(iv) **Examples of Chain Reactions.** 1. *Thermal Reaction between Hydrogen* Bromine. Linde and Bodenstein (1906) established the following rate for this reaction :

$$\frac{d\,[HBr]}{dt} = \frac{k\,[H_2]\,[Br_2]^{1/2}}{1 + m\,[HBr]\,/\,[Br_2]}$$

where k and m are constants.

Polanyi, Herzfeld and Christiansen (1920) suggested the following mechanism :

1. *Chain initiation :* $\qquad Br_2 \xrightarrow{k_1} 2Br \quad$ (slow)

2. *Chain propagation :* $Br + H_2 \xrightarrow{k_2} HBr + H \quad$ (slow)

$$H + Br_2 \xrightarrow{k_3} HBr + Br \quad \text{(fast)}$$

3. *Chain inhibition :* $\quad H + HBr \xrightarrow{k_4} H_2 + Br$

4. *Chain termination :* $Br + Br \xrightarrow{k_5} Br_2$
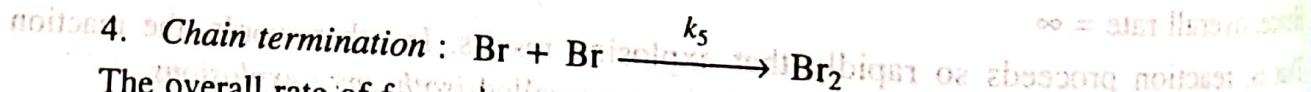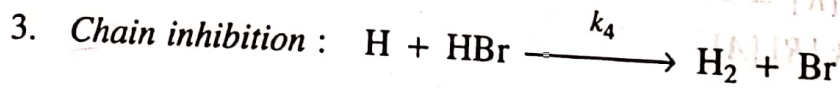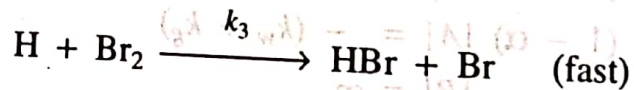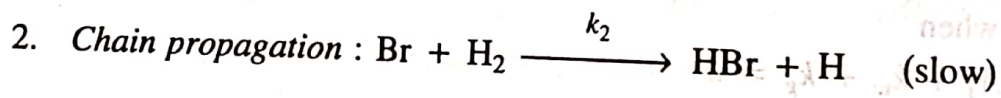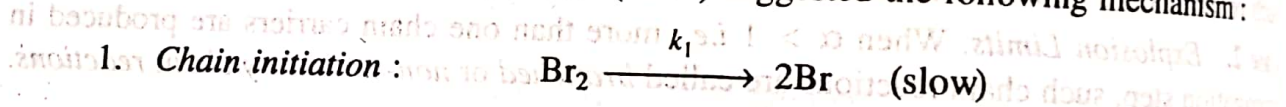
The overall rate of formation of HBr is

$$\frac{d\,[HBr]}{dt} = k_2\,[Br]\,[H_2] + k_3\,[H]\,[Br_2] - k_4\,[H]\,[HBr]$$

The Br-atoms and H-atoms are the active short-lived intermediate and must have concentrations. Hence steady-state concept can be applied in these intermediates and we have

$$\frac{d\,[Br]}{dt} = k_1\,[Br_2] - k_2\,[Br]\,[H_2] + k_3\,[H][Br_2] + k_4\,[H]\,[HBr] - k_5\,[Br]^2 = 0$$

$$\frac{d\,[H]}{dt} = k_2\,[Br]\,[H_2] - k_3\,[H]\,[Br_2] - k_4\,[H]\,[HBr] = 0$$

From equations (2) and (3), we get

$$k_1 [Br_2] - k_5 [Br]^2 = 0 \quad \text{or} \quad [Br] = \left(\frac{k_1}{k_5} [Br_2]\right)^{1/2} \qquad \text{... (4)}$$

From equation (3), we have

$$[H] = \frac{k_2 [Br] [H_2]}{k_3 [Br_2] + k_4 [HBr]} \qquad \text{... (5)}$$

Putting value of [Br] from (4) in (5), we get,

$$[H] = \frac{k_2 \cdot (k_1/k_5)^{1/2} \cdot [H_2] [Br_2]^{1/2}}{k_3 [Br_2] + k_4 [HBr]} \qquad \text{... (6)}$$

From (3), we have

$$k_2 [Br] [H_2] - k_3 [H] [Br_2] = k_4 [H] [HBr] \qquad \text{... (7)}$$

From (1) and (7), we get

$$\frac{d [HBr]}{dt} = 2k_3 [H] [Br_2] \qquad \text{... (8)}$$

Putting value of [H] from (6) in (8),

$$\frac{d [HBr]}{dt} = \frac{2k_3 k_2 (k_1/k_5)^{1/2} [H_2] [Br_2]^{3/2}}{k_3 [Br_2] + k_4 [HBr]}$$

$$= \frac{2k_3 k_2 (k_1/k_5)^{1/2} [H_2] [Br_2]^{3/2}}{k_3 [Br_2] \left(1 + \dfrac{k_4 [HBr]}{k_3 [Br_2]}\right)}$$

$$= \frac{2k_2 (k_1/k_5)^{1/2} [H_2] [Br_2]^{1/2}}{1 + \dfrac{k_4}{k_3} ([HBr] / [Br_2])} \qquad \text{... (9)}$$

The equation (9) is identical to that obtained by Linde and Bodenstein.

Discussion of equation (9). (a) In equation (9), since [HBr] term is present in denominator, increase in concentration of HBr will decrease overall rate of reaction. This is an example of inhibition.
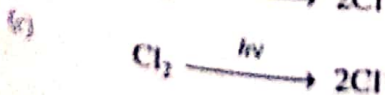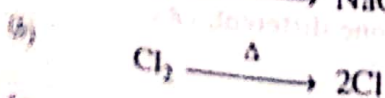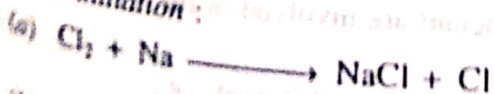
(b) In the beginning of reaction, *i.e.,* when $t = 0$;

$$[HBr] = 0$$

Then the equation (9) becomes

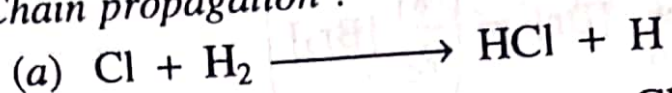$$\frac{d [HBr]}{dt} = 2k_2 (k_1/k_5)^{1/2} [H_2] [Br_2]^{1/2}$$

This equation gives order 1.5. Hence we can say that in the initial stages of reaction, the overall order of reaction is 1.5.

2. Reaction between Chlorine and Hydrogen. This reaction is initiated by chlorine atoms obtained by photo dissociation or thermal dissociation or from the reaction between chlorine gas and the atomic sodium introduced in the reaction mixture. The probable mechanism is as follows :
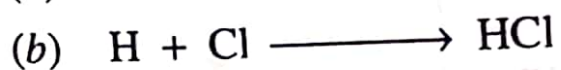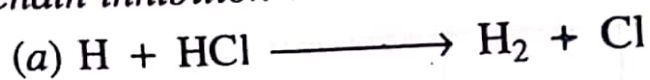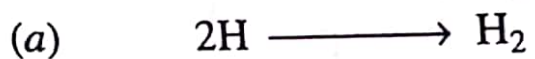
(i) Chain initiation :

(a) $Cl_2 + Na \longrightarrow NaCl + Cl$

(b) $Cl_2 \xrightarrow{\Delta} 2Cl$

(c) $Cl_2 \xrightarrow{h\nu} 2Cl$

(ii) *Chain propagation :*

    (a) $Cl + H_2 \longrightarrow HCl + H$

    (b) $H + Cl_2 \longrightarrow HCl + Cl$

(iii) *Chain inhibition :*

    (a) $H + HCl \longrightarrow H_2 + Cl$

    (b) $H + Cl \longrightarrow HCl$

(iv) *Chain Termination :*

    (a) $2H \longrightarrow H_2$

    (b) $2Cl \longrightarrow Cl_2$

3.   *Formation of phosgene.*   The overall reaction is