Module 4: Chemistry of combustion

Lecture 19: Law of Mass Action

The Lecture Contains:

- Law of Mass Action
- Collision Theory
- Elementary Reactions

Law of Mass Action

The rate of reaction, *RR* of a chemical species is proportional to the product of the concentrations of the participating chemical species, where each concentration is raised to the power equal to the corresponding stoichiometric coefficient in the chemical reaction.

$$RR_i \propto \prod_{i=1}^{N} C_{M_i}^{v_i}$$

$$RR_i = k \prod_{i=1}^{N} C_{M_i}^{v_i}$$

Where, k is the specific reaction rate or rate coefficient

Note :

k-depends on temperature and activation energy and not on concentration. Law of mass action holds good only for elementary reactions

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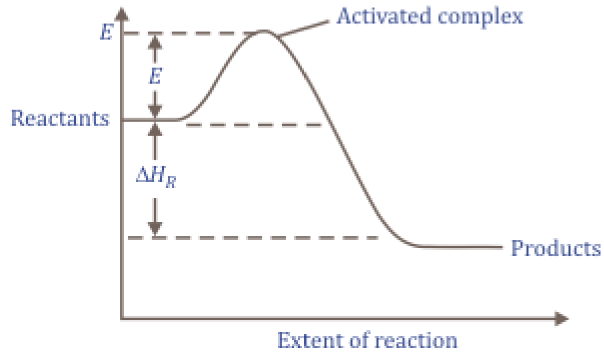
Collision Theory



(Figure 19.1)

The colliding molecules must possess higher energy than the mean energy

Boltzman's energy distribution law:

The probability of a molecule possessing the threshold energy, E is proportional to exp $(-E/R_u T)$

Conditions for chemical reactions to occur:

- Suitable molecule must collide with each other
- The molecules must collide with proper orientation (Determined by steric factor)
- Colliding molecules must possess energy greater than the threshold energy(E).

From collision theory,

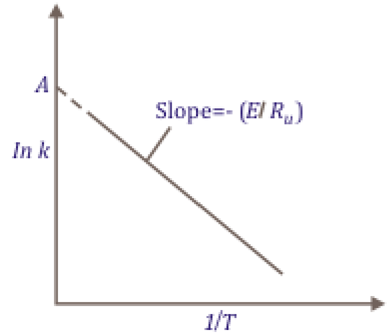
$$RR = Z_{AB} S\, e^{(-E/R_u T)}$$

Z_{AB} - Collision frequency,

S - Steric factor,

$e^{(-E/R_u T)}$ - Boltaman's energy probability factor

E - Activation energy



(Figure 19.2)

From kinetic theory,

$$Z_{AB} = C_A C_B \sigma_{AB}^2 [8\pi k_B T/\mu]^{0.5}$$

σ_{AB} - Average effective collision diameter between molecules A and B,

k_B - Boltaman's constant = 1.381 X 10^{-23} J/K

M_R - Reduced mass $[m_A m_b/(m_A + m_b)]$

Reaction rate

$$RR = C_A C_B \sigma_{AB}^2 [8\pi k_B T/M_R]^{0.5}\, S\, e^{(-E/R_u T)} = BT^{0.5} C_A C_B\, e^{(-E/R_u T)}$$

$k = BT^{0.5}\, e^{(-E/R_u T)} = A e^{(-E/R_u T)}$ $\quad A = BT^{0.5}$ (Pre-exponential Factor)

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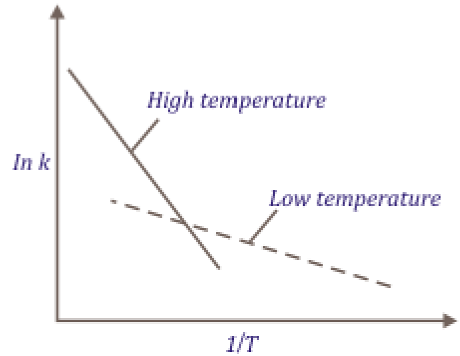
The form of equation in previous section is Arrhenius law

Limitations of Arrhenius law:

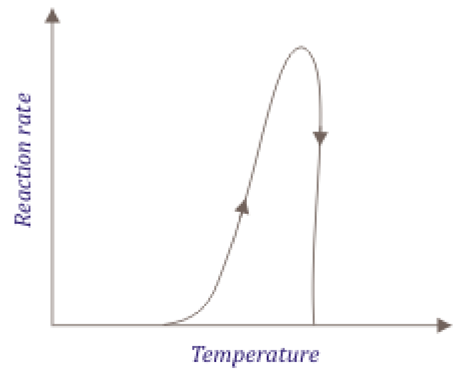
- It cannot simulate combustion process over wide range of temperature.
- Rate law matches experimental data at high temperature, but not so at low temperature.



(Figure 19.3)

Variation of RR with temperature:

- An increase in temperature by 10% for same activation energy can cause RR to be enhanced by 250 %



(Figure 19.4)

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Elementary Reactions

If the reaction occurs successfully at molecular level, the reaction is termed as elementary.

$$OH + H_2 \rightarrow H_2O + H$$

Molecularity :

Number of molecules or atoms participating in each reaction leading to product.

1. Unimolecular reaction $(N_2O_5 \rightarrow 2N_2O_4 + O_2)$
2. Bimolecular reaction $(CO_2 + H_2 \rightarrow H_2O + CO)$
3. Trimolecular reaction $(CO + O + M \rightarrow CO_2 + M)$

Order of Reaction:

Number of molecules or atoms whose concentration would determine the reaction rate.

Example: $(N_2O_5 \rightarrow 2N_2O_4 + O_2)$

$$\frac{dC_{N_2O_5}}{dt} = -k_f C_{N_2O_5}$$

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