Reactions for Energy -

Chemical Kinetics

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Learning objectives

- At what rate a reaction proceed?
- How does a reaction proceed?

Chemical kinetics

Why do we need to study?

Importance of chemical kinetics in reaction

Nature of reaction chemistry (1)

Global reaction

Elementary reactions

Reaction mechanisms:
The collection of elementary reactions that describe the overall global reaction is referred to as "reaction mechanism".

Nature of reaction chemistry (2)

Definitions:

Chain reaction

Those reactions in which an intermediate product produced in one step generates a reactive intermediate species in a subsequent step, then that intermediate generate another reactive intermediate and so on.

Free radicals

The chemical species, which have unpaired electrons and can react very actively with other molecules.

Nature of reaction chemistry (3)

Fuel	Species	# Steps
CH_4	53	400
C_2H_4	75	
C_3H_8	176	
Iso-octane	860	3606

4 main types of combustion related elementary reactions

1. Chain initiation
2. Chain branching
3. Chain propagation
4. Chain termination or recombination

Elementary reactions (1)

Chain initiation

- Free radicals are produced from this reaction

- Combustion reaction gets initiated through reaction involving a 3rd body

Elementary reactions (2)

Chain branching

- Ratio of number of free radicals in the product to that in the reactants >1

Elementary reactions (3)

Chain propagation

- Reactions involving radicals where the total number of radicals remain unchanged
- Total number of radicals in the reactant and product sides stays the same

Elementary reactions (4)

Chain termination or recombination

- When sufficient radicals or 3rd bodies are present, radicals can react among themselves to recombine or react to form stable species

Elementary reactions (5)

Example: Consider a 1 cm^3 container that initially contains 1 chain molecule i.e., 1 free radical per cm^3. Assume the number density to be 10^{19} molecules/cm^3 and the average collision rate is 10^9 collisions/s. If the reaction is a chain propagation reaction (one free radical can generate another free radical in the reaction), then

a. What is the time required for all the molecules to react?

b. Assuming a chain branching case, what is the time required?

Elementary reaction rate (6)

Law of mass action:

It states that the rate at which species are produced, also the rate at which reactant species are removed, is proportional to the product of the concentration of the reacting species, with the concentration of each species raised to the power of the stoichiometric coefficient.

Global reactions

Global reaction rate constant for hydrocarbon fuels

Fuel	A_o	E_A (kCal/mol)	n	m
CH_4	8.3×10^{5}	30	-0.3	1.3
C_2H_6	1.1×10^{12}	30	0.1	1.65
C_3H_8	8.6×10^{11}	30	0.1	1.65
C_8H_{18}	4.6×10^{11}	30	0.25	1.5
CH_3OH	3.2×10^{11}	30	0.25	1.5
C_2H_5OH	1.5×10^{12}	30	0.15	1.6
C_6H_6	2×10^{11}	30	-0.1	1.85

Relation between rate coefficient and equilibrium constants (1)

Example 1: $NO+O \rightarrow N+O_2$

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

Determine the reverse rate coefficient, k_r for the above reaction at 2300 K.

Relation between rate coefficient and equilibrium constants (2)

Example 2: The O atom is an important species involved in the formation of thermal NO. Estimate the mole fraction of radical O in atmospheric air in ppm when it is heated to 2000 K. At 2000 K, assume the reaction $O_2 \leftrightarrow 2O$ to be in equilibrium.

H_2-O_2 Explosion Limits

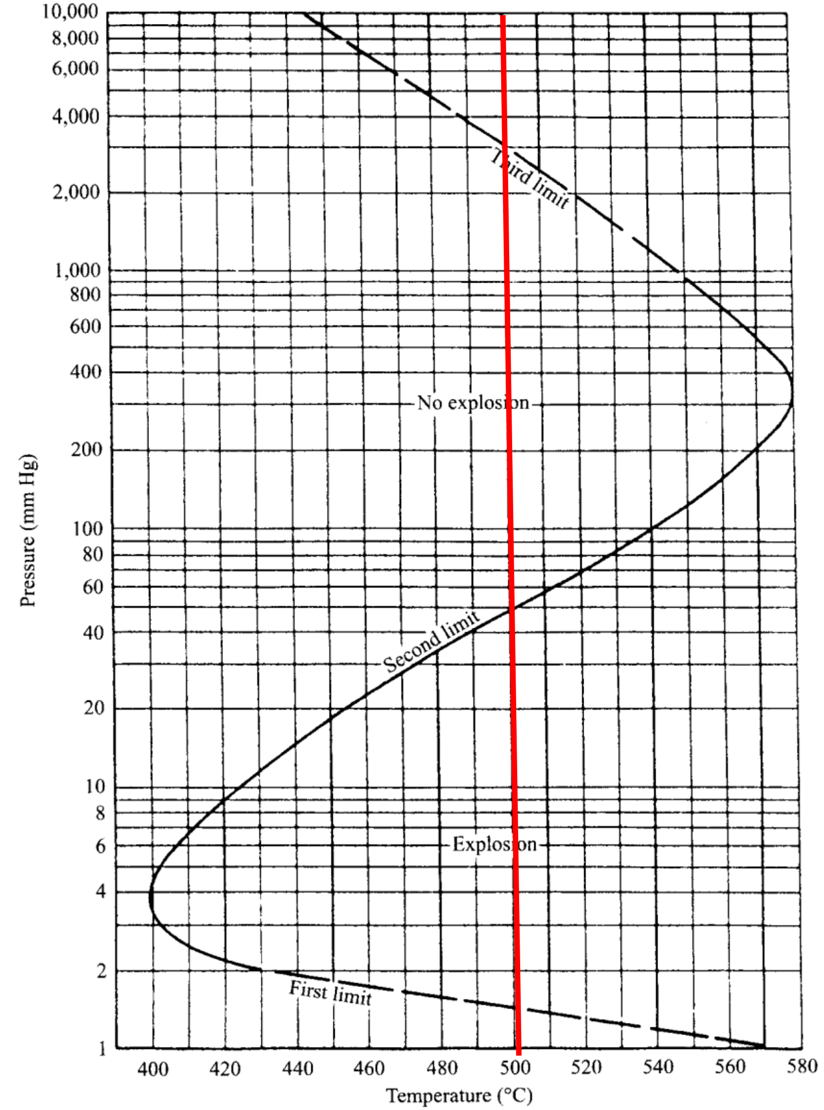

Figure 5.1 Explosion limits for a stoichiometric hydrogen–oxygen mixture in a spherical vessel.

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Next Lecture

- **Reactors**