Module 4: Chemistry of combustion
Lecture 20: Order reaction

The Lecture Contains:

- First Order Reaction
- Second Order Reaction
- Third Order Reaction
- Reverse Reaction
- Chain Reaction

First order reaction,
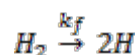
Consider the first order reaction,

$$H_2 \overset{k_f}{\rightarrow} 2H$$

Reaction rate,

$$-\frac{dC_{H_2}}{dt} = k_f C_{H_2} = \frac{1}{2}\frac{dC_H}{dt}$$
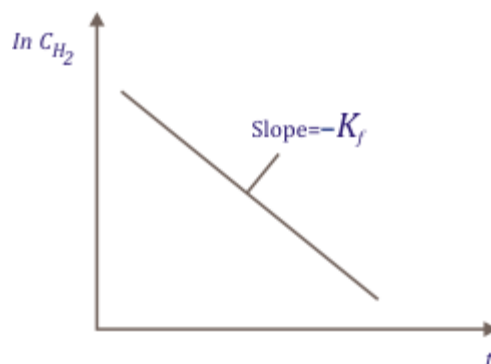
Sepatating the variables and integrating,

$$-ln\, C_{H_2}\Big|_0^t = k_f(t-0)$$

$$-ln\left(\frac{C_{H_2,0}}{C_{H_2,t}}\right) = k_f t$$

(**Figure 20.1**)

First order combustion reactions!

$$O_2 \rightarrow 2O$$

$$H_2O \rightarrow 2NO_2 + \frac{1}{2}O_2$$
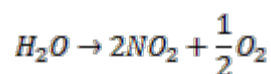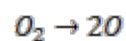
Note : H_2 concentration decreases exponentially with time (Refer Fig),

All unimolecular reactions obey first order kinetics!

All first order reactions need not to be unimolecular!!

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Second Order Reaction

Consider the second order bimolecular reaction,

$$H_2 + I_2 \xrightarrow{k_f} 2HI$$
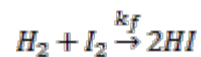
Reaction rate for the above reaction,

$$\frac{dC_{N_2}}{dt} = -k_f C_{H_2} C_{I_2}$$

General second order reaction

$$A + B \xrightarrow{k_f} C + D$$
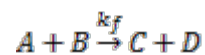
Concentration of species A and B

$$C_A = C_{A,}in - C_X \qquad C_B = C_{B,}in - C_X$$

Reaction rate for the above reaction,

$$-\frac{dC_X}{dt} = k_f\left(C_{A,in} - C_X\right)\left(C_{B,in} - C_X\right)$$

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Multiplying both sides by $\left(C_{B,in} - C_{A,in}\right)$

$$-\frac{\left(C_{B,in} - C_{A,in}\right)dC_X}{\left(C_{A,in} - C_X\right)\left(C_{B,in} - C_X\right)} = k_f\left(C_{B,in} - C_{A,in}\right)dt$$

Integrating,

$$-\int\left(\frac{1}{\left(C_{A,in} - C_X\right)} - \frac{1}{\left(C_{B,in} - C_X\right)}\right)dC_X = \int k_f\left(C_{B,in} - C_{A,in}\right)dt$$

Second order combustion reactions!

$$ln\left(\frac{\left(C_{B,in} - C_X\right)}{\left(C_{A,in} - C_X\right)}\right) = k_f\left(C_{B,in} - C_{A,in}\right)t + const$$

By applying $l.c,$ we will get

$$k_f = \frac{1}{\left(C_{A,in} - C_{B,in}\right)t}ln\left(\frac{C_{B,in}\left(C_{A,in} - C_X\right)}{C_{A,in}\left(C_{B,in} - C_X\right)}\right)$$

$$OH + H_2 \rightarrow H_2O + H$$
$$CO + O_3 \rightarrow CO_2 + 2O$$
$$O + H_2 \rightarrow OH + H$$
$$H + O_2 \rightarrow OH + O$$
$$OH + CH_4 \rightarrow H_2O + CH_3$$
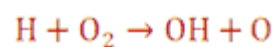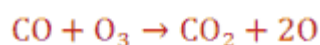
Third Order Reaction

Consider the third order, trimolecular reaction,

$$2NO + O_2 \xrightarrow{k_f} 2NO_2$$

$$-\frac{dC_{NO_2}}{dt} = k_f C_{NO}^2 C_{O_2}$$
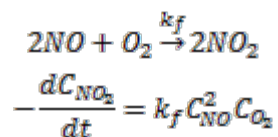
RR proportional to third power of concentration of participating species,

Third order combustion reactions !

$$H_2 + M \rightarrow H + H + M$$

$$HO + OM \rightarrow OH_2 + M$$

$$H + H + H \rightarrow H_2 + H$$

$$2NO + O_2 \rightarrow 2NO_2$$
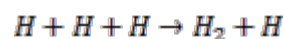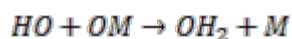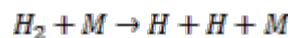
Reverse Reaction

Chemical reactions may proceed in both forward and reverse directions.
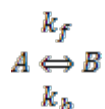
$$A \underset{k_b}{\overset{k_f}{\Longleftrightarrow}} B$$

Net rate of consumption of A,

$$-\frac{dC_A}{dt} = k_f C_A - k_b (C_{A,in} - C_A)$$

$$k_b = k_f C_{A,eq} / (C_{A,in} - C_{A,eq})$$

Substituting k_b in the above equation, we will get

$$-\frac{dC_A}{dt} = k_f C_{A,in} \left(\frac{C_A - C_{A,eq}}{C_{A,in} - C_{A,eq}} \right)$$

By integreting the above equation, we can get

$$\ln \left(\frac{C_A - C_{A,eq}}{C_{A,in} - C_{A,eq}} \right) = \left(\frac{k_f C_{A,in}}{C_{A,in} - C_{A,eq}} \right) t$$

k_f can be estimated from the knowledge of C_A

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Chain Reaction

In reality, combustion process involves several reactions
The overall stoichiometric chemical reaction is unlikely to occur in nature. The elementary reactions can be classified as;

- Chain initiating
- Chain branching
- Chain carrying
- Chain terminating

Chain branching

The ratio of number of free radicals in the product to the reactant > 1

Chain carrying

The ratio of number of free radicals in the product to the reactant = 1

Chain terminating

The ratio of number of free radicals in the product to the reactant < 1

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