Computer code for estimating the stationary multicomponent one-dimensional gas flow by the hypothesis of the local thermodynamic equilibrium in chemical processes

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1. Introduction. Many devices of the modern technology utilize one-dimensional stationary flows of multicomponent gas mixtures at high temperatures, ε.γ. high temperature pyrolysis, fuel boilers in old electric station, gaswelting apparatus, arc and high frequency plasmatrons, chemical reactors, nozzles of launch rockets and so on.

Designers and engineers have to know the parameters of the flow (velocity, pressure and temperature) and concentrations of the compounds in the flow. However, even application of the simplest one-dimensional stationary flow description for a reacting gas mixture happens to be quite difficult. The main reason is a lack of available and reliable numerical values of the rate constants which are necessary to describe time evolution of the species concentrations in multicomponent gases. The situation is far much better with the equilibrium constants. There are several extensive compilations (ε.γ. [1, 2]) which allow us to model high temperature gases at equilibrium quite accurately. Thus, as a first approximation to model the one-dimensional reacting gas flow a local thermodynamic equilibrium hypothesis (LTE) can be employed. The description of the code implementing

the latter approach - REACTOR - is given in the present paper.

2. Theory. The stationary one-dimensional gas flow system of equations with the external source of heat can be described by the conservation laws for mass, impulse and energy

$$\frac{d}{dx}(\rho Sv) = 0 \tag{1}$$

$$\frac{d}{dx}(p + \rho v^2)S = 0 \tag{2}$$

$$\frac{d}{dx}[(\rho v^2/2 + H_v)Sv - q] = 0 \tag{3}$$

where x is a coordinate along the axis; ρ is the mass density of the gas mixture; p is the pressure; T is the gas temperature; v is the flow velocity; S is a cross section of the pipe; H_v is the enthalpy of a unit volume; q is the power of the external energy source.

When eqs (1) to (3) are applied to multicomponent mixture one can say that ρ, p, and H are the total quantities which depend on the chemical composition of the gas. Let us assume that in the gas flow there are N chemical species formed from L elements and each species is a perfect gas (ideal association gas model). Then

$$p = \sum_i p_i \tag{4}$$

$$\rho = Mp/(RT) \tag{5}$$

$$H_v = (p/RT)H_m \tag{6}$$

where M is the average molecular mass and H_m is the molar enthalpy. Both latter quantities depend on the species mole fractions, x_i, as follows

$$M = \sum_i x_i M_i \tag{7}$$

$$H_m = \sum_i x_i H_i \tag{8}$$

$$x_i = n_i/\sum_i n_i \tag{9}$$

where summation is over all the species (i = 1, ..., N), M_i is the molecular mass, H_i is the molar enthalpy of the i-th species. It should be mentioned that H_i is a known function of temperature.

If the LTE hypothesis is accepted than the species mole fractions are the implicit functions of temperature and total pressure only. They can be found after the mole numbers n_i by minimizing the total Gibbs energy at given temperature and pressure (T, p = const)

$$\min_{n_i} G(n_i) = \sum_i n_i \left[\mu_i^o + RT \ln(p_i/p^o)\right] \tag{10}$$

subjected to mass balance constraints

$$\sum_i a_{ki} n_i = b_k \tag{11}$$

and the conditions $n_i \geq 0$. In eqs (10-11), μ_i^o is the standard chemical potential of the i-th species (a given function of the temperature), p^o is the standard pressure (101325 Pa), b_k is the total mole number of the k-th element (k = 1, ..., L), and a_{ki} is the number of the k-th element in the i-th species (a member of the formula matrix [3]). The value of b_k is should be known α πριορι and is constant along the x-axis.

3. Algorithm. It can be seen that three eqs (1) to (3) for the ideal associated gas (eqs (4) to (8)) under LTE hypothesis (eqs (9) to (11)) contain three unknowns: velocity, temperature and pressure. The density and enthalpy are the implicit functions of temperature and pressure under LTE hypothesis that allow us to estimate mole fractions. Others quantities should be given a priori.

The integration of eqs (1) - (3) reduces the task to a solution of the nonlinear algebraic equations which after employing eqs (4) to (8) can be written as follows

$$pMSv/(RT) = m \tag{12}$$

$$pS[1 + mv^2/(RT)] = I \tag{13}$$

$$SvP(mv^2 + H_m)/(RT) - Q = E \tag{14}$$

where m, I and E are the values of the mass, impulse and energy flows that must be constant along the axis and should be estimated at the initial cross section of the pipe. The symbol Q stands for the integral external heat

$$Q = \int_{x=0}^{x} dQ$$

Solving eqs (12) to (14) is possible by an iteration numerical process when the mole fractions and, thus the average molecular mass and molar enthalpy, are determined from the gas dynamics parameters, T and p of the mixture that in turn allow us to find these parameters more precisely.

It was found that before starting the numerical solution it is better to rewrite eqs (12) to (14) as follows

$$[m - (I - vm)Mv/(RT)]/m = 0 \qquad (15)$$

$$[mv^2/2 + (m/M)H_m - Q - E]/(Q + E) = 0 \qquad (16)$$

having solved the equation for pressure in the explicit form

$$p = (I - vm)/S \qquad (17)$$

It is convenient to divide eqs (15) and (16) by the factors m and (Q + E) accordingly because this improves convergence.

There are many good numerical tools for solving a system of nonlinear equations and computing the equilibrium composition of the gas mixture. To this end, ZXSSQ [4] and VCS [3] subroutines accordingly were chosen at the present work (we have had good impression for both of them for quite a time). The ZXSSQ is a minimization subroutine implementing finite-difference Levenberg-Marquardt method and does not require programming derivatives that is convenient for our problem. The objective function for ZXSSQ is chosen as the sum of squared deviations of eqs (15) and (16).

The approach discussed above was implemented in the algorithm presented below in pseudo-code (the identifiers in lower and upper case letters are different):

```
declaring subroutine to compute the deviates of eqs (15) and (16)
      EXTERNAL SS

reading initial values
  initial mole numbers of the elements b(k), k = 1, ..., L
  initial pressure p
  initial velocity v
  initial temperature T
  initial area cross section S
  initial average molecular mass M,
  initial molar enthalpy H

computing initial flows of mass, impulse and energy
      m = p*M*S*v/R/T
      I = p*S*(1. + m*v*v/R/T)
      E = S*v*p/R/T*(m*v*v/2 + H)

setting up initial estimates
      X1(1) = v
      X1(2) = T

starting loop
      DO

reading the current values
  position x
  area cross section S
  integral external heat Q

setting up parameters for ZXSSQ

starting ZXSSQ to solve eqs (15) and (16) by minimizing the sum of
squared deviates. Deviates are computed by SS which called from
inside the ZXSSQ
        CALL ZXSSQ(SS,NPar,NPar,NSIG,EPS,DELTA,MAXFN,IOPT,
     *           PARM,X1,SSQ,F,XJAC,NPoints,XJTJ,WORK,INFER,IER)

printing results
        v  = X1(1)
        T  = X1(2)
        p = (I - v*m)/S
M, H and mole fractions are computed by VCS which is called by SS

      END DO
      END

      SUBROUTINE SS(X, MM, NN, F)
      DIMENSION X(2), F(2)
X gives the current values for unknown v and P, F should return
two deviates for the given X

declaring common block to exchange variables with the main program

      v = X(1)
      p = (I - v*m)/S
      T  = X(2)
setting up parameters for VCS
calling VCS to compute equilibrium mole fractions at given p and T
      CALL VCS(0, 0, 0, MAXIT)
```

computing M and H with estimated equilibrium mole fractions

computing deviates, sum of squares of which should be minimized

```
      F(1) = (m*v**2/2d0 + m/M*H - Q - E)/(Q + E)
      F(2) = (m - P*M*S*v/R/T)/m
      RETURN
      END
```

4. Program REACTOR - calculating the pattern of the stationary four-component gas flow formed from O, H, N, and C& The program is working under MS-DOS (starting from version 3.3). 500 Kb of RAM is required and coprocessor is recommended. The more powerful computer the faster calculations. The program can be obtained by pointing World-Wide-Web browser at URL

http://www.chem.msu.su/people/rudnyi/reactor/reactor.zip

Use the utility PKUNZIP to retrieve the files as follows:

REACTOR.EXE - main module,

OHNCG.TDT - data file containing the Gibbs energies,

OHNCH.TDT - data file with the enthalpies,

REACTOR.PIF - file to run REACTOR.EXE under WINDOWS,

TEST.DAT - file to run the example described below,

README.TXT - manual.

The files OHNCG.TDT and OHNCH.TDT comprise the thermodynamic values of 63 molecules and ions which can be formed in the gas phase of O-H-N-C system. The values of $\Delta_f H^o_{298} - T*\Phi'^o$ in kJ/mol are presented as the Gibbs energies ($\Phi'^o = -(G - H^o_{298})/T$ is a free energy function) and the values of $\Delta_f H^o_{298} + \{H^o - H^o_{298}\}$ in kJ/mol are given as enthalpies. All thermodynamic values are calculated in accordance to reference book [1].

Let us consider how the REACTOR works in the next example. The mixture of molecular nitrogen with molecular oxygen (the flow of O_2 is 0.3 mol/s and the flow of N_2 is 0.7 mol/s) moves in a pipe with the constant circular cross section S = 3.14 cm^2. The

initial pressure in the pipe is 0.5 atm, the initial velocity is 2.7 m/s, and the initial temperature is 300 K. When distance (x) is changing from 0 to 10 cm, the pipe is heated with the power dQ/dx = 500 W (on each two centimeters of the way the mixture gets 1000 W of energy). From x equal to 10 cm to 11 cm the mixture gets no external power and then from x = 11 cm to 21 cm the energy is taken out by the law dQ/dx= -500 W.

The display output of the REACTOR to estimate flow pattern in the example above at x = 10 cm, when the integral external power is equal 5000 W, is shown below. Input of the user is given by ιταλιχ. For the sake of simplicity, a few lines are skipped that is shown by (...).

```
File name without extension to capture the output (NUL)? τεστ
File name without extension for full VCS output (NUL)?
Initial conditions: T/K, p/Pa, v/(m/s), S/(m^2)?
300  0.5ε5  2.7  3.14ε–4

Empty line to quit
Molecule and its initial flow in mol/s? O2  0.3
Molecule and its initial flow in mol/s? N2  0.7
Molecule and its initial flow in mol/s?
Initial element abundances (mol/s)
    e        O        H        N        C
0.00     0.60     1.00E-10  1.4     1.00E-10

Initial conditions
   p/Pa      v/(m/s)    T/K     S/(m^2)  M/(kg/mol)  H/(J/mol)
5.000E+04  2.70      300.     3.140E-04 2.921E-02  55.1

 mass/(kg/s)  impulse/(kg m/s)  energy(J/s)
   4.964E-04    15.7       0.938

x, S/(m^2), Q/W (Empty or incomplete line to quit)?
 0.1000   3.14–04  5000.

      v         p          T         M           H        SSQ
   2.700     5.0000E+04  300.0     2.9209E-02  55.10     0.9998
   2.700     5.0000E+04  300.0     2.9209E-02  55.10     0.9998
   2.700     5.0000E+04  300.0     2.9209E-02  55.10     0.9998
   6.538     4.9994E+04  730.6     2.9209E-02 1.3081E+04 0.9556
   19.95     4.9973E+04  2231.     2.9173E-02 6.7584E+04 0.7701
   32.08     4.9954E+04  3589.     2.5236E-02 1.7561E+05 0.3406
...
   50.43     4.9925E+04  4391.     2.2926E-02 2.3094E+05 3.2687E-06
   50.43     4.9925E+04  4391.     2.2926E-02 2.3093E+05 2.9452E-06
   50.43     4.9925E+04  4391.     2.2926E-02 2.3093E+05 2.9467E-06
```

```
   50.43     4.9925E+04  4391.     2.2926E-02 2.3093E+05 2.9436E-06
   50.43     4.9925E+04  4391.     2.2926E-02 2.3093E+05 2.9415E-06
   50.43     4.9925E+04  4391.     2.2926E-02 2.3093E+05 2.9489E-06
   50.43     4.9925E+04  4391.     2.2926E-02 2.3093E+05 2.9452E-06
   SSQ     INFER IER    GRAD   NFUC   NDIG      MPAR   NITER
 2.945E-06    3    0 4.521E-08   40  5.30     3.030E-03   11
 Name   mole fraction
e            0.0000142
O            0.4234635
O2           0.0101664
N            0.0067501
N2           0.5324757
NO           0.0271144
NO+          0.0000142
```

The REACTOR starts working with a dialog when a user should enter the information about the problem. The first two questions allow the user to save the output in to the files. The program uses the first file name (τεστ in the example) to echo all the display output to the file with the extension .LOG (TEST.LOG) and also to write the results in the tabular form into the file with the extension .LST (TEST.LST). The second file name is for the original output of the VCS subroutine. By default the REACTOR employs the name NUL which is the reserved MS-DOS name for the null device. It means that if the user keys in nothing (as in the example in the second question) the program will make no output to the file.

Then the user should type the initial values required (note the blank line employed to stop the cycle over the substances) and the REACTOR estimates the average molecular mass, the molar enthalpy, the mass, impulse and energy flows. In the example, the REACTOR used small non-zero values for amounts of carbon and hydrogen which should be absent because of the numerical limits of the VCS subroutine.

The main calculations (solution of the system of the nonlinear equations (15) and (16)) starts after input of the

current values of x, S and Q is finished. The ZXSSQ subroutine is changing velocity and temperature to find the values minimizing the sum of squared deviations of the eqs (15) and (16). Each move is displayed by the current values of v, T, p, M, H, and the square root of the objective function. The current values of M and H are estimated after solving the equilibrium problem by the VCS subroutine.

After the convergence criterion is reached, the final results are printed. The solution is given by the last line of values of v, T, p, M, H. Below the substances are listed with the equilibrium mole fraction more than 10^{-5}. Between, there is ZXSSQ's report on the properties of the solution that explained in details in the file README.TXT.

The REACTOR reads the data from the standard input that allows the user to automate calculations by redirecting input from the file. For example, if the user gives the command as follows

REACTOR < TEST.DAT

all the calculations will be made in a batch mode. Fig. 1 to 3 show the results which are plotted with use of the file TEST.LST by the utility XYLINE.

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9. Literature.

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