Gas-Phase Chemical Reactions

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

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Chemked is a program designed for creating and editing thermodynamic and chemical kinetics databases, for formation of reaction mechanisms and simulation of problems of complex gas-phase chemistry. The program will be useful for you, if you work in the field of the chemical kinetics and study the atmospheric chemistry, air pollution, combustion chemistry and waste gas treatment.
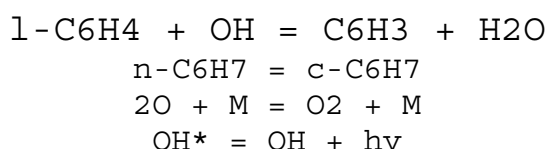
Contents

1   Introduction

Realistic description of some industrial processes and natural phenomena requires detailed knowledge of chemical conversions that take place in these systems. In many cases, modelling of the chemical processes is extremely tedious work. Chemked [1] is designed for this kind of work; the program will help the users to create reaction mechanisms and to solve problems of gas-phase chemical kinetics. Chemical reactions are the essential components that are present at each stage of the work. Because of this, we believe that the short review of general properties of chemical reactions will be useful for the Chemked users, especially, if they were not familiar with this subject previously.

A necessary part of each chemical model is the reaction mechanism that must adequately describe the chemical conversions in system under consideration. In the reaction mechanism, the chemical processes may have different level of description: from elementary reactions (one-step processes) to generalized reactions that represent multi-step chemical conversions. All reactions of these types can be used in Chemked, if they meet the following requirements.
- The stoichiometric equation of the reaction contains only integer coefficients.
- The order of forward (reverse) reaction is the sum of the stoichiometric coefficients of reactants (products).

In the following examples, the reactions are described by stoichiometric equations with integer coefficients.

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1-C6H4 + OH = C6H3 + H2O
     n-C6H7 = c-C6H7
     2O + M = O2 + M
      OH* = OH + hv
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This is the common reaction representation used in chemical kinetics databases [2, 3]. Reactions of this type are discussed in the following sections. Emphasis is given to the formal description of the reaction parameters and not to fundamental principles of chemical processes. The more detailed information on these subjects can be found in the literature (for example, [4-6]). In examples presented in the text, the reaction rate constants and the thermodynamic functions were taken from [7].

2   Chemical Reactions

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

$$\sum_n v'_{jn} \chi_n = \sum_n v''_{jn} \chi_n \, , \qquad (2.1).$$

where j is the reaction number, χ_n is the chemical symbol of species n, v_{jn} is the stoichiometric coefficient. The summations are over species involved in the reaction. The species in the left hand side of the reaction are reactants and the species in the right hand side are products. The superscript ' of the stoichiometric coefficients refers to the reactants, the superscript '' refers to the products. In this representation, all the v_{jn} coefficients are integer positive numbers or zeros. The both sides of the reaction equation are fully equivalent and can be interchanged.

In the chemical reaction, the conservation law of chemical elements (atoms) must be satisfied.

$$\sum_n v'_{jn} e_{nl} = \sum_n v''_{jn} e_{nl} \; , \tag{2.2}$$

where e_{nl} is the number of atoms of sort l in species n. The similar equation can be written for electrical charges of ions, if they are involved in the reaction.

In accordance with the law of acting masses, the forward and reverse rates and rate-of-progress of the $j$rth reaction are

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

$$q_{j,net} = q_{j,for} - q_{j,rev} \; , \tag{2.3}$$

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.

Remark ---
In Eq. (2.3), the powers of concentrations are reaction orders with respect to reactants. In more general expressions for reaction rates, the reaction orders are not necessarily equal to the stoichiometric coefficients v'_{jn} and v''_{jn}. Often, this situation shows up at description of non-elementary reactions, for example, gas-surface reactions. Nevertheless, in gas reaction systems, the approach used here is usually valid.
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The expressions (2.3) have clear physical meaning. The $q_{j,for}$ value is a frequency of events per unit volume, where a cooperative interaction of reactants yields products. Similarly, the $q_{j,rev}$ value is a frequency of events per unit volume, where a cooperative interaction of products yields reactants. And finally, $q_{j,net}$ is the total frequency per unit volume, where reactants are converted to products.

If we are interested in production of species n then the production rate of this species in the forward reaction is

$$\left(v''_{jn} - v'_{jn} \right) q_{j,for}$$

This expression reflects the fact that each event of the jth forward reaction yields the number $\left(v''_{jn} - v'_{jn} \right)$ of species n. Similarly, the production rate of the species n in the reverse reaction is

$$\left(v'_{jn} - v''_{jn} \right) q_{j,rev}$$

The total production rate is a sum of the production rates in forward and reverse reactions

$$w_{jn} = \left(v''_{jn} - v'_{jn} \right) q_{j,net} \; . \tag{2.4}$$

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The sign of w_{jn} shows the actual situation. If $w_{jn} > 0$, then the species n is produced; if $w_{jn} < 0$, then the species n is consumed.

Now we define an important reaction parameter, the reaction order (pay attention to the previous Remark on this page). The sum of the stoichiometric coefficients of reactants is the order $p_{j,for}$ of the forward reaction; the sum of the stoichiometric coefficients of products is the order $p_{j,rev}$ of the reverse reaction.

$$p_{j,for} = \sum_n v'_{jn} \qquad p_{j,rev} = \sum_n v''_{jn} \; . \qquad (2.5)$$

Units of the forward rate constant $k_{j,for}$ depend on the species concentration units and on the order of the forward reaction. If we denote the concentration units as U, then

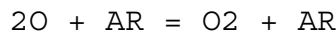$$\text{the } \; k_{j,for} \; \text{ units } \; \text{are } \; U^{-(p_{j,for}-1)} / \sec \; . \qquad (2.6)$$

Similarly,

$$\text{the } \; k_{j,rev} \; \text{ units } \; \text{are } \; U^{-(p_{j,rev}-1)} / \sec \; . \qquad (2.7)$$

The net reaction rates (Eq. 2.3) and the species production rate (Eq. 2.4) have the units of U/sec.

Example 1 ---
Consider a recombination reaction of atoms O diluted in argon. The reaction has the following stoichiometric equation

$$2O + AR = O2 + AR$$

The reaction rates are defined by Eq. (2.3)

$$q_{for} = k_{for} [O]^2 [AR], \quad q_{rev} = k_{rev} [O_2][AR], \quad q_{net} = q_{for} - q_{rev} \; .$$

The rate of species production is given by Eq. (2.4)

For atoms O: $\qquad\qquad v''_O = 0, \; v'_O = 2 \qquad w_O = -2 \, q_{net}$

For molecules O2: $\qquad\; v''_{O2} = 1, \; v'_{O2} = 0 \qquad w_{O2} = q_{net}$

For atoms AR: $\qquad\;\; v''_{AR} = 1, \; v'_{AR} = 1 \qquad w_{AR} = 0$

The units of the all reaction parameters are presented in Table1 1 with regard to the reaction orders $p_{for} = 3$ and $p_{rev} = 2$.

Table 1. Units of reaction parameters

Concentration Units	k_{for}	k_{rev}	$q_{for}, q_{rev}, q_{net}, w_O, w_{O2}$
$1/cm^3$	cm^6/sec	cm^3/sec	$1/cm^3$ sec
mol/cm^3	cm^6/mol^2 sec	cm^3/mol sec	mol/cm^3 sec

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2.2 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 process is a result of difference in energies between products and reactants. The heat of the jth reaction Q_j is defined as an amount of heat that must be exchanged

between reaction system and its surrounding to keep a fixed system temperature. Below we will consider two important cases when a reaction system is at constant pressure or at constant volume.

Constant pressure, $\Delta V \neq 0$. In this case, change in the internal energy ΔU_j must be equal to a sum of heat of reaction Q_{pj} and work $-P\Delta V$ due to expansion (contraction) of the gas volume (first low of the thermodynamics). Then the heat of reaction is

$$Q_{pj} = \Delta U_j + P\Delta V, \tag{2.8}$$

whre the subscript p indicates constant pressure. It is convenient to use the enthalpy instead of the internal energy. By definition, enthalpy of the nth species is

$$H_n = U_n + PV. \tag{2.9}$$

where H_n and U_n are the enthalpy and the internal energy of species n. Taking into account Eq.(2.9), we may rewrite Eq.(2.8) in the form:

$$Q_{pj} = \Delta H_j, \quad \Delta H_j = \sum_n (v''_{jn} - v'_{jn})H_n. \tag{2.10}$$

Constant volume, $\Delta V = 0$. Under these conditions the gas does not make any work ($P\Delta V = 0$) and the heat of reaction Q_{vj} is equal to change in internal energy.

$$Q_{vj} = \Delta U_j, \quad \Delta U_j = \sum_n (v''_{jn} - v'_{jn})U_n. \tag{2.11}$$

where the subscript v indicates constant volume process.

Rate of heat production. This value is given by the expression

$$s_j = -Q_j q_{j,net}. \tag{2.12}$$

where $q_{j,net}$ is rate-of-progress of the jth reaction, Eq.(2.3). Eq (2.12) can be rewritten in terms of production rate of species involved in reaction (Eq. 2.4).

$$s_{pj} = -\sum_n w_{jn} H_n, \tag{2.13a}$$

$$s_{vj} = -\sum_n w_{jn} U_n, \tag{2.13b}$$
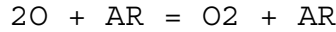
The sign of s_j shows the actual situation. If $s_j < 0$, then the heat is consumed; if $s_j > 0$, then the heat is released. The heat of reaction Q_j (like H_n and U_n) has the units of energy per mole, (J/mol) or (cal/mol). The rate-of-progress $q_{j,net}$, as well as the production rates of species w_{jn}, must have the units of molar production, (mol/cm^3 sec). Then the s_j values describe the rate of heat production in the jth reaction per unit volume, (J/cm^3 sec) or (cal/cm^3 sec).

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In many data sources, the thermodynamic functions of species are given for standard state, at pressure 1 atm. These values have a standard designation with superscript 'o', for example H^o_n. However, for ideal gases, the thermodynamic functions don't depend on pressure and the standard-state values are the actual values. Because of this in this section and in the following consideration, the superscript 'o' is not used and the attribute "standard-state" is omitted.

Example 2 --
Here we continue discussion of Example 1, assuming that gas mixture O/O2/AR is kept at constant pressure.

$$2O \ + \ AR \ = \ O2 \ + \ AR$$

Let the gas have the temperature T = 2700K. The molar enthalpies of species at this temperature are

$$H_O \ = 299.48 \ \text{kJ/mol and} \ H_{O2} = 86.21 \ \text{kJ/mol.}$$

The heat of the reaction (Eq. 2.10) is

$$Q_p = \Delta H = H_{O2} - 2H_O \ = \ \text{-512.75 kJ/mol.}$$

The equation implies that recombination of two moles of oxygen atoms yields one mole of oxygen molecules and the heat of 511 kJ. Note that the AR contribution is zero.

The rate of heat production in the reaction at T = 2700K is given by

$$s_p = 512.75 \ q_{net} \ \text{kJ/cm}^3 \ \text{sec.}$$
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2.3   Equilibrium Constant

A reacting system without external influence goes to an equilibrium state, where the net rates of all chemical reactions are zeros and, consequently, the species concentrations remain constant. Then from Eq. (2.3) at $q_{j,net} = 0$ the following relation can be obtained:

$$\frac{k_{j,for}}{k_{j,rev}} = \frac{\prod_n [X_n]_o^{v''_{jn}}}{\prod_n [X_n]_o^{v'_{jn}}} , \tag{2.14}$$

where the superscript 'o' refers to the equilibrium species concentrations. The right hand side of the Eq. (2.14) is a definition of the reaction equilibrium constant.

$$K_{cj} \ = \ \frac{\prod_n [X_n]_o^{v''_{jn}}}{\prod_n [X_n]_o^{v'_{jn}}} , \tag{2.15}$$

where K_{cj} is the equilibrium constant of the *j*th reaction. The superscript *c* indicates that the equilibrium constant has the concentration units; these units and the units of the species concentrations $[X_n]_o$ must be identical.

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The equilibrium constant can be expressed in terms of the equilibrium partial pressures $P_{n,o}$ of species involved in the reaction.

$$K_{pj} = \frac{\prod_n P_{n,o}^{v''_{jn}}}{\prod_n P_{n,o}^{v'_{jn}}} \cdot \qquad (2.16)$$

Here the superscript p refers to the equilibrium constant in the units of pressure (atm). The equilibrium constant K_{cj} is related to K_{pj} by the expression

$$K_{cj} = K_{pj}\left(\frac{C_{STP}T_s}{T}\right)^{\Delta p_j}, \quad \Delta p_j = p_{j,rev} - p_{j,for}, \qquad (2.17)$$

where T is the gas temperature, Δp_j is the difference in the orders of reverse and forward reactions, C_{STP} is the gas concentration under standard temperature $T_s = 273.15$ K and pressure $P_s = 1$ atm (101.325 kPa). If we want to express K_{cj} in the cm^{-3} units, then $C_{STP} = L$, where $L = 2.687E+19$ cm^{-3} is the Loschmidt constant. If the K_{cj} units must be mol/cm^3, then $C_{STP} = L / A$, where $A = 6.022E+23$ 1/mol is the Avogadro constant.

Remark --
If the order of the forward reaction is equal to the order of the reverse reaction ($\Delta p_j = 0$), then $K_{j,c} = K_{j,p}$.
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The equilibrium constant is a thermodynamic quantity and can be defined through the reaction thermodynamic functions.

$$K_{pj} = \exp\left(-\frac{\Delta G_j}{RT}\right), \qquad (2.18)$$

where ΔG_j is the Gibbs energy change of the jth reaction, R is the universal gas constant (R = 8.314 J/K mole or 1.987 cal K mole).

$$\Delta G_j = \Delta H_j - T \cdot \Delta S_j, \qquad (2.19)$$

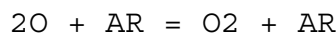where ΔH_j is defined by Eq. (2.10), ΔS_j is the entropy change of the jth reaction.

$$\Delta S_j = \sum_n (v''_{jn} - v'_{jn})S_n \cdot \qquad (2.20)$$

Here S_n is the molar entropy of species n in the units of (J/mol K) or (cal/mol K).

Example 3 ---
Here we continue discussion of the reaction from Examples 1 and 2.

$$2O + AR = O2 + AR$$

In Example 2, the change of enthalpy in the reaction at T = 2700K has been calculated (Eq. 2.10).

$$\Delta H = H_{O2} - 2H_{O} \; = \; \text{-512.75 kJ/mol.}$$

The molar entropies of species at T = 2700K are

$$S_O = \text{208.50 J/mol K and } S_{O2} = \text{280.34 J/mol K.}$$

Eq. (2.20) defines the change of the entropy in the reaction

$$\Delta S = S_{O2} - 2S_{O} \; = \; \text{-134.66 J/mol K.}$$

Then the K_p is

$$K_p = \exp\left(-\frac{\Delta G}{RT}\right) = \; 767.96 \;\; \text{atm}^{-1}.$$

Eq. (2.17) gives the equilibrium constant in concentration units

$$K_c = \frac{[O2]_o}{[O]_o^2} \; = \text{1.70E+08 (mol/cm}^3)^{-1} \text{ or 2.82E-16 cm}^3.$$

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2.4   Reaction Rare Constants

There are several types of chemical reactions that differ by their nature. For example, the reaction can be a result of molecular collision, rearrangement of molecular structure or photon absorption. It is obvious that in each case the reaction has its own pathway from reactants to products. Nevertheless, there are several common features that characterize all types of the reactions. The most important of them is the reaction activation energy E_j. The activation energy is the minimum energy of reactants when the reaction will take place. This energy is the kinetic energy of colliding reactants, the energy released by rearrangement of molecular structure or the photon energy.

Another reaction feature results from the assumption that all internal degrees of freedom (rotations, vibrations and electronic levels) of molecules are in equilibrium with translational degrees of freedom. In this case the reaction rate is a function of one temperature, namely, the gas temperature T. This assumption is valid for many practicable situations including thermal systems.

In view of this discussion, different representations of the reaction rate constants are used; among these representations the Arhenius form is used most frequently.

$$k_{j,for} = A_{j,for} T^{a_{j,for}} \exp\left(-\frac{E_{j,for}}{RT}\right), \tag{2.21}$$

where $A_{j,for}$, $a_{j,for}$ and $E_{j,for}$ are parameters that are available in chemical kinetics databases, for example [1, 2]. Eq. (2.21) includes both features discussed; the form is a function of one temperature T and contains the activation energy $E_{j,for}$.

Remark ---
Eq. (2.21) is one of the simplest expressions of the rate constant; in many cases the more sophisticated expressions must be employed. For example, there are reactions that proceed via intermediates. The decay of the intermediate goes through

several channels. The decay probability into some channels can depend on gas pressure P. In this case the reaction rate constant is a complex function of T and P. More about this and other reaction types can be found in [2-6],

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In principle, the expression (2.21) can be used for calculation of the rate constants of forward and reverse reactions; the corresponding parameters may be obtained, for example, from different independent sources. However, it is best to calculate the reverse rate constant through equilibrium constant (Eq. 2.15):

$$k_{j,rev} = \frac{k_{j,for}}{K_{j,c}} . \qquad (2.22)$$

When using this approach, the equilibrium gas composition will be predicted with confidence.

Example 4 --
Here we continue discussion of the reaction from Examples 1 - 3.

```
2O + AR <=> O2 + AR          1.00E+17        -1         0
```

The numbers after the stoichiometric equation are parameters of Eq. 2.21:

$A = 1.0E+17$ cm^6/mol^2 sec, $a = -1$, $E = 0$; at $T = 2700$k $k_{for} = 3.7E+13$ cm^6/mol^2 sec.

The reverse rate constant k_{rev} is given by Eq. (2.22)
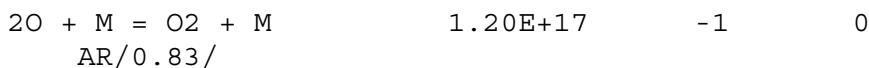
$$k_{rev} = k_{for} / K_c = 2.2E+05 \text{ cm}^3/\text{mol sec},$$

where the equilibrium constant $K_c = 1.70E+08$ cm^3/mol has been calculated in Example 3.

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3 Irreversible Reactions

Under real-world conditions every chemical reaction is reversible. If the rate constant of a forward reaction is distinct from zero, then the rate constant of the reverse reaction must be nonzero as well. This statement follows from the principle of detailed balance. Nevertheless, when simulating reaction systems, in specific cases the reverse reactions can be omitted. Reasons of the omitting are the lack of information or simplification of reaction set. Reactions, where the reverse rate constant is zero ($k_{rev} = 0$), are denoted as irreversible reactions. The use of irreversible reactions leads to disturbances in solution of chemical kinetics problems; the possible error depends on the conditions under consideration. Here we present several examples that demonstrate the effect of the reaction irreversibility.

We will consider evolution of a gas mixture that consists of AR with a minor concentration of atoms O. Only the reaction of atoms O recombination takes place in the mixture.

```
2O + M = O2 + M          1.20E+17        -1         0
    AR/0.83/
```

This is a three-body reaction; the M symbol denotes an arbitrary species in the gas mixture. Actually, this form is a compact representation of N reactions with different third body enhanced efficiencies b_{jn}, (N is the number of species in the gas mixture). The rates of the three-body reaction in general form are given by

$$q_{j,for} = k_{j,for} F_j \prod_{n=1} [X_n]^{v'_{jn}}, \qquad q_{j,rev} = k_{j,rev} F_j \prod_{n=1} [X_n]^{v''_{jn}}, \qquad F_j = \sum_{n=1}^{N} b_{jn} [X_n].$$

For the considered reaction, the reaction rates are (compare with Example 1)

$$q_{for} = k_{for} F [O]^2, \qquad q_{rev} = k_{rev} F [O_2], \qquad q_{net} = q_{for} - q_{rev},$$

where

$$F = [O] + [O2] + 0.83[AR].$$

The b_j values, which are used in the F expression, are placed below the stoichiometric equation; the default values are equal to 1. Eq. (2.21) is used for k_{for} calculations; the reverse rate constant k_{rev} is defined through k_{for} and equilibrium constant, Eq. (2.22).

Differential equations presented in Appendix are used for modeling chemical kinetics of the oxygen recombination. The equations include rate productions of species w_O and w_{O2}, and rate production of heat s_p in chemical reactions; these parameters are calculated with Eq. (2.4) and (2.13a). The differential equations have been integrated with the Chemked solver [1]; the results are species concentrations and gas temperature.

Initial conditions.
Constant pressure $P=1$ atm, initial temperature $T=2700K$, initial mole fractions [O] : [AR] = 0.05 : 0.95.
Three runs were made.
1. Constant temperature, irreversible reaction.
2. Constant temperature, reversible reaction.
3. Reversible reaction and temperature equation.

The results are presented in Figure 1. First we compare runs #1 and #2. In the initial stage, the irreversibility hasn't any effect on the species mole fractions (profiles *1* and *2*). The error can be quite considerable in the final stage, where the reversible reaction goes to a constant equilibrium value (profile *2*)), while the irreversible reaction removes atoms O completely (profile *1*).

If an irreversible reaction makes a substantial contribution to the temperature equation, the effect on the results can be more appreciable. In run #3, the final equilibrium concentration of atoms O is greater then in run #2 due to temperature elevation, profiles *2* and *3*. As a result the difference between run #1 (irreversible reaction) and run #3 (reversible reaction and temperature equation) is drastically increases, profiles *1* and *3*.
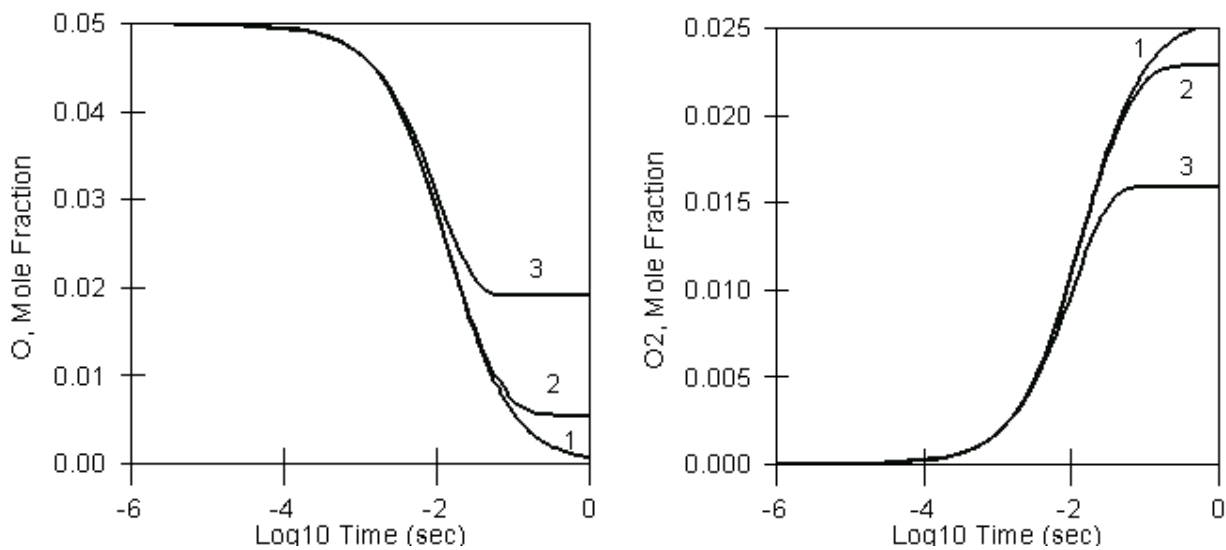

Fig. 1. Mole fraction profiles in O-AR mixture

The irreversible reactions always introduce errors in calculations. Nevertheless in many cases, the errors are negligible and the assumption of reaction irreversibility is valid. For example, the runs #1 and #2 give essentially identical results, if the initial temperature is 1500K. Thus, before using the approach of the reaction irreversibility, the user must closely examine conditions, under which the reactions will be employed, in order to make a correct decision.

Appendix. Conservation Equations for Species and Energy

In this section, the differential equations of species and energy conservation are given for problems of gas-phase chemistry at constant pressure. The equations are presented without derivation, for more information see [6, 8]. The equations are used in the Section 3 to illustrate effect of reaction irreversibility.

$$\frac{dY_n}{dt} = \frac{m_n}{\rho} \sum_j w_{jn} \; ,$$
(A.1).

$$\frac{dT}{dt} = \frac{1}{C_{mol}\hat{C}_p} \sum_j s_{pj} \; ,$$
(A.2).

where t is time, Y_n is the mass fraction of species n, m_n is the molecular weight of species n, ρ is the mixture-averaged mass density, C_{mol} is the total molar concentration, $\hat{C}_p$ is the mean molar heat capacity at constant pressure. The rate of species production w_{jn} is defined by Eq. (2.4) and must have the units of (mol/cm^3 sec), the rate of heat production s_j is defined by Eq. (2.13a). The summations are over all reactions.

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