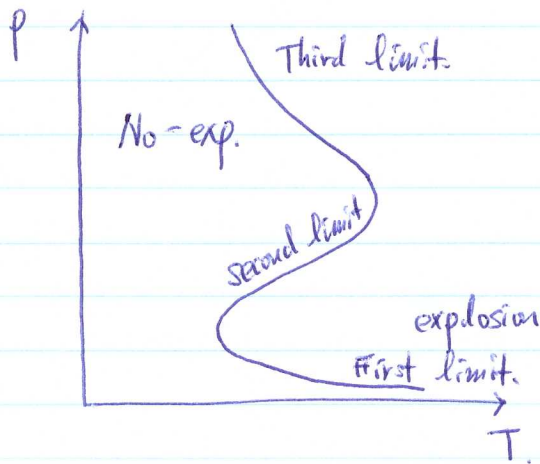


<Chemical Kinetics IV>

1



Recall $\beta \equiv 1 + \frac{[A][M] + k_w/k_t}{k_b[A]/k_t} = \alpha$

- First limit. low pressure $\Rightarrow [M] \ll 1$.

$$\therefore \beta \approx 1 + k_w/(k_b[A])$$

\Rightarrow competition between wall recombination rxn & branching rxns.

- Second limit. moderate pressure

$$\beta \approx 1 + k_t[M]/k_b$$

\Rightarrow competition between gas phase termination and branching rxns.

- Third limit does not exist for all fuels.

H_2/O_2 systems have third limit governed by chemical kinetics.

* Explosions are characterized by time delays before the onset of combustion. (induction period)

\Rightarrow ignore initiation/termination rxns.

$$\frac{d[R]}{dt} = (\alpha - 1)k_b[R][A] \Rightarrow \text{exponential growth of } [R]$$

$$\frac{t_{\text{induction}}}{\tau} = \ln \frac{[R]_{\text{crit.}}}{[R]_{\tau}}$$

$$\tau = \frac{1}{(\alpha - 1)k_{\text{total}}} \quad (\text{recall } \alpha > 1)$$

during the induction time period

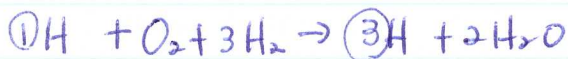
2



Termination rxns are insignificant,

$\therefore [R]$ is small

(less than 10% H_2 consumed)



$$n-1=2$$

\Rightarrow explosive branching, but temp. rise is not significant.
 \therefore termination rxns are exothermic.

At higher pressure. HO_2 radical explains the drastic shift in mechanism.

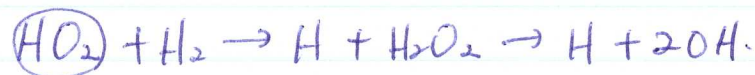


\rightarrow at low temperature, $\textcircled{1}$ rxn dominates

while as the temp. increases $\textcircled{2}$ becomes the dominant rxn.

$\therefore HO_2$ is stable radical

\rightarrow in the second limit. $\textcircled{1}$ is termination rxn, however HO_2 radical leads to production of chain carriers.



$\textcircled{2}$ CO oxidation.

\rightarrow CO is generated during the oxidation of any hydrocarbons.

\therefore CO oxidation is a part of hydrocarbon combustion mechanism.

\Rightarrow "wet" (including hydrogen) mechanism.

* high-temperature sequence



* low-temperature high pressure

dominant CO oxidation channel



P.E. assumption for CO-H₂-O₂ reaction



P.E. for (1)-(3)

\Rightarrow Equilibrium constant K_1, K_2, K_3 .

$$K_1 = \frac{[\text{H}_2\text{O}][\text{H}]}{[\text{OH}][\text{H}_2]}, \quad K_2 = \frac{[\text{OH}][\text{O}]}{[\text{H}][\text{O}_2]}, \quad K_3 = \frac{[\text{OH}][\text{H}]}{[\text{O}][\text{H}_2]}$$

\Rightarrow useful to eliminate radical concentrations.

$$\text{eg. } -\frac{d[\text{CO}]}{dt} = k_f [\text{OH}][\text{CO}]$$

$$K_2 \cdot K_3 = \frac{[\text{OH}]^2}{[\text{O}_2][\text{H}_2]} \Rightarrow [\text{OH}] = (K_2 K_3)^{1/2} [\text{O}_2]^{1/2} [\text{H}_2]^{1/2}$$

$$\therefore -\frac{d[\text{CO}]}{dt} = k_f [\text{CO}] \left(K_2 K_3 [\text{O}_2][\text{H}_2] \right)^{1/2}$$

\Rightarrow In practice, H₂ is minor species in many combustion systems.

assume another P.E. for



$$K_5 \equiv \frac{[O_2]}{[O]^2} \Rightarrow [O] = ([O_2]/K_5)^{1/2}$$

$$\frac{K_1}{K_2} = \frac{[H_2][O_2]}{[H_2O][O]}$$

$$[H_2] = \left(\frac{K_1}{K_2}\right) \frac{[H_2O]}{([O_2]K_5)^{1/2}}$$

$$-\frac{d[CO]}{dt} = k_f (K_2 K_3)^{1/2} [CO][O_2]^{1/2} \left(\frac{K_1}{K_2}\right)^{1/2} \frac{[H_2O]^{1/2}}{([O_2]K_5)^{1/4}}$$

$$= \boxed{k_{emp} [CO][H_2O]^{1/2} [O_2]^{1/4}}$$

$$k_{emp} = k_f \left(\frac{K_1 K_3}{K_5^{1/2}}\right)^{1/2}$$

$\Rightarrow \frac{d[A_c]}{dt}$ estimation. using concentrations of stable species.

(Use Q.S.S. and/or P.E. assumptions
to eliminate radical concentrations which are
typically hard to measure.)