Use of Chemked for Simulation of Gas-Phase Chemical Reactors

Chemked – A Program for Chemical Kinetics of Gas-Phase Reactions

M. Jelezniak and I. Jelezniak
Home page: http://www.chemked.com/, email: info@chemked.com
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1. Introduction

Chemked [1] is a program designed for creating and editing thermodynamic and chemical kinetics databases, for formation of reaction mechanisms. The program incorporates a solver for solving the differential equations of gas-phase chemical kinetics at constant pressure and at constant volume without mass and heat transfer. Such approach is an idealized description of processes that take place in nature and industry. Although the approach is very simple, it has been successfully employed for simulation of reaction chemistry behind shock waves in gases [2, 3].

In Chemked, the following differential equations for species and gas temperature are employed for simulation processes at constant pressure.

$$\frac{dY_n}{dt} = \frac{m_n}{\rho} \sum_j w_{jn} \ , \tag{1.1}$$

$$\frac{dT}{dt} = \frac{1}{\rho \hat{c}_p} \sum_j u_j \ , \tag{1.2}$$

where t is time, Y_n and m_n are the mass fraction and the molecular weight of species n, ρ is the mass density, T is temperature, $\hat{c}_p$ is the mean heat capacity at constant pressure, w_{jn} is the rate of species production, u_j is the rate of heat production. The summations are over all reactions. The equations (1.1, 1.2) in conjunction with the equation of state form the governing equations, whose solution gives the temporal development of the chemically reacting system.

The objective of this work is to demonstrate the capability of Chemked for simulation of the processes in gas-phase chemical reactors. First we will define the general gas parameters (Section 2) and give the expressions for calculation of reaction rates and heat production rates (Section 3). In Section 4, the equations (1.1, 1.2) are derived from a more general set of equations; simple models of the chemical reactors based on these equations are discussed. In Section 5, the computational models are validated against experimental data.

2. Gas Parameters and Variables

Here we specify gas parameters that are used as variables in the conservation equations or are useful for analysis of results.

2.1 Mixture-Averaged Gas Parameters
The choice of some variables is obvious and does not require special comments. These variables are the mixture-averaged gas parameters.

Temperature T, [K]
Pressure P, [atm]
Total gas concentration $C_{tot,}$, [$1/cm^3$] or [mol/cm^3].

For given P and T, the C_{tot} value is found from the ideal-gas equation of state.

$$C_{tot} = \frac{P}{RT},$$

(2.1)

where R is the universal gas constant.

2.2 Species Concentration

Species concentration is denoted as $[X_n]$ and has the units of $[1/cm^3]$ or $[mol/cm^3]$. The obvious formula relates the $[X_n]$ values to the total concentration C_{tot}.

$$C_{tot} = \sum_n [X_n],$$

(2.2)

where the summation is over all species of the gas mixture. The species concentrations can be expressed also through the mole fraction X_n.

$$X_n = \frac{[X_n]}{C_{tot}}.$$

(2.3)

The mass fraction Y_n of the nth species is defined as

$$Y_n = \frac{m_n [X_n]}{\rho}.$$

(2.4)

Here m_n is the molecular weight of the nth species in the units of (g/mol). The mass density ρ (g/cm^3) can be calculated by

$$\rho = \sum_n m_n [X_n].$$

(2.5)

3 Chemical Reactions

In this section, we give only a short description of chemical reactions; more detailed information on this subject can be found in literature, for example, in [4-6].

3.1 Reaction Rate

The stoichiometric equation of a chemical reaction can be written in the following general form:

$$\sum_n v'_{jn} s_n = \sum_n v''_{jn} s_n,$$

(3.1).

where the subscript j is the reaction number, s_n is the chemical symbol of species n, v_{jn} is the stoichiometric coefficient. The summations are over species involved in the reaction. The superscript ' of the stoichiometric coefficients refers to the reactants, the superscript " refers to the products. In this representation, the v_{jn} coefficients are integer positive numbers or zeros.

The forward, reverse and net reaction rates are

$$q_{j,for} = k_{j,for} \prod_n [X_n]^{v'_{jn}} , \qquad q_{j,rev} = k_{j,rev} \prod_n [X_n]^{v''_{jn}} ,$$

$$q_{j,net} = q_{j,for} - q_{j,rev} , \qquad\qquad (3.2).$$

where $k_{j,for}$ and $k_{j,rev}$ are the forward and reverse rate constants of the jth reaction, $[X_n]$ is the concentration of species n. The Arhenius form is used most frequently for calculation of the reaction rate constant:

$$k_{j,for} = A_{j,for} T^{a_{j,for}} \exp\left(-\frac{E_{j,for}}{RT} \right) , \qquad\qquad (3.3)$$

where $A_{j,for}$, $a_{j,for}$ and $E_{j,for}$ are the parameters that ate available in chemical kinetics databases, for example [7]. The reverse rate constant is related to the forward rate constant by

$$k_{j,rev} = \frac{k_{j,for}}{K_j} , \qquad\qquad (3.4)$$

where K_j is the equilibrium constant of the jth reaction.

Remark --
The Arhenius form is one of the simplest expressions of the rate constant; in many cases the more sophisticated expressions are required. Description of other reaction types can be found in 4-6].
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Each event of the Jth reaction yields the number $\left(v''_{jn} - v'_{jn} \right)$ of species n. Then production rate of species n in the jth reaction is given by

$$w_{jn} = \left(v''_{jn} - v'_{jn} \right) q_{j,net} . \qquad\qquad (3.5)$$

The sign of w_{jn} shows the actual situation. If $w_{jn} > 0$, then the species n are produced; if $w_{jn} < 0$, then the species n are consumed. The reaction rates (Eq. 3.2) and the species production rate (Eq. 3.5) have the units of $(1/cm^3$ sec) or $(mol/cm^3$ sec).

3.2 Heat of Reaction

The final products of a chemical reaction are not only new chemical compounds, but releasing (consuming) of heat as well. The last processes are described by the reaction thermochemistry. The basic thermochemical quantity is the heat of reaction ΔH_j, which closes the energy balance of the reaction. The heat of reaction ΔH_j is the difference in the enthalpies of the products and reactants at constant pressure and at a definite temperature. This value is calculated from the molar enthalpies H_n of species involved in the reaction.

$$\Delta H_j = \sum_n (v''_{jn} - v'_{jn}) H_n . \qquad\qquad (3.6)$$

The rate of heat production in the Jth reaction is given by

$$u_j = -\Delta H_j q_{j,net}.\tag{3.7}$$

The sign of u_j shows the actual situation. If $u_j < 0$, then the heat is consumed; if $u_j > 0$, then the heat is released.

The heat of reaction ΔH_j has the units of energy per mole, (J/mol) or (cal/mol). Correspondingly, the reaction net rate $q_{j,net}$ must have the units of molar production, (mol/cm^3 sec). Then the u_j values describe the rate of heat production in the jth reaction per unit volume, (J/cm^3 sec) or (cal/cm^3 sec).

4. Chemical Reactors

In this section, a simplified description of chemical processes in plug flow and batch reactors are presented. We will consider reactors of constant pressure and without surface reactions. In addition we will neglect diffusion processes and heat transfer in the reactor volume. The equations obtained here are the conservation equations for total mass, species and enthalpy. These are a simplified version of the more general equations from [4, 5]. The more detailed information on chemical reactors can be found in [5, 8, 9].

4.1 Plug Flow Reactor
Let a tube with a variable cross-sectional area $A(x)$ be a working section of a plug flow reactor, Fig .4.1. A stirred gas mixture of reagents enters the section at $x = 0$. The initial gas parameters (mass density ρ_0, temperature T_0, velocity U_0 and chemical composition X_{n0}) are known. The chemical reactions proceed when the gas mixture moves through the working section. The products of the chemical reactions are removed from the exit of the section ($x = L$). Below we will discuss the equations that describe the processes in such reactor.
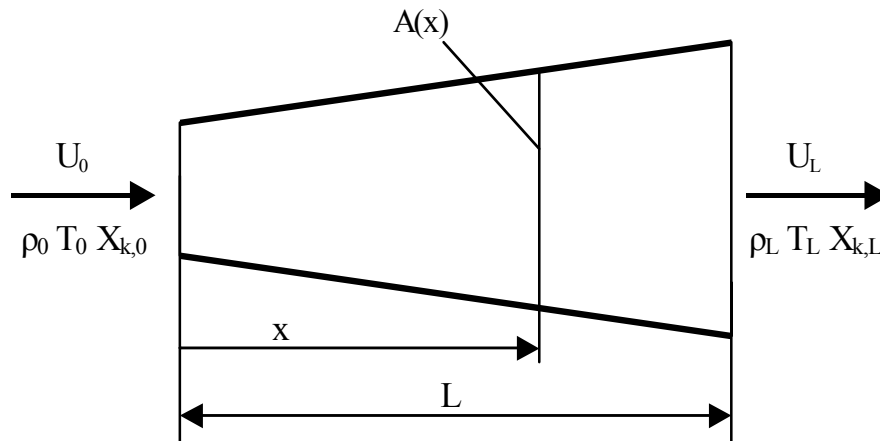

Fig. 4.1. Schematic diagram of plug-flow reactor

When describing the reactor the following assumptions will be used.
- All the processes are steady state
- Gas flow is subsonic (low Mach number)
- The reactor walls are well insulated

- There are no surface reactions
- There is no upstream or downstream mixing
- There is perfect mixing in the transversal direction.

4.1.1 Conservation of Total Mass

The steady-state equation of total mass conservation is

$$\frac{dQ}{dx} = 0 \ , \quad Q = A\rho U \ ,$$

(4.1)

where U is axial flow velocity, Q is mass flux across a surface A (the total mass of molecules which move across A per unit time, the Q units are g/sec). Eq. (4.1) corresponds to a gas flow without mass accumulation in the reactor volume.

4.1.2 Conservation of Momentum

The steady-state momentum equation without surface reactions is written as

$$\frac{dP}{dx} + \rho U \frac{dU}{dx} + \frac{1}{A}\frac{dF}{dx} = 0 \ ,$$

(4.2)

where F is the drag forces exerted on the gas by the tube wall (viscous term), the second term is responsible for the change of momentum of the gas. In subsonic gas flows (low Mach number), when the flow velocity U is much less than the mean thermal gas velocity, it is often possible to neglect the pressure changes due to both the drag forces and changing the flow velocity. Then $dP/dx = 0$ and the assumption of the constant pressure can be applicable.

4.1.3 Conservation of Species

Similar to Eq.(4.1), we can write the continuity equation for each species.

$$\frac{1}{A}\frac{d}{dx}\left(QY_n\right) = m_n \sum_j w_{jn}$$

(4.3)

Here QY_n is the mass flux of species n across a surface A, the units are (g/sec). The right-hand side of Eq.(4.3) is the mass production rate of the nth species by gas-phase reactions (Eq. 3.5). Differentiating the left-hand side leads to

$$\frac{Y_n}{A}\frac{d}{dx}\left(Q\right) + \frac{Q}{A}\frac{d}{dx}\left(Y_n\right) = m_n \sum_j w_{jn} \ .$$

(4.4)

If we taken into account Eq.(4.1) and use the relation $dt = dx/U$, then the differential equations for mass fraction of species n may be written as

$$\frac{dY_n}{dt} = \frac{m_n}{\rho} \sum_j w_{jn} \ .$$

(4.5)

This equation is fully coincident with Eq.(1.1) used in Chemked.

4.1.4 Conservation of Energy

The energy equation will be obtained under the assumptions discussed in the beginning of this section. The steady-state energy equation for a gas flow in a tube with chemically non-reactive and insulated walls without heat transfer and diffusion may be written as

$$\frac{1}{A} \frac{d}{dx} Q\left(h + \frac{1}{2}U^2\right) = 0 \ ,$$

(4.6)

where h is mean specific enthalpy,

$$h = \sum_n Y_n h_n \ .$$

(4.7)

Here h_n is the specific enthalpy of the nth species in the units of (J/g) or (cal/g); the summation is over all species of the gas mixture.

This equation (4.6) represents the conservation of the total gas energy that is the sum of enthalpy and kinetic energy. Again, as in Section 4.1.2, we will consider subsonic gas flows at low Mach numbers, where $h >> U^2/2$. Under these conditions the kinetic energy term can be omitted. Differentiating out the products gives

$$\frac{h}{A} \frac{dQ}{dx} + \frac{Q}{A} \frac{dh}{dx} = 0 \ .$$

(4.8)

The first term is equal to zero (Eq. 4.1), then Eq.(4.8) can be written in the form

$$\rho \frac{d}{dt} \sum_n Y_n h_n = 0 \ .$$

(4.9)

Here, as in Section 4.1.3, we use the relation $dt = dx/U$. The ideal-gas specific enthalpy h_n is function of the gas temperature only. Then the h_n derivative can be written as

$$\frac{dh_n}{dt} = c_{pn} \frac{dT}{dt} \; , \quad c_{pn} = \frac{dh_n}{dT} \; , \tag{4.10}$$

where c_{pn} is the specific heat capacity of the nth species at constant pressure; the units are (J/g K) or (cal/g K). After differentiating the sum in Eq.(4.9), we obtain the final equation for the gas temperature.

$$\frac{dT}{dt} = \frac{1}{\rho \hat{c}_p} \sum_j u_j \; , \tag{4.11}$$

where the rates of heat production in reactions u_j are defined by Eq.(3.7); the summation is over all reactions. Mean specific heat capacity at constant pressure $\hat{c}_p$ is

$$\hat{c}_p = \sum_n Y_n c_{pn} \; . \tag{4.12}$$

Eq.(4.11) is fully coincident with Eq.(1.2) used in Chemked.

4.1.5 Initial Conditions

Conservation equations (4.1, 4.5, 4.11) and the equation of state (2.1) describe the temporal development of chemically reacting gas mixture in a plug flow reactor. These equations must be accompanied by initial conditions; values U, P, T, ρ and Y_n must be known at $t = 0$, that is, at $x = 0$, Fig.4.1.

4.1.6 Reaction Time and Axial Distance

The solution of Eqs.(2.1, 4.5, 4.11) with initial conditions at $t = 0$ gives the gas parameters T, ρ, Y_n versus time t We denote the time t as reaction time. The reaction time is a time required for reagents to pass from the inlet of the working section to a position x. The function $x(t)$ is important for reactor engineering and is defined by the differential equation:

$$\frac{dx}{dt} = U \; . \tag{4.13}$$

The desirable function $x(t)$ is a simultaneous solution of the equations (4.1) and (4.13). In Eq.(4.1), the cross-sectional aria $A(x)$ is specified as a parameter of the problem and the function $\rho(t)$ must be taken from the numeric solution. The simplest solution of Eq.(4.13) can be obtained for reactors with a constant cross-sectional aria.

$$x(t) = \rho_0 U_0 \int_0^t \frac{dt'}{\rho(t')} \; , \tag{4.14}$$

Equations (4.13) and (4.14) also relate the two important reactor parameters: reactor length L and residence time t_r. The residence time is a time required for reagents to pass from the inlet ($x = 0$) to exit of the working section ($x = L$).

4.1.7 Output Characteristics of Reactor

When designing a reactor, the basic problem is to achieve the largest reagent conversion in minimal reactor volume. Solution of the problem requires optimization of the reactor parameters; this problem isn't discussed here. We believe that all the reactor characteristics are specified. Then the solution of Eqs.(2.1, 4.5, 4.11) gives directly parameters of the reactor product, namely, the species mass fractions $Y_n(t_r)$ at the exit of the working section ($x = L$). If the yield must be expressed in concentrations $[X_n]$, then the $Y_n(L)$ values must be reduced to $[X_n]$ through Eq.(2.4).

An essential characteristic of the reactor is the production rate of the nth species $Q_n(t_r)$. This value has the units of (g/sec) and can be calculated as

$$Q_n(t_r) = Q(0) \cdot Y_n(t_r). \qquad (4.15)$$

4.2 Batch Reactor

A batch reactor consists of a vessel with a means to stir the gas mixture (Fig. 4.2). After charge of reagents, the vessel is closed and the chemical processes are initiated. When the chemical conversion of reagents is completed, the vessel is opened and the products are removed. In contrast to the plug flow reactor (Section 4.1), which can work in steady-state mode, the batch reactor works only transiently. Nevertheless, the chemical processes in the batch and plug flow reactors are very similar; in particular, the courses of chemical reactions in time are identical.

Here we will consider a batch reactor that is held at constant pressure P_0. In order to sustain the constant pressure a special tool is required; this tool is depicted schematically as bellows in Fig. 4.2. In addition we believe that the stirring time of the gas is much less than the times of chemical conversion of reagents. Again, as is done for plug flow reactor (Section 4.1), we will consider reactor with insulated walls and without surface reactions. Therefore, the batch reactor processes take place in well-stirred gas at constant pressure and at unchanged total mass and enthalpy of the gas.
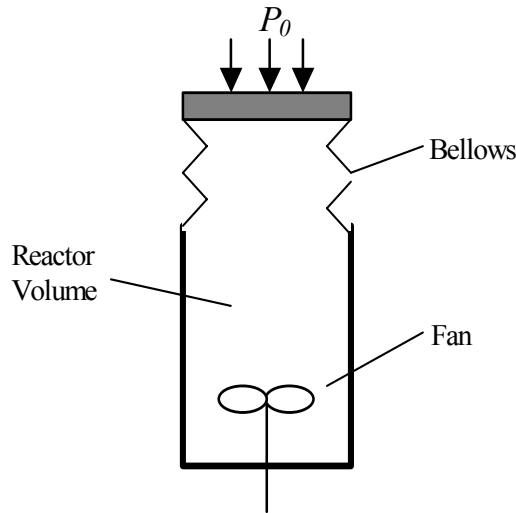
Fig. 4.2. Schematic diagram of batch reactor

If the total gas mass in the reactor volume is denoted as Q, then the conservation of the total mass can be written as

$$\frac{dQ}{dt} = 0 \ , \quad Q = V\rho \ , \tag{4.16}$$

where V is the reactor volume and ρ is the mass density; these values can change in order to keep the constant pressure. Using the conservation equation (4.16), we can directly obtain equations for species mass fractions (4.5) and temperature (4.11).

Thus Eqs. (2.1, 4.16, 4.5, 4.11) with corresponding initial conditions for V, P, T, ρ, Y_n at $t = 0$ describe the temporal change of the gas parameters in the batch reactor. The solution of these equations gives specific gas parameters (per unit of mass), which can be used as source data for calculation of reactor parameters. In particular, the yield of the nth species $Q_n(t_r)$ can be calculated, as before, by Eq.(4.15); the yield has the units of (g).

The enthalpy equation Eq.(4.11) was obtained for insulated walls. However in batch reactor, a mode of constant gas temperature can be realized as well. Thus mode takes place, if there is a strong thermal interaction between gas and vessel walls, and if wall temperature is kept constant. In this case Eq.(4.11) may be omitted and the reactor performance is described by Eqs. (2.1, 4.16 and 4.5).

Remark ---
When describing the batch reactor, a stirring means (fan) is usually introduced. Actually the fan isn't required, if the initial distribution of the gas parameters is uniform and the effect of the reactor walls is negligible. Then the gas will stay uniform during the course of chemical conversion.

For this reason, the batch reactor equations can be employed for description of a uniform reacting area in the atmosphere. This approach is valid, if the reacting area is a result of a short discharge of pollutants and if the area size is much larger than the mixing layer with surrounding air.
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5. Comparison to Experiments

In this section, the conservation equations (4.1, 4.5, 4.11), which are derived previously, are validated against experimental data for plug flow and batch reactors.

5.1   Plug Flow Reactor

Here the numerical calculations compare with experiments [11]. In [11], the methanol oxidation has been examined at wide ranges of temperatures and pressures. We do not discuss the full set of the data [11] and will consider only an experiment matching a plug flow conditions.

5.1.1   Mixing and Working Sections of Flow Reactor

In section 4.1, an idealized description of a plug flow reactor is given. Actually the gas flow in the reactor has much more complex structure; a sketch of the flow is shown in Fig. 5.1. The reactor duct consists at least of two main parts: mixing section and working section. The mixing section includes injectors for introduction of reactants into carrier gas. Well-designed mixing section provides a well-stirred and uniform gas mixture at the inlet of the working section. The main experimental study of the chemical processes is carried out in the working section.
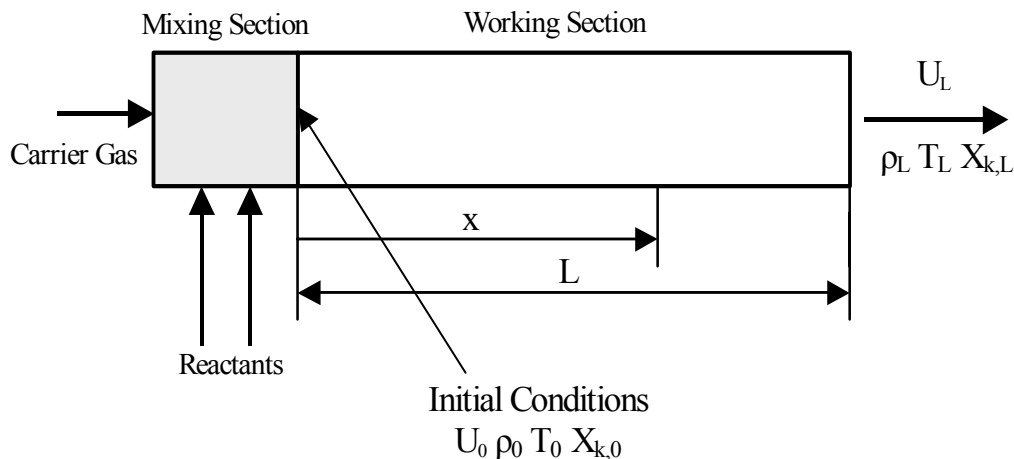

Fig 5.1 Sketch of plug flow reactor

Experimental data must be referred to a coordinate system. Normally the axial distance x from the inlet of the working section is used as a coordinate (Fig. 5.1). The reaction time t, connected with a gas element, has the origin at the instant, when this element goes into the working section ($t = 0$ at $x = 0$). Here, at $t=0$, we must know the gas parameters that are the initial conditions for Eqs. (4.1, 4.5, 4.11). But in many cases the exact determination of these parameters isn't achievable due to very sophisticated arrangement of the mixing flow and possible chemical reactions during the mixing process. As a consequence, special approaches must be used; an approach for comparison between experimental and calculated data will be discussed below.

5.1.2 Methanol Oxidation

Now we turn to a close examination of the chemical processes in a flow reactor under conditions of the works [11]. In this work, the methanol oxidation under wide ranges of temperatures and pressures is investigated. On the bases of the experimental data a detailed reaction mechanism has been developed and tested. In order to validate Eqs. (2.1, 4.1, 4.5, 4.11) for plug flow conditions, an experiment from [11] has been chosen. The chosen data are shown in Fig.5.2; the conditions are presented in the figure caption (φ is the equivalence ratio).

For simulation of the chemical processes, the reaction mechanism [11] consisting of 22 species and 97 reactions is used. The reactions from the mechanism are used to calculate the reaction rates that are formed right-hand sides of the differential equations of species and energy. These equations must be accompanied by initial conditions for T and Y_n at the reactor inlet ($t = 0$). Nevertheless, as mentioned above, there are difficulties with definition of the initial conditions (Section 5.1.1). In this connection the authors [11] recommend the following procedure for comparing calculations with experiments.

- The initial conditions for the differential equations are defined in accordance to the flow rates of the carrier gas and reagents at inlets of the mixing sections (for the considered experiment, these conditions are shown in the caption of Fig. 5.2).
- The set of chemical kinetics equations are solved with these initial conditions.
- The calculated species profiles are translated along the time axis to achieve minimum distinctions between calculated and experimental data.

This procedure has been carried out in the work [11]; the results are shown in Fig. 5.1a. It must be emphasized that in Fig. 5.2a the point $t = 0$ corresponds to the inlet of the working section ($x = 0$). In order to bring the calculation and experiment into agreement, the calculated profiles have been shifted by $t_{sh} = 0.05$ sec towards the origin. In the work [11], the calculations have been made with the standard CHEMKIN package [5].

Now we will compare calculations performed with Chemked [1] to the results [11]. The flow reactor [11] has operated under a constant pressure and the effect of walls of the working section was negligible. These are just the conditions, under which Eqs. (2.1, 4.1, 4.5, 4.11) incorporated in Chemked can be used. In our calculation, the reaction mechanism [11] is employed as well. As previously, the initial conditions are stated according to the flow rates of the carrier gas and reagents at inlets of the mixing sections. The species profiles obtained with Chemked are presented in Fig. 5.2b. To compare the calculations with the experiment [11], we will follow the recommendations [11] discussed above. As may be seen, the Chemked profiles will coincide with calculation and experiment [11], if they are shifted by $t_{sh} = 0.05$ sec. The agreement testifies that Chemked can be used for simplified description of plug flow reactors.
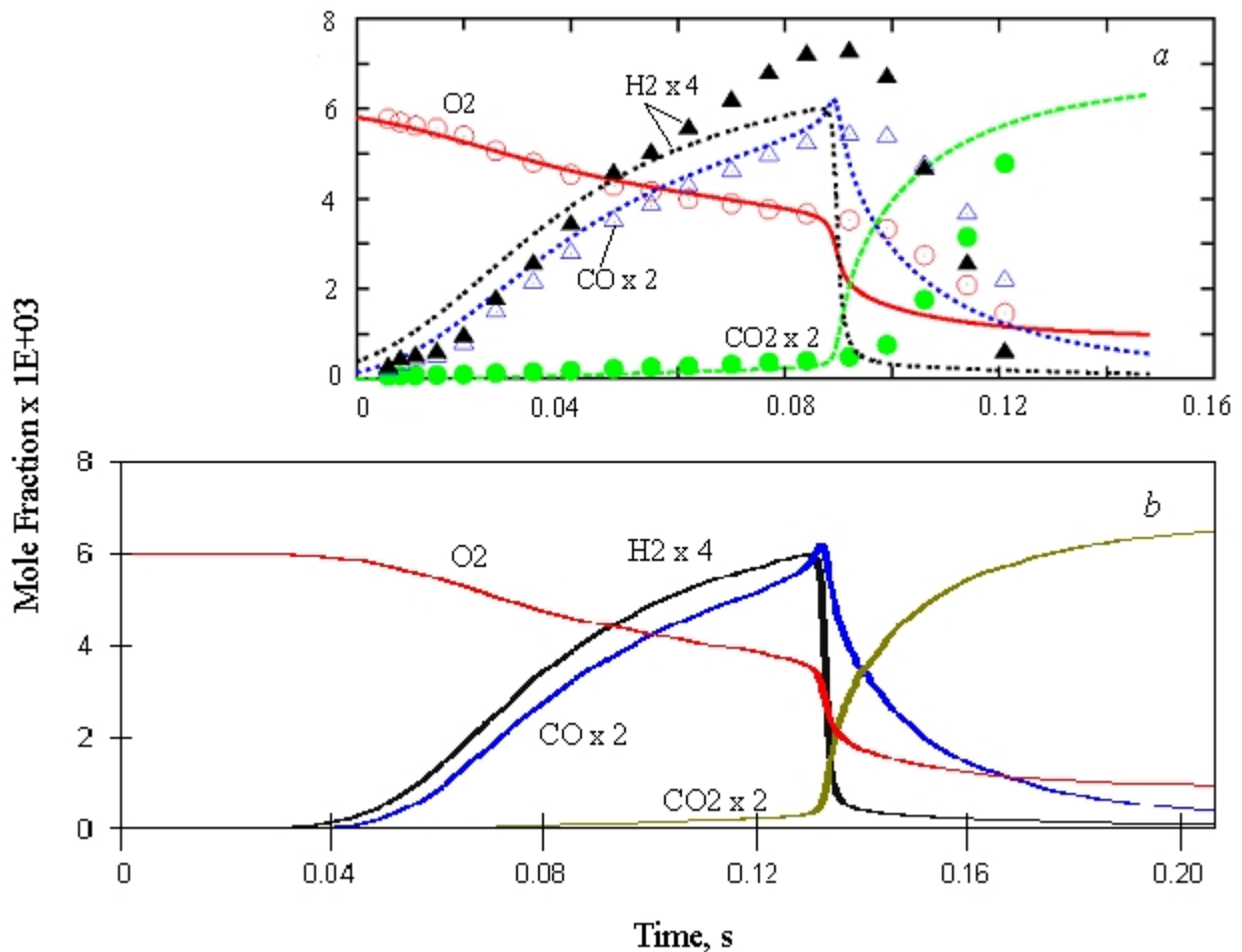
Fig 5.2. Species profiles of methanol oxidation products in plug flow reactor
Gas mixture: CH3OH/N2/O2, P = 1atm, T_0 = 1043K, $X_{CH3OH,0}$ = 3.44E-03, φ = 0.86
a - experiment [11] (symbols), calculations [11] (lines), b – this calculation

It should be noted that the discussed method for validation of reaction mechanism isn't fully substantiated due to the lack of exact initial values at the entrance of the working section. However, this method has been successfully employed in other works, for example, in [12] where the ethanol oxidation reaction mechanism was developed. The agreement between experiments and calculations is excellent.

5.2   Methanol Oxidation in Batch Reactor

Here, as in Section 5.1, we consider the kinetics of methanol oxidation using results of the work [11]. In [11], a proposed reaction mechanism was validated against experiments [13] obtained in a laboratory batch reactor. The experiments were carried out in a constant reactor volume. In addition, due to strong thermal interaction the temperatures of the gas and vessel walls were identical, and this common temperature was kept constant. Experimental [13] and calculated [11] species profiles are shown in Fig.5.3; the conditions are presented in the figure caption (φ is the equivalence ratio).

Some problems arise from the use of Chemked for description of the experiments [13]. In the constant volume batch reactor, the pressure can change due to chemical reactions, even though the gas temperature is constant. Chemked isn't meant for problems with variable pressure. Nevertheless, an approximate approach can be formulated. In the [13], the gas mixture consists of an inert gas (N_2) with small-admixed reagents (CH_3OH and O_2). Then, the chemical reactions don't cause great changes of the pressure, and numeric simulation can be made at a mean constant pressure.

Besides, there is a chemical interaction between the vessel walls and the gas; this interaction can substantially control the chemical processes. In particular, the surface reaction of hydrogen peroxide decomposition was found to be important under conditions of Fig. 5.3 [11].

(R)   H2O2 (+ wall) => H2O + 0.5 O2 $k = 0.35$ s

This isn't an elementary reaction. In order to include the reaction (R) in the reaction mechanism of the methanol oxidation we replace this with two elementary reactions.

(R1)   H2O2 => H2O + OW $k_1 = 0.35$ s
(R2)   OW + OW => O2 $k_2 = 1E+18$ mol/cm^3 s

where the symbol OW denotes atomic oxygen absorbed on the walls. In Chemked there are no tools for processing the surface reactions, and we will consider the reactions (R1, R2) as gas-phase ones. In this case the reaction (R2) must be very fast, for example, must have the reaction rate constant $k_2 = 1E+18$ mol/cm^3 s. Then the concentration OW will be always small and the action of the reactions (R1, R2) will be equal to the action of the reaction (R).

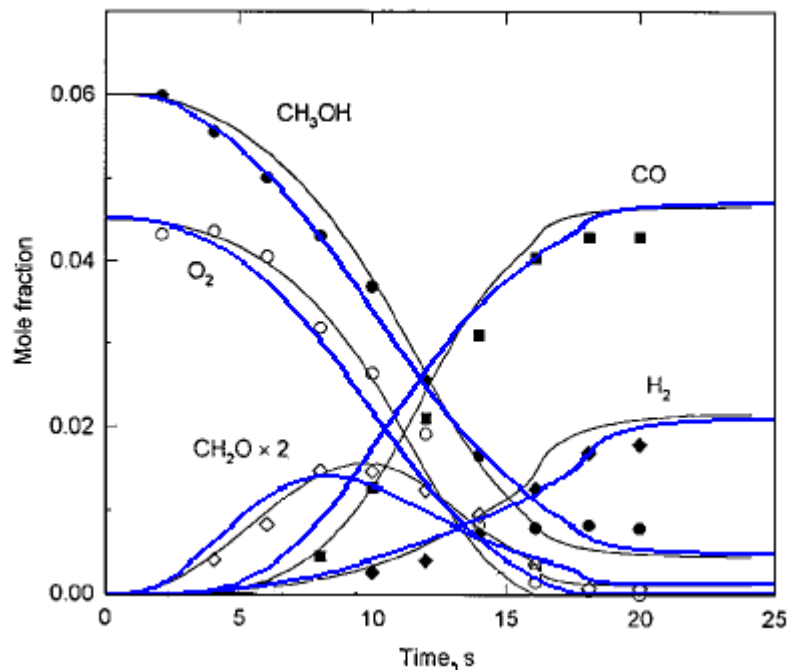Fig 5.3. Methanol oxidation in batch reactor
Gas mixture: CH3OH/N2/O2, $X_{CH3OH,0} = 0.06$, $\varphi = 2$, $T = 823K$
Calculated [11] (black lines) and measured [13] (symbols) species profiles, $P_0 = 200$ torr
Constant pressure calculation, this work (blue lines), $P = 205$ torr

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Thus, the simulation of the methanol oxidation in the batch reactor [13] is made under constant pressure ($P = 205$ toor) and constant temperature (823 K) with using the reaction mechanism [11] and the reactions (R1, R2). Generally the full set of equations Eqs. (2.1, 4.1, 4.5, 4.11) is required for description of the reactor performance. However, under discussed isothermal conditions the enthalpy equation (4.11) can be omitted and only equations (2.1, 4.1, 4.5) may be used. These equations are solved with Chemked [1]. Some calculated profiles of species mole fractions are presented in Fig.5.3 (blue lines). These results are in reasonable agreement with the experiments [13] and calculations [11], which are made with the standard CHEMKIN package [5]. This agreement testifies that Chemked can be used for simulation of constant pressure batch flow reactors.

Remark --
When using the reaction (R), we implicitly suppose that the number of oxygen atoms absorbed on the wall is much less than the number of the atoms in the gas-phase oxygen molecules. In this calculation, this requirement is always met; the mole fraction of the OW species is less than 10^{-8}.
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6 Conclusion

We have demonstrated the capability of Chemked for solving the complex problems of gas-phase chemical kinetics. This study focuses on the application of the conservation equations of species and enthalpy (1.1, 1.2) for description of gas-phase chemical reactors. Simplified computational models of the reactors are presented and validated against experimental data. Besides, the previous works [2, 3] showed that Eqs. (1.1, 1.2) also describe the reaction kinetics behind shock waves, if the shocked gas mixture consists of an inert gas with a small amount of chemically reactive substances. Thus, the equations (1.1, 1.2) can adequately simulate a wide class of reacting systems.

On the basis of this and previous studies we can summarize the requirements for the use of Eqs. (1.1, 1.2). Let us consider a gas-phase reacting system. We select a uniform area inside the system. The selected area can be at rest or can move with a gas flow; the volume and the form of the area can change due to chemical processes and gas movement. The equations (1.1, 1.2) describe the temporal behavior of the selected area, if the following conditions are satisfied.

- There are no mass fluxes through the boundary of the area; the gas mass in the area is constant.
- There are no enthalpy fluxes through the boundary of the area; the gas enthalpy in the area is constant.
- There are no temperature and species gradients within the area; the gas in the area is always uniform.
- Total gas pressure in the area is constant.

If the gas temperature in the area is constant, then only the equation (1.1) must be used for calculation of gas composition.

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Nomenclature

A	cross-sectional area	cm^2
c_{pn}	specific heat capacity at constant pressure of the nth species	(cal / g K), (J / g K)
$\hat{c}_p$	mean specific heat capacity at constant pressure	(cal / g K), (J / g K)
C_{pn}	molar heat capacity at constant pressure of the nth species	(cal / mol K), (J / mol K)
$\hat{C}_p$	mean molar heat capacity at constant pressure	(cal / mol K), (J / mol K)
C_{tot}	total gas concentration	$(1/cm^3)$, (mol/cm^3)
h_n	mean specific enthalpy of the nth species	(cal / g), (J / g)
h	mean specific enthalpy of a mixture	(cal / g), (J / g)
H_n	molar enthalpy of the nth species	(cal / mol), (J / mol)
L	reactor length	cm
$k_{j,for}$	forward rate constant of the jth reaction	depends on reaction
$k_{j,rev}$	reverse rate constants of the jth reaction	depends on reaction
K_j	equilibrium constant for the jth reaction	depends on reaction
m_n	molecular weight of the nth species	g / mol
M	mean molecular weight of a gas mixture	g / mol
P	pressure	atm
$q_{j,for,}$	forward rate of the jth reaction	$(1/ cm^3$ sec), $(mol / cm^3$ sec)
$q_{jrev,}$	reverse rate of the jth reaction	$(1/ cm^3$ sec), $(mol / cm^3$ sec)
q_j	net rate of the jth reaction	$(1/ cm^3$ sec), $(mol / cm^3$ sec)
Q	mass flux across a surface (for plug flow reactor)	g / sec
	total gas mass in the reactor volume (for batch reactor)	g
R	universal gas constant	(cal / mol K), (J / mol K)
s_n	chemical symbol of the nth species	
t	time	sec
t_r	reactor residence time	sec
T	temperature	K
u_j	rate of heat production in the jth reaction	(cal / cm^3 sec), (J / cm^3 sec)
U	axial gas velocity in a plug flow reactor	cm / sec
V	volume of a batch reactor	cm^3
w_{jn}	production rate of species n in the jth reaction	$(1/ cm^3$ sec), $(mol / cm^3$ sec)
x	axial distance	cm
X_n	mole fraction of the nth species	
$[X_n]$	molar concentration of the nth species	$(1/ cm^3)$, (mol / cm^3)
Y_n	mass fraction the nth species	
v_{jn}	stoichiometric coefficient of the nth species in the jth reaction	
ρ	mass density	g / cm^3
φ	equivalence ratio	