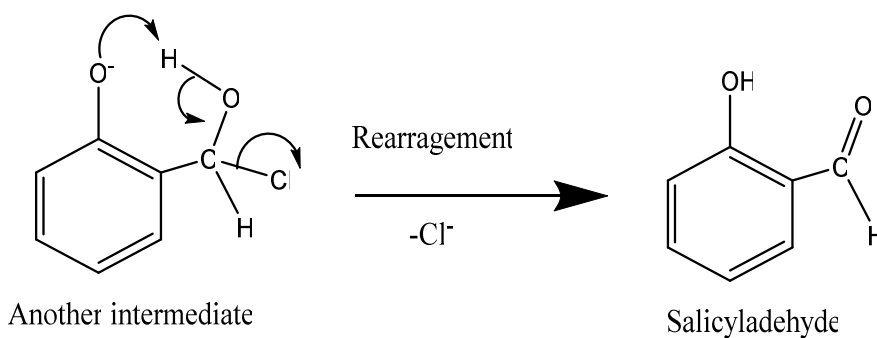
b) Attack of electrophile on ortho position phenol and to form intermediate product



c) Intermediate compound undergoes rearrangement and followed by addition of base to form another intermediate compound

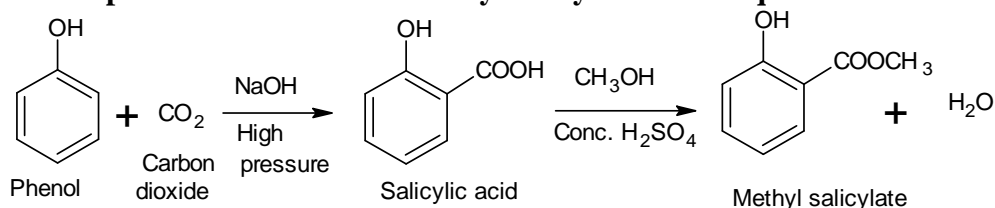


d) Finally another intermediate undergoes rearrangement to form salicylaldehyde



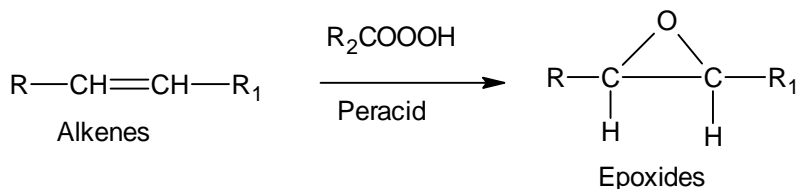
23(b) **How is phenol converted into methyl salicylate? Give equation.**

Ans



24(a) **What are epoxides? How they are prepared from peracids?**

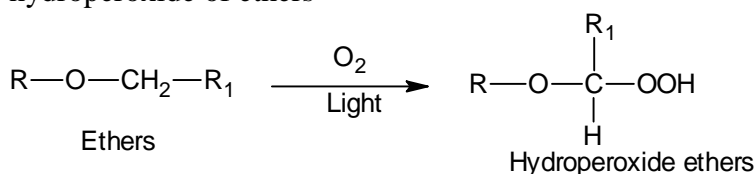
Epoxides are the three membered heterocyclic compound containing oxygen as heteroatom.



24(b) **Explain auto-oxidation reaction in ethers.**

Ans

Ethers undergo self oxidation when contact with air, oxygen or light to form hydroperoxide of ethers



<p>25(a) Ans</p>	<p>Explain the manufacture of urea. Mention its uses.</p> <p>Manufacture of urea involved following steps</p> <p>Step 1: Crude naphtha obtained from oil refineries is subjected to partial combustion in specially designed burners to get a mixture of H₂ and CO.</p> <p>Step 2: This mixture is made to react with steam in presence of Fe, Cr, Co catalyst.</p> $\text{H}_2 + \text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$ <p style="margin-left: 20px;"> H₂ + CO + H₂O </p> <p>Water gas</p> <p>Step 3: CO₂ is separated from H₂ by washing with water under pressure or by treatment with KHCO₃.</p> <p>Step 4: H₂ is separated from mixture is mixed with Nitrogen and passed over heated Fe₂O₃ with Cr₂O₃ as promoter at 450– 500° C, and 200 atm. Pressure, Ammonia thus formed is mixed with gaseous CO₂, at 200atm pressure when unstable Ammonium carbamate is formed. This Ammonium carbamate further decomposes to produce Urea.</p> $2\text{NH}_3 + \text{CO}_2 \longrightarrow \text{NH}_2\text{COONH}_4 \xrightarrow{\Delta} \text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 + \text{H}_2\text{O}$ <p>It is used as nitrogenous fertilizer</p>	<p>1</p> <p>1</p> <p>1</p> <p>1</p>
<p>25(b) Ans</p>	<p>Name any two fertilizer industries in India.</p> <ol style="list-style-type: none"> 1) National fertilizers Ltd. New Delhi. 2) Chambal fertilizers & chemicals Ltd (KK Birla) Rajasthan. 3) Rashtriya chemicals & fertilizers Ltd. Mumbai 4) Zuari Agro chemicals Ltd, Goa 5) Gujarat Narmada Valley fertilizers & chemicals Ltd. Gujarat. 6) Deepak fertilizers & petrochemicals corporation Ltd. Pune , Maharashtra. 7) Nagarjuna fertilizers and chemicals Ltd. Kakinada, Andhra Pradesh. 8) Mangalore chemicals & Fertilizers Ltd. Karnataka. 	<p>2</p>

Scheme Prepared by Shivappa Jugale, Associate Professor, Department of Chemistry
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