Course Name: Theory of Fire Propagation (Fire Dynamics)

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Week – 04

Lecture – 01

Module 2 – Review of thermo-chemistry, chemical equilibrium & kinetics

Molecularity of elementary reaction:

An elementary reaction is written at the molecular level. For example, the reaction, $CO + OH \leftrightarrow CO_2 + H$, indicates that one molecule of CO reacts with one molecule of OH to produce one molecule of CO_2 and one H atom. The molecularity of this reaction is 2.

This reaction takes place in one step. That is, a CO molecule collides with an OH molecule, with the necessary force and proper orientation to break the bonds in them and to form new bonds to produce CO2 and H. Similarly, as per the prevailing temperature, a reverse reaction produces CO and OH. The amounts of CO, OH, CO_2, and H present are dependent on the value of the equilibrium constant at a given temperature and pressure.

Law of mass action:

The molecularity of most of the reactions is two. This is because the probability of more than two molecules colliding with each other during a reaction is much lower. There are very few reactions with a molecularity of three. In dissociation reactions, molecularity is one. The rate of a reaction is defined by the Law of Mass Action. This states that the rate of a chemical reaction is proportional to the concentrations of the reacting species. The concentrations of reactants are raised to appropriate powers (integers or decimal numbers) depending on if the reaction is global or elementary. The order of a reaction is the sum of the powers of the concentrations of the reactants participating in the rate equation.

Molecularity and order:

Order and molecularity of an elementary reaction have the same value. For example, in the reaction, $CO + OH \leftrightarrow CO_2 + H$, the molecularity is two as seen earlier. The rate of the forward reaction using the law of mass action is written as, $d[CO]/dt = k\ [CO]^1[OH]^1$. Here, [CO] indicates the concentration of CO and [OH] is the concentration of OH.

The rate at which reaction takes place is the rate at which the concentration of CO varies (decreases) with time. It is easy to note that at the same rate [OH] decreases with time and $[CO_2]$ and [H] increases with time when the forward reaction takes place.

Overall order of this reaction is sum of powers of [CO] and [OH], which is equal to $1 + 1 = 2$, same as the molecularity.

Rate of a reaction:

It is shown that for the reaction, $CO + OH \leftrightarrow CO_2 + H$, the rate of the forward reaction using the law of mass action is written using the concentrations of the reactants, as, $d[CO]/dt = k\ [CO]^1[OH]^1$.

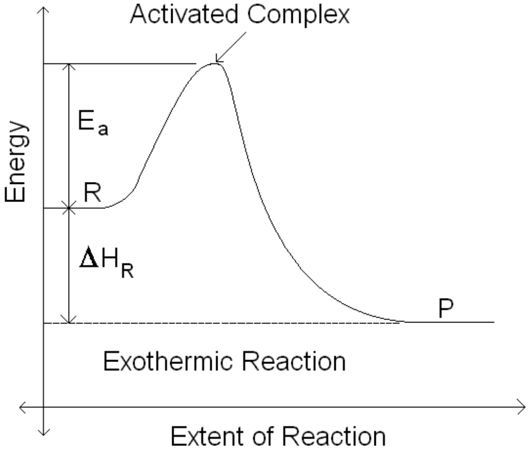
Here, k is called reaction coefficient and it varies strongly as a function of temperature.

For elementary reactions, there is a kinetic theory basis for defining and evaluating the value of k, even though experimental data fit is required to correlate this completely. For successful occurrence of a chemical reaction, as consolidated by Arrhenius and vant Hoff, the following conditions are required.

1. Suitable molecules must collide. (CO and OH)
2. Collisions must be in proper orientation. (O atoms should collide)
3. Collisions must be energetic enough. (strong enough to break bonds)

Rate of a Reaction–activated complex:

The energy of reactants has to be increased to a level where they are in the form of activated complexes, which can form products subsequently, as shown in the figure. Collisions between the reactant molecules should be strong enough for this to happen. The difference between the energy levels of the activated complex and the reactants is called Activation Energy (E_a). Other factors of proper orientation and probability that a collision results in a reaction are included in a term, A.



Rate coefficient:

Using the activation energy, E_a, and the term, A, the rate coefficient is written in Arrhenius form as,

$k(T) = A \exp(-E_a/R_uT)$.

This equation shows the exponential dependence of k on T. Since, A appears before the exponent term, A is often called pre-exponential factor. If the range of temperature for the rate coefficient is wider, a third term is added as,

$k(T) = A\, T^m \exp(-E_a/R_uT)$.

Reaction rate in kmol/m^3-s for $CO + OH \leftrightarrow CO_2 + H$, is written as,

$d[CO]/dt = A\, T^m \exp(-E_a/R_uT)\, [CO]\, [OH]$

Rate coefficient – measurement:

Forward reaction rate for $CO + OH \leftrightarrow CO_2 + H$, is,

$d[CO]/dt = A\ T^m \exp(-E_a/R_uT)\ [CO]\ [OH]$

Controlled experiments in *isothermal conditions* are carried out. Concentrations of CO and OH as a function of time are recorded. By getting this data for various temperatures, the values of A and E_a are derived. Order of the reaction is also evaluated using these experiments. In the case of elementary reactions, the order is a whole number. Either forward or reverse reaction rate coefficient is obtained from the experiments. Uncertainty involved in the estimation of the reaction rate coefficient is quite high. Therefore, the reverse (or the forward) reaction rate coefficient is estimated using thermodynamic procedure, once the other rate coefficient is determined from experiments.

Equilibrium Constants:

Considering, $CO + OH \leftrightarrow CO_2 + H$, let k_f is the forward rate coefficient and k_r is the reverse rate coefficient. At thermodynamic equilibrium (given temperature and pressure) the rate of forward reaction is equal to the rate of reverse reaction. That is,

$k_f\ [CO][OH\} = k_r\ [CO_2][H]$

Or, $k_f/k_r = [CO_2][H]\ /\ [CO][OH] = K_C$

Here, K_C is the equilibrium constant written in terms of concentrations of products and reactants. This can be related to the equilibrium constant, K_p, which is evaluated using Standard Gibbs function change at a given temperature and written in terms of partial pressures of products and reactants.

Relation between Equilibrium Constants:

Consider a general elementary reaction, aA + bB ↔ cC + dD. The equilibrium constant based on concentrations is written as,

$$\frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_C$$

Above equation is called Guldberg and Waage's Law of chemical equilibrium. Relation between K_C and K_p is given as,

$$[A] = \frac{a}{V} = \frac{p_A}{R_u T} \Rightarrow K_C = \frac{\left(\frac{p_C}{R_u T}\right)^c \left(\frac{p_D}{R_u T}\right)^d}{\left(\frac{p_A}{R_u T}\right)^a \left(\frac{p_B}{R_u T}\right)^b} = K_p \left(\frac{p^0}{R_u T}\right)^{\Delta n_R}$$

$$\Delta n_R = (c+d) - (a+b)$$

Net reaction rates:

Consider as an example, a reaction mechanism consisting of four elementary reversible reactions, given as,

$$H_2 + O_2 \xleftrightarrow{k_{f1},\, k_{r1}} HO_2 + H \qquad (R-1)$$

$$H + O_2 \xleftrightarrow{k_{f2},\, k_{r2}} OH + O \qquad (R-2)$$

$$OH + H_2 \xleftrightarrow{k_{f3},\, k_{r3}} H_2O + H \qquad (R-3)$$

$$H + O_2 + M \xleftrightarrow{k_{f4},\, k_{r4}} HO_2 + M \qquad (R-4)$$

Here, k_{fi} and k_{ri} represent forward and reverse rate coefficients of the elementary reaction i. Net rate of production or consumption of any species is written considering the reactions in which the species is involved and taking both forward and reverse rates into account. For instance, the net rate of production or consumption of O_2 is written as,

$$\frac{d[O_2]}{dt} = k_{r1}[HO_2][H] + k_{r2}[OH][O] + k_{r4}[HO_2][M] - \\ k_{f1}[H_2][O_2] - k_{f2}[H][O_2] - k_{f4}[H][O_2][M]$$

Similarly for H atom,

$$\frac{d[H]}{dt} = k_{f1}[H_2][O_2] + k_{f3}[OH][H_2] + k_{r2}[OH][O] + k_{r4}[HO_2][M] - \\ k_{r1}[HO_2][H] - k_{f2}[H][O_2] - k_{r3}[H_2O][H] - k_{f4}[H][O_2][M]$$

Production terms are added and consumption terms are subtracted.

Global reaction rate:

Reaction rate of a global reaction is obtained by careful experiments conducted for certain purpose. This may be for determining ignition delay or flame extinction and so on. Such global reaction can be economically applied to simulate flames from practical burners and for carrying out design calculations. For the reaction between methane and air, $CH_4 + 2(O_2 + 3.76\ N_2) \rightarrow CO_2 + 2\ H_2O + 7.52\ N_2$, the global reaction rate is written as,

$$\mathbf{d[CH_4]/dt = A\ exp(-E_a/R_uT)\ [CH_4]^m\ [O_2]^n}$$

Values of A, E_a, m and n are obtained from careful experimental data. Here, m and n need not be integers.

Overall order is m + n and this lies in between 1.7 to 2.2 for hydrocarbons.