

# MATHEMATICAL MODELS IN CHEMICAL PHYSICS AND COMBUSTION THEORY

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## Summary

A brief review of mathematical models in chemical physics is given. More attention is devoted to the theory of chain reactions. This theory was created by N.N. Semenov. Chain theory is theoretical foundation of modern models. Being extremely significant in the field of chemistry, chain processes are investigated by experimental methods as well as by mathematical models. The results of calculations are given in terms of parameters of the model: temperature, form of vessel (plane, cylindrical or spherical) etc. Different questions are discussed: link between energy and kinetics of reaction, a length of chains, development of chains in time, paths of chain breaking - a breaking of chains in volume and on a surface. The modified Chester–Chisnell–Whitham (CCW) model has been examined to account for reactive mixtures and to describe detonation wave propagation, diffraction, and reflection. This model makes it possible to investigate the behavior of detonation propagation and reflection near and at the Chapman–Jouguet (CJ) point. Model of the temporal evolution of a reduced combustion chemical system with an artificial neural network and a model for calculating heat release in premixed turbulent flames are briefly discussed.

## 1. Introduction

All mathematical models in chemical physics describe molecular reactions. If a reaction develops spontaneously in space and in time, the latter implies that this reaction has a

chain nature. The theory of chain reactions was created by N.N. Semenov. Chain theory is a theoretical foundation of modern combustion models. Being extremely significant in chemistry, chain processes are investigated by experimental methods as well as by mathematical modeling.

## 2. Chain Reactions

The number of molecules with great energy is determined by four processes:

1. Creation of fast molecules owing to collisions.
2. Disappearing of fast molecules owing to collisions.
3. Creation of fast molecules of initial substances as the result of a reaction.
4. Disappearing of fast molecules owing to a reaction.

Assume that the thermal motion produces  $H$  particles with energy  $E$  every second, and time interval, during which a particle preserves its energy from dissipation, is  $\Delta\theta$ . Let  $\Delta\tau$  be the mean time, reckoned from the appearance of an active particle up to its entry into reaction. And, finally, concentration of active particles is  $\Pi$ . Each particle can disappear either due to a reaction, or owing to energy dissipation. In such a case the mean time of its life, irrespective of the mode of disappearance, will be

$$t = \frac{1}{\frac{1}{\Delta\theta} + \frac{1}{\Delta\tau}} \quad (1)$$

All  $n$  active molecules available at the same instant of time, will disappear during the time interval  $t$ . From here, the number of the disappeared molecules in unit time will be:

$$\frac{n}{t} = \left( \frac{1}{\Delta\theta} + \frac{1}{\Delta\tau} \right) \quad (2)$$

$n/\Delta\tau$  molecules will react and  $n/\Delta\theta$  will disappear as a result of energy dissipation. So:

$$\omega = \frac{n}{\Delta\tau} \quad (3)$$

Each reaction creates particles with energy which is equal to  $Q + E$ . These particles, being products of reaction, cannot react. However their interaction with a molecule of an initial substance may lead to energy transfer. As a result, new active molecules will be created. If  $\varepsilon$  is the average number of active molecules established as a result of one elementary reaction ( $\varepsilon$  can be a small fraction or a value greater than unity), the reaction will deliver  $\varepsilon\omega = n\varepsilon/\Delta\tau$  active particles every second. So, the total number of generated active particles will be (per second):

$$\begin{aligned} \frac{dn}{dt} &= H + \frac{n\varepsilon}{\Delta\tau} - n\left(\frac{1}{\Delta\theta} + \frac{1}{\Delta\tau}\right) = H - n\left(\frac{1}{\Delta\tau} - \frac{\varepsilon}{\Delta\tau} + \frac{1}{\Delta\theta}\right) \\ &= H - \frac{n}{\Delta\tau}\left(1 - \varepsilon + \frac{\Delta\tau}{\Delta\theta}\right) \end{aligned} \quad (4)$$

If reaction does not take place, i.e.  $\Delta\tau = \infty$ , then  $dn/dt = H - n/\Delta\theta$ . Under the condition of thermal balance  $dn/dt = 0$ , or  $n_g = H \Delta\theta$ . In this case  $n_g$  is the number of molecules with energy greater than  $E$ . The validity of Maxwell-Boltzman distribution is supposed in this situation. As a first approximation  $n_g = Ne^{-E/RT}$ , where  $N$  is a total number of molecules in a unit volume.

When reaction occurs the situation changes. Admit, that the values  $H$ ,  $\Delta\tau$ ,  $\Delta\theta$  and  $\varepsilon$  do not depend on reaction rate  $w$ , or, in other words, do not depend on concentration  $n$  of active molecules. Then the equation

$$\frac{dn}{dt} = H - \frac{n}{\Delta\tau}\left(1 - \varepsilon + \frac{\Delta\tau}{\Delta\theta}\right) \quad (5)$$

at increase of  $t$  gives a stationary solution only in the case, when

$$1 - \varepsilon + \frac{\Delta\tau}{\Delta\theta} > 0$$

or

$$\frac{\varepsilon}{1 + \frac{\Delta\tau}{\Delta\theta}} = \alpha < 1. \quad (6)$$

Suppose  $dn/dt = 0$ , the equation will be:

$$n = \frac{H\Delta\tau}{1 - \varepsilon + \frac{\Delta\tau}{\Delta\theta}} = \frac{H\Delta\theta}{1 + \frac{\Delta\theta}{\Delta\tau} - \varepsilon \frac{\Delta\theta}{\Delta\tau}} = \frac{H\Delta\theta}{1 + \frac{\Delta\theta}{\Delta\tau}(1 - \varepsilon)} = \frac{n_g}{1 + \frac{\Delta\theta}{\Delta\tau}(1 - \varepsilon)} \quad (7)$$

It is obvious that in the presence of a reaction the amount of active molecules, with energy greater than  $E$ , differs from an equilibrium value  $n = n_g$ .

Thus, if  $\varepsilon < 1$ , then  $n < n_g < 1$ , or, the number of high energy molecules diminishes as compared to an equilibrium amount. When  $\varepsilon$  is less than  $1 + \Delta\tau/\Delta\theta$ , but nevertheless greater than unity, then  $n > n_g$ . In this case, the number of high energy particles will be greater than in the case of the temperature balance. If  $\varepsilon$  is very close to  $1 + \Delta\tau/\Delta\theta$ , the value  $1 + \Delta\theta/\Delta\tau(1 - \varepsilon)$  will be close to zero, and it will receive enormous deviations from equilibrium distribution in the tail of the curve. The reaction rate, according to the formulae (3) and (7), is

$$\omega = \frac{H}{1 - (\varepsilon - \Delta\tau/\Delta\theta)} = \frac{H}{1 + \Delta\tau/\Delta\theta} \left(1 - \frac{\varepsilon}{1 + \Delta\tau/\Delta\theta}\right)^{-1} \quad (8)$$

The value  $\frac{H}{1 + \Delta\tau/\Delta\theta} = H \frac{1/\Delta\tau}{1/\Delta\tau + 1/\Delta\theta}$  means the part of active molecules  $H$  which will react, remaining molecules  $\frac{H}{1 + \Delta\theta/\Delta\tau} = H \frac{1/\Delta\theta}{1/\Delta\tau + 1/\Delta\theta}$  disappear owing to energy dissipation.

Designate the value  $\frac{H}{1 + \Delta\tau/\Delta\theta}$  as  $n_0$ . Apparently,  $n_0$  presents number of elementary reactions, which arise in unit time due to the thermal activation. Therefore,  $n_0$  is the number of primary centers. Reaction rate:

$$\omega = \frac{n_0}{1 - \frac{\varepsilon}{1 + \Delta\tau/\Delta\theta}} = \frac{n_0}{1 - \alpha} \quad (9)$$

Here

$$\alpha = \frac{\varepsilon}{1 + \Delta\tau/\Delta\theta} \quad (10)$$

It is obvious that the total number of elementary reactions occurring in unit time, exceeds the number of primary reactions by the factor

$$\frac{1}{1 - \alpha} = \nu \quad (11)$$

In other words, each elementary reaction causes a chain of secondary reactions, and the amount of secondary reactions in a chain (length of a chain) is  $\nu$ .

The value  $\varepsilon$ , according to the definition, is the number of active molecules arising as a result of any (primary or secondary) elementary reaction. Part  $\frac{\varepsilon}{1 + \Delta\tau/\Delta\theta}$  of these  $\varepsilon$  active molecules will react.

$\alpha$  is the mean number of elementary reactions provided by each given particle, therefore it is the probability of the prolongation of a chain. Thus, however, it is necessary to remember, that  $\alpha$  can be greater than unity, and consequently the term "probability" is used conventionally in a case when  $\alpha > 1$ . Finally, if  $\varepsilon > 1 + \Delta\tau/\Delta\theta$  or  $\alpha > 1$ , the stationary state is impossible in general, as  $dn/dt$  will be more than 0 at any time. The number of active molecules will grow continuously, irrespective of specific values  $H$  and  $n_0$ . In this case the presence of a small number of active molecules at the initial

moment starts the reaction. Accordingly the reaction rate  $w$  will grow infinitely.

In a case of stationary current reaction, i. e. under the condition  $\alpha < 1$ , its rate, being proportional to  $H$  or  $n_0$ , depends significantly on the number of initial centers of reaction, formed by the thermal motion. If values  $H$  and  $n_0$  are reduced to zero, for example by instant cooling of a reaction mixture, the reaction will stop.

In the case of an auto-accelerating reaction, when  $\alpha > 1$ , the interruption of initial centers producing at some moment will not influence the auto-acceleration of reaction. It is clear from the following equation

$$\frac{\Delta\tau}{1+\Delta\tau/\Delta\theta} \frac{dw}{dt} = \frac{H}{1+\Delta\tau/\Delta\theta} - \frac{w(1-\varepsilon+\Delta\tau/\Delta\theta)}{1+\Delta\tau/\Delta\theta} \quad (12)$$

$$= n_0 - w(1-\alpha)$$

which is obtained from the Eq. (4) multiplying by  $\frac{1}{1+\Delta\tau/\Delta\theta}$  and replacing  $n$  by its value  $w\Delta\tau$ .

If  $\alpha < 1$ , at  $n_0 = 0$  reaction rate will decrease down to zero. If  $\alpha > 1$ , and  $n_0 = 0$  reaction will be auto-accelerated ad infinitum.

*Example:* active centers are the products of dissociation of mother substances (for example, atoms  $H$  in reaction  $H_2 + O_2$ ).

In such a case the lifetime  $\Delta\theta$  of such active molecules will be in inverse proportion to the concentration of atoms  $H$  (because  $H$  disappearing happens owing to contact of two  $H$  atoms). So,  $\Delta\theta = k/n$ , where  $n$  concentration of active molecules, (4) will transform to:

$$\frac{dn}{dt} = H - \frac{n}{\Delta\tau} \left(1 - \varepsilon + \frac{\Delta\tau}{k} n\right) \quad (13)$$

Suppose that after the reaction had started, production of initial centers was interrupted. Then,  $H$  is reduced to zero. Then if  $\varepsilon > 1$ , the number  $n$  will decrease until the value  $c = 1 - \varepsilon + n \Delta\tau/k$  does not become equal to zero.

Further decrease of  $n$  will make  $c < 0$ , i. e.  $dn/dt > 0$ . But in such a case the number  $n$  again will begin to increase as far as  $1 - \varepsilon + n \Delta\tau/k = 0$ . And if the value  $1 - \varepsilon + n \Delta\tau/k = 0$ , then  $\alpha = 1$ .

Thus, number of initial centers is of no significance. Reaction supports a steady deflection from a Maxwell-Boltzman distribution. The stationary number of active molecules, in this case, is  $(\varepsilon - 1)k/\Delta\tau$ . Therefore, one can expect stationary reactions. This stationary reaction can exist because  $\alpha$  is automatically maintained around unity.

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### Biographical Sketch

**Valentin I. Korotkov**, was born in 1947. In 1965-1971 he was a student at the Department of Physics of St-Petersburg State University and graduated from chair of photonics. After one year in State Optical Institute he returned to the Physical Department and got the PhD degree in 1976. In 1976 he became associate professor of the chair of General Physics where he got the second scientific degree of Dr. Sc. and professorship in 1998. For more than 20 years Prof. Korotkov delivered lectures in General Physics and Modern Science. He is author of 107 papers and 16 text-books. For three years he had grant of Soros

foundation. His main fields of scientific interest are photo-physical and photo-chemical processes in complex organic molecules located at the interface. He is member of European photo-chemical association and World Theoretical Organic Chemistry Organization.

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