

Chemical Kinetic Modeling and its Principles

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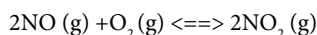
Abstract

The emphasis will be to demonstrate the fundamental mathematical concepts in calculating rates of reactions and the meaning of chemical reaction mechanisms. Reactions as mentioned in a previous chapter can be frequently classified as homogeneous or heterogeneous. Homogeneous reactions occur in a single phase for example, the gas phase reaction involving NO and Oxygen.

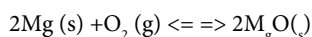
Keywords: Chemical kinetics; Polymerization

Introduction

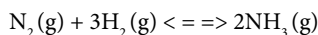
Chemical kinetics is the study of the rates of chemical reactions, the means by which reaction rates may be controlled, and the ways in which reactions proceed on the atomic-molecular level [1].



Heterogeneous reactions take place on a phase boundary, e.g., the formation of solid Magnesium oxide,



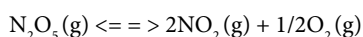
Reactions are also classified as reversible or irreversible. The reaction to produce ammonia below is an example of reversible reaction or,



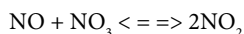
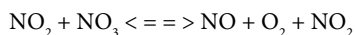
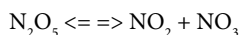
Depending on conditions of temperature and pressure the reaction leads to the formation of Ammonia, if conditions are suddenly changed such as lowering the reaction pressure substantially, ammonia dissociates back into Nitrogen and Hydrogen.

Reaction mechanisms and elementary reactions

Other important concepts to understand are reaction mechanisms and elementary reactions. This can be demonstrated by considering the gas-phase decomposition of $\text{N}_2\text{O}_5(\text{g})$ [2], The overall reaction is



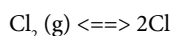
The actual decomposition of N_2O_5 occurs via three “elementary” steps or “molecular events”,



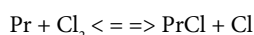
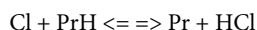
Another important example are “chain reaction mechanisms” since they provide an explanation for important process such as photochemical, combustion, and polymerization.

Chain reactions consist of three kinds of elementary steps initiation (or activation) step, propagation, and termination. As an example consider the gas-phase chlorination of propane (PrH) [2].

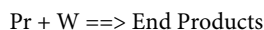
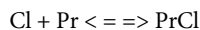
Initiation



II. Propagation



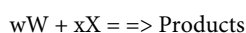
III Termination



In the initiation step Cl atoms can be generated thermally at high temperatures. The propagation step produces unstable radical intermediates such as Pr. Both Pr and Cl in the Propagation step are considered chain carriers. The Propagation step is responsible for the high rate of reaction since the chain carriers are produced. The Termination step reduces the overall rate of reaction and results in the formation of the end products homogeneously or heterogeneously (where W, reactor wall surface).

Concentration and reaction rates

The chemical law of mass action states that, in general, for any single step or elementary reaction (or for one step of a multistep mechanism) such as the rate equation [3] is

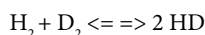


$$\text{Reaction rate} = k[\text{W}]^w[\text{X}]^x = d[\text{Products}]/dt$$

where k is the rate constant. The order of the reaction is given by the sum of the exponents of the concentrations appearing in the rate equation or

$$\text{Reaction order} = w + x + \dots$$

For example, The experimentally determined rate law for the overall reaction (Gardiner), rate,



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$$R = \frac{1}{2} \frac{d[HD]}{dt} = k(T) [H_2]^{0.38} [D_2]^{0.66} [Ar]^{0.98}$$

The order or sum of exponents is 2.0 and the reaction is 0.38 and 0.66 order with respect to Hydrogen and deuterium respectively.

If the reaction is an elementary reaction, the sum of the exponents is then the molecularity of the elementary reaction: one for a unimolecular reaction, two for a bimolecular reaction, and three for a termolecular reaction.

Temperature and reaction rates

Theoretically (Kinetic Theory of Reactions), the temperature dependence of the reaction rate is due to two important factors: the rate of molecular collisions (proportional to $T^{1/2}$) and the increasing probability of high energy encounters (varies as $\exp(-\text{const}/T)$). Based on experimental evidence Savante Arrhenius arrived at the following expression for the temperature dependence of the rate constant, $k(T)$

$$K(T) = A \exp(-E_a/RT)$$

The exponential factor is the most important factor, although the constant A is also known to have temperature dependence. The A factor is related to the molecular encounter frequency as well as

encounter geometry. The activation energy factor E_a is related to the strength of the chemical bonds that are broken and formed, and is the most important factor in the Arrhenius equation.

As noted above, the activation energy factor can be derived from the Maxwell-Boltzmann Distribution Law of molecular energy in the Kinetic Theory of Gases.

Mathematical description of chemical kinetics in solution (Batch)

The mathematical treatment of rate equations lead to integral forms as shown in Table 1 [2]. For example, for a zero order elementary reaction in a batch and isothermal system, the integration of the rate equation leads to:

$$D[A]/dt = -k_0$$

$$[A] = [A]_0 - k_0 t$$

Where $[A]_0$ is the initial concentration of species $[A]$ and t is time.

Other types of reactions can be similarly analyzed mathematically and analytical solutions found for composition of the solution in a batch reactor as shown in Table 1.

Reaction	Order	Rate Equation	Integral Equation
Irreversible Reactions: A ==> B	0	$-\frac{d[A]}{dt} = k_0$	$[A] = [A]_0 - k_0 t$ $t \frac{1}{2} = \frac{[A]_0}{2k_0}$
A ==> B	1	$-\frac{d[A]}{dt} = k_1[A]$	$\ln \frac{[A]}{[A]_0} = -k_1 t$ $t \frac{1}{2} = \frac{1}{k_1} \ln 2$
A + A ==> P	2	$-\frac{d[A]}{dt} = k_2[A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_0} = k_2 t$ $t \frac{1}{2} = \frac{1}{k_2[A]_0}$
aA + bB ==> P	2	$-\frac{d[A]}{dt} = k_2[A][B]$	$\ln \frac{[A]_0 - [X]}{[B]_0 - b/a[X]} = \ln \frac{[A]}{[B]}$ $= \frac{b[A]_0 - a[B]_0}{a} k_2 t + \ln \frac{[A]_0}{[B]_0}$ $t \frac{1}{2} = \frac{a}{k_2(b[A]_0 - a[B]_0)}$ $\times \ln \frac{a[B]_0}{2a[B]_0 - b[B]_0}$
Reversible Reactions: A <==> B	1	$[A]_{eq} = \frac{[B]_0 + [A]_0}{K + 1}$	$\frac{[A] - [A]_{eq}}{[A]_0 - [A]_{eq}} = e^{-k_{eff}t}$ $k_R = \frac{k_1(K + 1)}{K}$ $[A]_{eq} = \frac{[B]_0 + [A]_0}{K + 1}$
A + B <==> C + D	2	$\ln \frac{[A]_0 - [X]}{[B]_0 - b/a[X]} = \ln \frac{[A]}{[B]}$ $= \frac{b[A]_0 - a[B]_0}{a} k_2 t + \ln \frac{[A]_0}{[B]_0}$ $t \frac{1}{2} = \frac{a}{k_2(b[A]_0 - a[B]_0)}$ $\times \ln \frac{a[B]_0}{2a[B]_0 - b[B]_0}$	$q^{1/2} t = \ln \frac{\{2\gamma[X]/(\beta - q^{1/2})\} + 1}{\{2\gamma[X]/(\beta - q^{1/2})\} - 1}$ $[X] = [A]_0 - [A]$

Table 1: Reaction Rates for Simple Reactions.

A more complete treatment of closed isothermal systems can be found in "Mathematical description of Chemical Kinetics in Solutions" by Capellos and Bielski [3].

In Table 1 for the 2nd order reversible reaction the constant q , α , β , γ are as follows:

$$\alpha = k_2 \left\{ [A_0][B_0] - \frac{1}{K} [C_0][D_0] \right\}$$

$$-\beta = k_2 \left\{ [A_0] + [B_0] - \frac{1}{K} [C_0] + [D_0] \right\}$$

$$\gamma = k_2 \left(1 - \frac{1}{K} \right)$$

$$q = \beta^2 - 4\alpha\gamma$$

And K is the reaction equilibrium constant.

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2. Smith JM (1970) Chemical Engineering Kinetics. 2nd edn.
3. Capellos C, Bielski BHJ (1980) Mathematical Description of Chemical Kinetics in Solution.

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