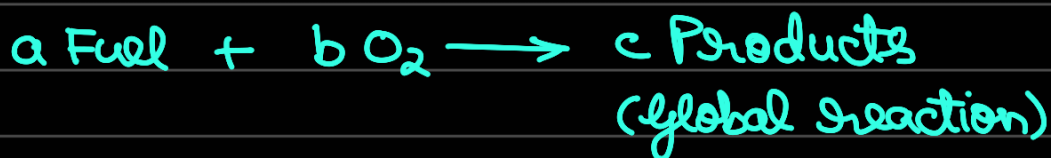


Day-13

→ Pressure dependence of rate of reaction -



$$\begin{aligned}\text{Rate of reaction} &= A_0 \exp\left(\frac{-E_A}{R_u T}\right) [\text{Fuel}]^n [\text{O}_2]^m \\ &= A_0 \exp\left(\frac{-E_A}{R_u T}\right) \left(\frac{\chi_{\text{fuel}} P_T}{R_u T}\right)^n \left(\frac{\chi_{\text{O}_2} P_T}{R_u T}\right)^m\end{aligned}$$

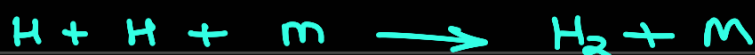
[Using $PV = NR_u T$

$$\Rightarrow \frac{N}{V} = \frac{P}{R_u T}$$

$$\text{so } [\text{Fuel}] = \frac{P_{\text{fuel}}}{R_u T} = \frac{\chi_{\text{fuel}} P_{\text{Total}}}{R_u T}$$

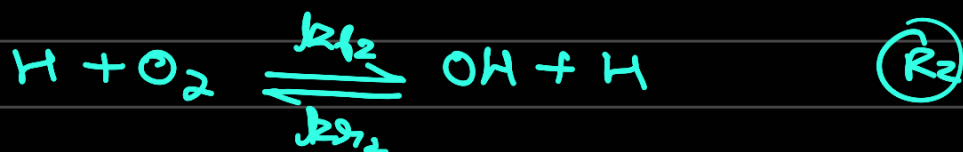
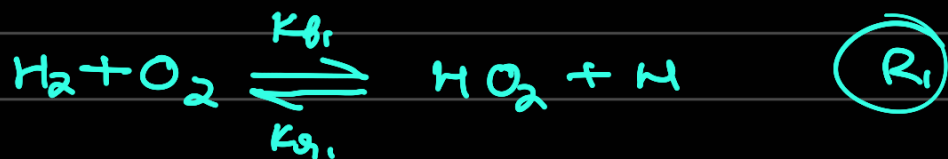
$$= A_0 \exp\left(\frac{-E_A}{R_u T}\right) \chi_{\text{fuel}}^n \chi_{\text{O}_2}^m \left(\frac{P_{\text{Total}}}{R_u T}\right)^{n+m}$$

→ Trimolecular reaction -



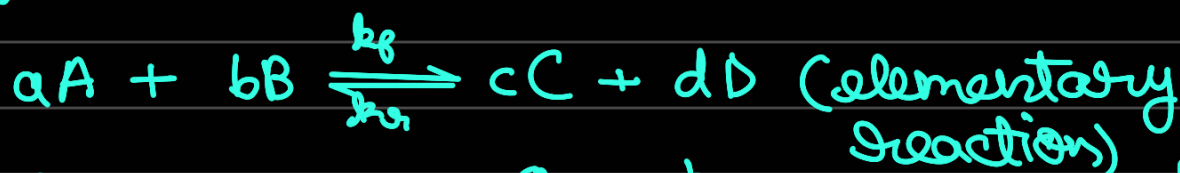
↓
Solid catalyst not
considered in molecularity
of reacⁿ, since its
molecules actually don't
collide.

→ multi-step:



$$\frac{d[\text{O}_2]}{dt} = -k_{f1}[\text{H}_2][\text{O}_2] + k_{r1}[\text{HO}_2][\text{H}] - k_{f2}[\text{H}][\text{O}_2] + k_{r2}[\text{OH}][\text{H}]$$

general:



$$\frac{1}{a} \frac{d[\text{A}]}{dt} = -k_f [\text{A}]^a [\text{B}]^b + k_{r1} [\text{C}]^c [\text{D}]^d$$

$$\text{At equilibrium, } \frac{d[\text{A}]}{dt} = 0$$

$$\Rightarrow k_f [\text{A}]^a [\text{B}]^b = k_{r1} [\text{C}]^c [\text{D}]^d$$

$$\Rightarrow \frac{k_f}{k_{r1}} = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} = K_c$$

↓
Equilibrium constant
based on concⁿ

$$K_p = \frac{(P_c/P_0)^c (P_d/P_0)^d}{(P_a/P_0)^a (P_b/P_0)^b}$$

$$= \frac{\left(\frac{[\text{C}]R_v T}{P_0}\right)^c \left(\frac{[\text{D}]R_v T}{P_0}\right)^d}{\left(\frac{[\text{A}]R_v T}{P_0}\right)^a \left(\frac{[\text{B}]R_v T}{P_0}\right)^b}$$

$$\Rightarrow K_p = K_c \left(\frac{R_u T}{P_0} \right)^{c+d-(a+b)}$$

$$= \frac{K_f}{K_r} \left(\frac{R_u T}{P_0} \right)^{\Delta n_g}$$



$$k_f = 3.8 \times 10^9 T \exp. \left(\frac{-20820}{T} \right) \text{ cm}^3/\text{mol-s}$$

$$T = 2300 \text{ K, find } k_r.$$

$$\text{Ans:} \rightarrow K_c = K_p$$

$$\Rightarrow k_r = \frac{K_f}{K_p}$$

$$K_p = \exp. \left(\frac{61243 + 101627 - 326331 - 0}{8.314 \times 2300} \right)$$

$$= 1.94 \times 10^{-4}$$

$$k_f = 3.8 \times 10^9 \times 2300 \exp. \left(\frac{-20820}{2300} \right)$$

$$= 1.024 \times 10^9$$

$$\text{So } k_r = \frac{1.024 \times 10^9}{1.94 \times 10^{-4}}$$

$$= 0.5278 \times 10^{13}$$

$$= 5.278 \times 10^{12} \text{ cm}^3/\text{mol-s}$$