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LSENS: Multipurpose Kinetics and Sensitivity Analysis Code for Homogeneous Gas-Phase Reactions

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LSENS is a multipurpose chemical kinetics and sensitivity analysis code for the solution of complex, homogeneous, gas-phase reactions. The main features of LSENS are its accuracy, efficiency, flexibility, and convenience for treatment of many different chemical reaction models, including static system; steady, one-dimensional, inviscid flow; incident-shock initiated reaction in a shock tube with corrections for frictional losses; perfectly stirred reactor; and perfectly stirred reactor followed by a plug flow reactor. In addition, equilibrium computations can be performed for several assigned states. An implicit numerical integration method, LSODE, which works accurately and efficiently for the extremes of very fast and very slow reactions, is used to solve the "stiff" ordinary differential equation systems that arise in chemical/combustion kinetics. For static and one-dimensional flow reactions, including those behind an incident shock wave and following a perfectly stirred reactor calculation, LSENS uses the decoupled direct method to calculate the sensitivity coefficients of dependent variables and of their derivatives with respect to the initial values of dependent variables and/or the rate coefficient parameters. Solution methods for the equilibrium and postshock conditions and for perfectly stirred reactor problems are either adapted from or based on procedures built into the chemical equilibrium and applications code CEA.

Introduction

THE multipurpose kinetics and sensitivity analysis code LSENS[1–3] was developed for the solution of complex, homogeneous, gas-phase, chemical reaction problems. The motivation for developing LSENS is the continuing interest in elucidation of detailed chemical reaction mechanisms for complex reactions (such as the combustion of fuels and pollutant formation and destruction) and reduced mechanisms for specific applications (such as computational fluid dynamic simulations). Here, a detailed chemical reaction mechanism denotes the set of all elementary chemical reactions, that is, real molecular events, required to describe the process of interest.[4,5]

Mathematical descriptions of chemical kinetics problems constitute sets of coupled, nonlinear, first-order ordinary differential equations (ODEs).[4,6] The number of ODEs can be very large because of the numerous chemical species involved in the reaction mechanism. A further difficulty includes the many simultaneous reactions needed to describe the chemical kinetics of practical fuels. For example, the mechanism describing the oxidation of the simplest hydrocarbon fuel, methane, involves over 25 species and 100 elementary reaction steps.[7]

Validating a chemical reaction mechanism requires repetitive solutions of the governing ODEs for a variety of reaction conditions. Analytical solutions to the systems of ODEs describing chemical kinetics are not possible except for the simplest cases, which are of little or no practical value. Consequently, fast and reliable numerical techniques are required for chemical kinetics problems.

In addition to solving the ODEs describing chemical kinetics, it is often necessary to know how variations in either initial condition values or chemical reaction mechanism parameters affect the solution. Such needs arise in the development of reaction mechanisms from experimental data.[8] The rate coefficients are often not known with great precision, and, in general, the experimental data are not sufficiently detailed to determine accurately the rate coefficient parameters. The development of a reaction mechanism is, therefore, facilitated by a systematic sensitivity analysis, which establishes relationships between the predictions of a kinetics model and the input parameters of the problem.[6,9,10]

LSENS has been designed for accuracy, efficiency, flexibility, and convenience. A variety of chemical reaction models is considered: 1) static system; 2) steady, one-dimensional, inviscid flow; 3) reaction behind an incident shock wave, including boundary-layer correction; 4) perfectly stirred (highly backmixed) reactor; and 5) perfectly stirred reactor followed by a plug flow reactor. In addition, the chemical equilibrium state can be computed for the following assigned states: 1) temperature and pressure, 2) enthalpy and pressure, 3) temperature and volume, and 4) internal energy and volume. For static and one-dimensional flow problems, including those behind an incident shock wave and following a perfectly stirred reactor calculation, the first-order sensitivity coefficients of dependent variables and of their derivatives can be computed with respect to the initial values of the dependent variables and/or the rate coefficient parameters of the chemical reactions. A unique feature of the code is the capability of solving multiple problems in a single computer run.

LSENS is the product of an ongoing effort at NASA John H. Glenn Research Center at Lewis Field to develop and upgrade algorithms and computer codes for chemical kinetics applications. The first kinetics code, GCKP, was developed by Bittker and Scullin in 1972 (Ref. 11). This code uses the implicit integration method of Tyson[12] with some modifications due to Bittker and Scullin.[11] Subsequently, many integration methods and computer codes were developed for the efficient integration of ODEs in general, and chemical kinetics equations in particular. (See Ref. 13 for details.) GCKP was replaced with GCKP84 (Ref. 14), which uses the GEAR package,[15] as modified by Zeleznik and McBride[16] to integrate the chemical kinetics ODEs. Critical analyses and comparisons[17–21] showed that, among the methods and codes examined, LSODE[22,23] was the most efficient and accurate code for chemical kinetics applications. The solver used in GCKP84 was, therefore, replaced with LSODE, and the novel capability of performing sensitivity analysis for nonisothermal problems, that is, combustion kinetics, was incorporated into the new code, GCKP86 (Ref. 24). The sensitivity analysis computations use the decoupled direct method,[1,13,25,26] as implemented by Dunker[25,27] for isothermal kinetics and modified by Radhakrishnan[26] for combustion kinetics. This method resulted in greater efficiency and stability, with equal or better accuracy, compared to other methods of sensitivity analysis.[1,13,25,26] Many improvements and new options

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were incorporated into GCKP86, and the present version, LSENS, replaces the previous general chemical kinetics codes GCKP,[11] GCKP84 (Ref. 14), GCKP86 (Ref. 24), and GCKP87 (Ref. 26). (Details regarding code availability and procurement can be obtained at https://technology.grc.nasa.gov/software/.)

Description of Code and Capabilities

LSENS is designed for solving several problem types arising in chemical/combustion kinetics. These problem types and the options built into the code are summarized in Table 1 and briefly described hereafter. The code solves constant-density and assigned-pressure static reaction problems. In the latter case, the pressure is specified as constant, a polynomial function of up to third degree in time, or in tabular form as a function of time. For all static problems, the temperature can be similarly assigned. Alternatively, the problem can be adiabatic or the heat transfer rate specified as a polynomial function of up to fourth degree in temperature. [See Eq. (10).]

Steady, one-dimensional flow reaction problems are solved with either pressure or area profile assigned. The independent variable can be either time or axial distance. The pressure/area profile is assigned as constant or as a function of either time or axial distance, irrespective of the independent variable. For any flow problem, the temperature can be specified as constant, as a polynomial function of up to third degree in time or axial distance, or in tabular form as a function of time or axial distance. Alternatively, the flow problem can be adiabatic or the heat transfer rate to the environment prescribed as a polynomial function of temperature [see Eq. (10)] or by means of empirical correlations built into the code [see Eq. (11)]. For any flow problem, several rocket performance parameters may be computed; thus, LSENS can be used to explore the differences between kinetically limited and equilibrium computations for a given nozzle geometry.

The same heat transfer options are available for the reacting flow problem behind an incident shock wave. For this problem type, the code computes the frozen and equilibrium postshock states and includes boundary-layer corrections to account for frictional losses.

LSENS also includes provisions for studying chemical reactions in a perfectly stirred reactor (PSR). The user can perform two types of calculations: assigned mass flow rate and assigned temperature. In either case, the reactor can be adiabatic or the heat transfer rate prescribed as a polynomial function of temperature [see Eq. (10)]. The PSR problem can be followed by a one-dimensional flow reaction, that is, a plug flow reactor problem; this combination is sometimes used as a simplified representation of a gas-turbine combustor.

For all static and one-dimensional flow reactions, including those behind an incident shock wave and following a PSR calculation, LSENS will perform a systematic sensitivity analysis. In particular, first-order sensitivity coefficients [Eq. (18)] can be generated with respect to the initial condition values of dependent variables and the chemical reaction mechanism parameters.

Equilibrium computations are available for all problem types. Specifically, the equilibrium state is calculated for the following assigned states: 1) temperature and pressure, 2) mass-specific enthalpy and pressure, 3) temperature and volume, and 4) mass-specific internal energy and volume. Thus, a convenient method is provided to determine how fast and how closely the finite rate chemical kinetic process approaches the equilibrium state or to assess completeness of the reaction mechanism.

LSENS was developed on an IBM 370/3033$^{\mathrm{TM}}$ computer using the TSS$^{\mathrm{TM}}$ operating system (OS) and the Amdahl 5870$^{\mathrm{TM}}$ computer using the UTS$^{\mathrm{TM}}$ OS. The code was subsequently modified suitably to enhance portability, and it has been executed successfully on various computer systems, using different operating systems and FORTRAN compilers. (See Ref. 2 for details.) LSENS is arranged in a highly "modular" fashion, with different subprograms performing different tasks; hence, the number of subprograms is fairly large. The modular feature of the code aids in both its understanding and, if desired, its modification. Therefore, as improvements are made in any calculation procedures or methods built into the code, only the subprograms using these procedures need to be replaced. An example is the computation of thermodynamic data. The relations currently built into the code are based on fitting data over two temperature ranges. Work is now underway to extend the temperature range over which the calculations are valid.[28]

The different subprograms that comprise the LSENS package are arranged in three separate groups. The first group contains the MAIN program and those related to thermodynamic, transport, and kinetics computations. This group also includes the numerical procedures for equilibrium and postincident shock states and PSR problems; the solution methods were either adapted from or based on the chemical equilibrium and applications code, CEA.[28] The second group includes the subroutines required for sensitivity analysis; several of these routines were adapted from the code CHEMDDM.[27] The last group contains the subprograms included in the code LSODE,[22,23] which is used to solve the governing ODEs.

Communication among different subprograms is accomplished by means of calling sequences and common blocks, which are used extensively in LSENS. The use of common blocks avoids lengthy calling sequences, which can significantly deteriorate the efficiency of the program. Each subprogram contains type declarations for all

Table 1 Computational capabilities of LSENS

Problem type	Options
Constant-density static reaction and constant-pressure static reaction	Constant temperature, temperature assigned as polynomial function of time or in tabular form as function of time, adiabatic, heat transfer rate assigned as polynomial function of temperature
Assigned-pressure static reaction	Pressure assigned as polynomial function of time or in tabular form as function of time, constant temperature, temperature assigned as polynomial function of time or in tabular form as function of time, adiabatic, heat transfer rate assigned as polynomial function of temperature
One-dimensional flow reaction at constant pressure and one-dimensional flow reaction in constant-area duct	Independent variable: time or axial distance, constant temperature, temperature assigned as polynomial function of time or axial distance or in tabular form as function of time or axial distance, adiabatic, heat transfer rate assigned as polynomial func tion of temperature, heat transfer rate given by built-in correlations
One-dimensional flow reaction at assigned pressure and one-dimensional flow reaction in assigned-area duct	Independent variable: time or axial distance, pressure/area assigned as polynomial function of time or axial distance or in tabular form as function of time or axial distance, constant temperature, temperature assigned as polynomial function of time or axial distance or in tabular form as function of time or axial distance, adiabatic, heat transfer rate assigned as polynomial function of temperature, heat transfer rate computed by using built-in correlations
Reaction behind incident shock wave	Flow area profile corrected for frictional losses (laminar and turbulent boundary layers)
Perfectly stirred reactor	Assigned mass flow rate, assigned temperature, adiabatic, heat loss rate assigned as polynomial function of temperature
Perfectly stirred reactor and one-dimensional flow reaction (assigned area/pressure)	Any combination of options just given for perfectly stirred reactor problems and flow problems
One-dimensional flow reaction	Rocket performance parameters calculation
All static and flow reactions	Sensitivity analysis with respect to specified initial conditions and rate coefficient parameters, sensitivity coefficients of first-order derivatives, reaction importance list
All problem types	Equilibrium calculation for following assigned states: temperature and pressure, enthalpy and pressure, temperature and volume, and internal energy and volume

variables used within it. Such declarations are useful for debugging and provide a list of all variables that occur in a routine. The type declarations are arranged in a specific order to enhance their utility.

The remainder of this section describes briefly the computational capabilities of LSENS. Convenience features and the calculation procedures used for thermodynamic and transport properties are also discussed. Detailed descriptions of the code, the theory and numerical solution procedures built into it, its usage, and accuracy and efficiency comparisons with other methods and codes are given by Radhakrishnan,[1] Radhakrishnan and Bittker,[2] and Bittker and Radhakrishnan.[3]

Types of Chemical Reaction and Rate Coefficient

Many different types of elementary chemical reactions are considered. In addition, provision has been made for both reversible and irreversible reactions. For a reaction mechanism involving N_R elementary reactions among N_S species, the jth elementary step, $j = 1, \ldots, N_R$, can be written symbolically in the general form

$$\sum_{i=1}^{N_s} \nu'_{ij} S_i \underset{k_{-j}}{\overset{k_j}{\rightleftharpoons}} \sum_{i=1}^{N_S} \nu''_{ij} S_i, \qquad j = 1, \ldots, N_R \tag{1}$$

where ν'_{ij} is the stoichiometric coefficient, that is, number of moles, of reactant species i in reaction j, ν''_{ij} the stoichiometric coefficient of product species i in reaction j, and S_i the chemical symbol for species i. The arrows indicate the direction, that is, forward or reverse, of the chemical reaction, and k_j and k_{-j} are, respectively, the forward and reverse rate coefficients of reaction j. Because the reaction given by Eq. (1) involves all species (reacting and inert), it includes third-body collisional reactions. In addition, photochemical reactions can be specified. For each reaction j, irrespective of its type, the forward rate coefficient k_j is usually given by the empirical expression[4]

$$k_j = A_j T^{n_j} \exp(-E_j/RT) \tag{2}$$

where the preexponential factor A_j, the temperature exponent n_j, and the activation energy E_j are constants; R is the universal gas constant; and T is the temperature. Each reaction may be irreversible, that is, in the forward direction only, $k_{-j} = 0$, or reversible, that is, bidirectional. For a reversible elementary reaction, either the user may specify the reverse rate coefficient or it is computed within the code by using the principle of detailed balancing or microscopic reversibility[4]:

$$k_{-j} = k_j / K_{C,j} \tag{3}$$

where $K_{C,j}$, the concentration equilibrium constant for reaction j, is a function of only temperature for ideal gases.

Thermodynamic and Transport Properties

The thermodynamic properties of the species are computed by using the empirical equations given by Gordon and McBride.[28] For each species i, the nondimensional properties molar-specific heat at constant pressure ($\mathcal{c}_{p,i}/R$), molar-specific enthalpy ($\mathcal{h}_i/RT$), and the one-atmosphere molar-specific entropy ($\mathcal{s}_i^\circ/R$) are specified as functions of temperature as follows:

$$\mathcal{c}_{p,i}/R = a_{i,1} + a_{i,2}T + a_{i,3}T^2 + a_{i,4}T^3 + a_{i,5}T^4 \tag{4}$$

$$\mathcal{h}_i/RT = a_{i,1} + (a_{i,2}/2)T + (a_{i,3}/3)T^2 + (a_{i,4}/4)T^3 + (a_{i,5}/5)T^4 + a_{i,6}/T \tag{5}$$

$$\mathcal{s}_i^\circ/R = a_{i,1} \ln T + a_{i,2}T + (a_{i,3}/2)T^2 + (a_{i,4}/3)T^3 + (a_{i,5}/4)T^4 + a_{i,7} \tag{6}$$

where $a_{i,1}$–$a_{i,7}$ are least-squares coefficients and the degree sign denotes standard conditions (here, pressure of 1 atm). For each species, two sets of coefficients for use on two adjacent temperature intervals, 300–1000 K and 1000–5000 K, are included. The data are constrained to give the same results at 1000 K. The thermodynamic properties of the reacting gas mixture are evaluated by applying the Gibbs theorem (see Ref. 29), that is, by simply summing the contributions made by all species. For example, the mixture mass-specific enthalpy h is given by

$$h = \sum_{i=1}^{N_s} \sigma_i \mathcal{h}_i \tag{7}$$

where σ_i is the mass-specific mole number of species i, that is, number of moles of species i per unit mass of mixture.

The transport properties of the species are computed by using the empirical equations given by Svehla.[30] For each species i, the dynamic viscosity μ_i and thermal conductivity κ_i are specified as functions of temperature, in the form used by Maitland and Smith[31]:

$$\ln \mu_i = a_{i,\mu} \ln T + b_{i,u}/T + c_{i,\mu}\big/T^2 + d_{i,\mu} \tag{8}$$

$$\ln \kappa_i = a_{i,\kappa} \ln T + b_{i,\kappa}/T + c_{i,\kappa}\big/T^2 + d_{i,\kappa} \tag{9}$$

The coefficients in these equations are obtained by least-squares fitting. The gas mixture dynamic viscosity μ and thermal conductivity κ are computed using formulas suggested by Wilke,[32] Bromley and Wilke,[33] and Lindsay and Bromley.[34]

Heat Transfer Models

The heat transfer rate between a reacting system and its surroundings is, in general, a function of the reacting gas and ambient temperatures, as well as flow rate and geometry. It is most likely that exact heat exchange rates will not be known when modeling an experimental reacting system. Therefore, the main usefulness of the code will be in determining the effects of various assumed heat transfer rates. The default method is to prescribe the heat loss rate $\dot{Q}$, for static problems, or the heat loss rate per unit length in the flow direction $\dot{Q}'$, for flow problems as a polynomial function of the reacting mixture temperature:

$$\dot{Q} \text{ (or } \dot{Q}') = H_0 + H_1T + H_2T^2 + H_3T^3 + H_4T^4 \tag{10}$$

where the $\{H_k\}$ are user-specified constants. For one-dimensional flow problems, the code contains an alternate option for computing $\dot{Q}'$; the built-in procedures use the empirical expression[35]

$$\dot{Q}' = \mathcal{H} L_w (T - T_w) \tag{11}$$

where $\mathcal{H}$ is the heat transfer coefficient, L_w the perimeter of the flow cross section, and T_w the wall temperature. Standard correlations are used for the heat transfer coefficients for laminar and turbulent pipe flows, as functions of the Reynolds and Prandtl numbers (for example, Ref. 35).

Chemical Kinetics Problems

To describe the temporal or spatial evolution of homogeneous chemical reaction systems, equations are needed for species concentrations, temperature, density, pressure, and, possibly, velocity.[4] Mathematical descriptions of combustion kinetics problems constitute sets of coupled, first-order ODEs, which can be generalized as follows:

$$\frac{d\boldsymbol{y}}{d\xi} \equiv \dot{\boldsymbol{y}} = \boldsymbol{f}(\boldsymbol{y}) \tag{12}$$

In Eq. (12), $\boldsymbol{y}$ is the solution vector with N components, where N depends on the problem type, and ξ is the independent variable: time t or axial distance x. The solution vector contains appropriate mass-specific species mole numbers, $\{\sigma_i\}$, thermodynamic variables, and, when necessary, the reacting gas velocity. For clarity in presentation, the dependence of $\boldsymbol{f}$ on the rate coefficient parameters, the heat transfer rate, etc., has been suppressed.

The initial value problem is to solve for the species mass-specific mole numbers, thermodynamic properties and, for a flow problem, the velocity at one or more ξ values in a prescribed integration interval $[\xi_0, \xi_{\text{end}}]$, given the initial conditions [that is, ξ_0 and $\boldsymbol{y}(\xi_0)$], reaction mechanism, and rate coefficient parameters, where ξ_{end} denotes the endpoint of the integration interval.

Numerical Integration Procedure

LSENS uses the double precision version of the packaged code LSODE[22,23] to solve the ODEs arising in combustion chemistry. LSODE includes a variable-step, variable-order implicit Adams method and a variable-step, variable-order backward differentiation formula (BDF) method. Both methods are step-by-step methods; that is, starting with the known initial conditions $\boldsymbol{y}(\xi_0)$ at ξ_0, the methods generate a sequence of approximate solutions $\boldsymbol{Y}_n$ at the discrete points ξ_n, $n = 1, 2, \ldots$, until the end of the integration interval, ξ_{end}, is reached. Extensive experimentation showed that the BDF method is consistently superior to the Adams method for chemical kinetics applications (see Ref. 1), and is, therefore, the default method in LSENS. At each integration step $[\xi_{n-1}, \xi_n]$ the BDF method advances the numerical solution by using linear multistep formulas of the type

$$\boldsymbol{Y}_n = \sum_{j=1}^{q_n} \alpha_j \boldsymbol{Y}_{n-j} + h_n \beta_0 \boldsymbol{f}_n \tag{13}$$

In this equation, q_n is the method order for the current step, the coefficients $\{\alpha_j\}$ and β_0 depend on q_n, $\boldsymbol{Y}_{n-j}$ is the numerical solution vector at ξ_{n-j}, h_n $(= \xi_n - \xi_{n-1})$ is the step size for the current step, and $\boldsymbol{f}_n$ $[= \boldsymbol{f}(\boldsymbol{Y}_n)]$ is the approximation to the exact derivative vector at ξ_n, $\dot{\boldsymbol{y}}_n$ $[= \boldsymbol{f}(\boldsymbol{y}_n)]$.

Equation (13) is solved by using a predictor–corrector scheme, wherein at each step $[\xi_{n-1}, \xi_n]$ an initial guess $\boldsymbol{Y}_n^{[0]}$ for the solution vector at ξ_n is first produced, and then the guess is improved upon by iteration. Thus, starting with the predicted value $\boldsymbol{Y}_n^{[0]}$, improved estimates $\boldsymbol{Y}_n^{[m]}$, $m = 1, 2, \ldots$, are generated until the iteration converges. A variety of iteration techniques is provided, but for chemical kinetics applications the most efficient and accurate technique is Newton–Raphson iteration (see Ref. 1), which is given by the recursive relation

$$P\left(\boldsymbol{Y}_n^{[m+1]} - \boldsymbol{Y}_n^{[m]}\right) = \sum_{j=1}^{q_n} \alpha_j \boldsymbol{Y}_{n-j} + h_n \beta_0 \boldsymbol{f}\left(\boldsymbol{Y}_n^{[m]}\right) - \boldsymbol{Y}_n^{[m]} \tag{14}$$

where the $N \times N$ iteration matrix P is

$$P = I - h_n \beta_0 J \tag{15}$$

Here, I is the $N \times N$ identity matrix and J is the Jacobian matrix, with element $J_{i,j}$ defined as

$$J_{i,j} = \frac{\partial f_i}{\partial y_j}, \qquad i, j = 1, \ldots, N \tag{16}$$

A useful feature of LSODE is that it will estimate the elements of the Jacobian matrix by finite difference approximations, if the user chooses not to provide analytical expressions. However, this method requires $(N + 1)$ derivative evaluations for a system of N ODEs and is, therefore, much more expensive than the use of an analytical Jacobian, especially for large N (see Ref. 1). Therefore, for all problem types, LSENS contains analytical Jacobians, whose use is the default option.

At each solution step $[\xi_{n-1}, \xi_n]$ LSODE controls the error incurred in the numerical solution by ensuring that the converged solution satisfies the inequality

$$\sqrt{\frac{1}{N} \sum_{i=1}^{N} \left(\frac{d_{i,n}}{\text{RTOL}_i |Y_{i,n-1}| + \text{ATOL}_i} \right)^2} \leq 1 \tag{17}$$

where $d_{i,n}$ is the estimated local truncation error in $Y_{i,n}$, the ith solution component at ξ_n; RTOL_i and ATOL_i are, respectively, the user-supplied local relative error tolerance and local absolute error tolerance for the ith solution component; and the vertical bars denote absolute value. The local error tolerances RTOL $(= \{\text{RTOL}_i\})$ and ATOL $(= \{\text{ATOL}_i\})$ determine both the nature of the local error control performed by LSODE and the magnitude of the error introduced into the numerical solution. Both RTOL and ATOL can be specified either as scalars, so that the same error tolerances are used for all variables, or as arrays, so that different tolerances are used for different variables. For reasons discussed by Radhakrishnan[1] LSENS uses a scalar RTOL (= EMAX) and an array ATOL. For convenience, the same value of ATOL (= ATOLSP) is assigned for the mass-specific mole numbers of all reacting species. For inert species, temperature, density, and velocity, ATOL is set equal to zero.

Sensitivity Analysis

For static and one-dimensional flow reaction problems, the first-order sensitivity coefficients $\{S_{ij}$ $(= \partial Y_i / \partial \eta_j)\}$ can be computed. Here, Y_i is the numerical solution for the ith, $i = 1, \ldots, N$, dependent variable and η_j is either an initial condition value or a rate coefficient parameter [that is, A_j, n_j, or E_j, Eq. (2)]. The ODEs for the sensitivity coefficients with respect to η_j are obtained by differentiating the model equations (12), with respect to η_j and then interchanging the order of differentiation with respect to ξ and η_j. The result is

$$\frac{\mathrm{d}\boldsymbol{S}_j}{\mathrm{d}\xi} \equiv \dot{\boldsymbol{S}}_j = J\boldsymbol{S}_j + \left.\frac{\partial \boldsymbol{f}}{\partial \eta_j}\right|_{\boldsymbol{y}} \tag{18}$$

where J is the Jacobian matrix [Eq. (16)] and $\boldsymbol{S}_j = \partial \boldsymbol{Y} / \partial \eta_j$. The initial value of $\boldsymbol{S}_j$, $\boldsymbol{S}_j(\xi_0)$, depends on the sensitivity parameter η_j. If η_j is the jth element of $\boldsymbol{y}_0$, that is, an initial condition value, $\boldsymbol{S}_j(\xi_0)$ is equal to the jth column of the $N \times N$ identity matrix; if, however, η_j is a rate coefficient parameter, $\boldsymbol{S}_j(\xi_0) = 0$.

The sensitivity analysis computations use the decoupled direct method (DDM).[1,13,25,26] The DDM solves the sensitivity equations separately from, but sequentially with, the model equations. The same algorithm that solves the ODEs for the chemistry also solves for the sensitivity coefficients. The rationale for using the same solver is that the two systems of ODEs have the same Jacobian. If the BDF method of order q_n [Eq. (13)] is used to solve Eq. (18), the resulting formula for the step $[\xi_{n-1}, \xi_n]$ is given by

$$\boldsymbol{S}_{j,n} = \sum_{k=1}^{q_n} \alpha_j \boldsymbol{S}_{j,n-k} + h_n \beta_0 \dot{\boldsymbol{S}}_{j,n} \tag{19}$$

which, upon using Eq. (18), can be rewritten as

$$P\boldsymbol{S}_{j,n} = \sum_{k=1}^{q_n} \alpha_j \boldsymbol{S}_{j,n-k} + h_n \beta_0 \frac{\partial \boldsymbol{f}}{\partial \eta_j}(\xi_n) \tag{20}$$

where P is given by Eq. (15).

Note that Eq. (20) can be obtained by differentiating Eq. (13) with respect to η_j. Although the model solution vector $\boldsymbol{Y}$ is defined only at discrete points in time or space, it can still be considered as a continuous function of the $\{\eta_j\}$ (Ref. 25). Thus, the sensitivities $\{\partial Y_i / \partial \eta_j\}$ calculated from Eq. (20) are the exact sensitivities of $\boldsymbol{Y}$ (but not necessarily of $\boldsymbol{y}$) with respect to η_j, apart from computer roundoff error, provided, of course, that the Jacobian matrix is accurate. Note also that because Eq. (18) is linear, Eq. (20) is linear. Hence, the solution can be obtained explicitly; that is, without an iterative predictor–corrector procedure. Thus, unlike the calculation procedure for the model solution, there is no need to measure or control the error incurred by the sensitivity coefficients. Of course, to guarantee accuracy of the computed sensitivities, one must ensure that the model solution is sufficiently accurate.

Equations (14) and (20) show the similarity between the model and sensitivity equations. The DDM exploits this similarity by alternating the solution of Eq. (20) with that of Eq. (14). At each step

$[\xi_{n-1}, \xi_n]$ the solution to the model problem is advanced by solving equation (14). Then the new solution $\boldsymbol{Y}_n$ is used in Eq. (20) to advance the $\{\boldsymbol{S}_{j,n}\}$ over the same step. This process of sequentially advancing $\boldsymbol{Y}$ and then the $\{\boldsymbol{S}_j\}$ by the same step size is repeated until the end of the integration interval.

An important feature of LSENS is that it can be used to generate sensitivity coefficients with respect to any number of parameters from just one initial condition or one rate coefficient parameter of one reaction to the full set of all N initial conditions and all $3 \cdot N_R$ rate coefficient parameters, where N_R is the total number of reactions. Finally, the linear sensitivity coefficients of the first-order derivatives of the dependent variables, that is, $\{\partial \dot{\boldsymbol{Y}}/\partial \eta_j\}$, may also be computed. Such a capability is useful, for example, in modeling combustion–acoustics interactions, by generating the sensitivity coefficients of the heat release rate with respect to the inflow state.[36,37]

Provision is made for the user to specify a cutoff level, TINY, for the normalized sensitivity coefficients. Any normalized sensitivity coefficient that is smaller in magnitude than TINY is set equal to zero. For rate coefficient parameters, an option to tabulate and print nonzero normalized sensitivity coefficients in decreasing magnitude is provided. Thus, for each dependent variable, the user can obtain a list of reaction numbers in order of decreasing importance.

Chemical Equilibrium

The code has built-in procedures for computing the equilibrium composition for the following four assigned states: 1) temperature and pressure, 2) mixture mass-specific enthalpy and pressure, 3) temperature and specific volume, and 4) mixture mass-specific internal energy and specific volume. For cases 2 and 4, the equilibrium temperature is also determined. The code automatically performs the appropriate type of equilibrium calculation, depending on the kinetics problem being solved.

The calculation procedures for the equilibrium states were adapted from CEA.[28] The equilibrium state is obtained by minimizing either the Gibbs or Helmholtz function. In either case, the chemical equilibrium criterion that must be satisfied by the system is given by[38]

$$\sum_{j=1}^{N_s} \mu_j d\sigma_j = 0 \tag{21}$$

where μ_j is the chemical potential of species j. This minimization is subject to several constraints imposed by the conservation of atomic species (all cases):

$$b_i = \sum_{j=1}^{N_s} a_{ij}\sigma_j = b_{i,0}, \qquad i = 1, \ldots, N_E \tag{22}$$

where b_i is the total number of atoms of element i in unit mass of mixture, $b_{i,0}$ the value of b_i for the initial mixture, a_{ij} the number of atoms of element i in one molecule of species j, and N_E the total number of elements. If charged or ionic species are present in the gas mixture, the element list includes the electron in addition to the atomic species, and some a_{ij} have negative values; otherwise, all a_{ij} are positive.

For cases 2 and 4, additional constraints must be satisfied. For case 2, enthalpy conservation,

$$h = \sum_{j=1}^{N_S} \sigma_j \mathfrak{h}_j = h_0 \tag{23}$$

where h_0 is the assigned mixture mass-specific enthalpy, is used to solve for the temperature. For assigned internal energy problems (case 4), the required equation is given by energy conservation:

$$u = \sum_{j=1}^{N_S} \sigma_j \mathfrak{u}_j = u_0 \tag{24}$$

where u is the mixture mass-specific internal energy, u_0 the assigned mixture mass-specific internal energy, and $\mathfrak{u}_j$ the molar-specific internal energy of the jth species.

The resulting nonlinear algebraic equations are solved by using a descent Newton–Raphson iteration method, which automatically limits the size of the corrections at each iteration to avoid convergence difficulties. Also, to prevent negative concentrations and temperature, the code solves for the logarithm of the variables.

Incident Shock

LSENS includes an option to compute the thermodynamic state and velocity behind an incident shock. Two types of computations are performed. First, the code solves for the "equilibrium" shock conditions; that is, after the shock initiated reactions have equilibrated. The second calculation produces the "frozen" shock conditions immediately after shock passage, when the composition is unchanged from its initial value. In both cases, the postshock conditions are obtained by solving the mass, momentum, and energy conservation equations describing steady, one-dimensional, inviscid flow of an ideal gas mixture:

$$\rho_1 V_1 = \rho_2 V_2 \tag{25}$$

$$p_1 + \rho_1 V_1^2 = p_2 + \rho_2 V_2^2 \tag{26}$$

$$h_1 + V_1^2\big/2 = h_2 + V_2^2\big/2 \tag{27}$$

In these equations, which assume that the coordinate system is attached to the shock, ρ, V, p, and h are, respectively, the mixture mass density, velocity, pressure, and mass-specific enthalpy. The subscripts 1 and 2 indicate conditions upstream and downstream of the shock, respectively.

The calculation procedure for both the frozen and equilibrium states were adapted from CEA.[28] Starting with a guess for the postshock state, a Newton–Raphson iteration procedure, which automatically limits the size of the corrections to minimize convergence difficulties, is used. To avoid negative variables during the solution procedure, the equations are cast in terms of the logarithm of the variables.

Postshock Kinetics Problem

Starting with the frozen shock state, LSENS follows the progress of the chemical reaction in the shocked gas by integrating the ODEs describing one-dimensional flow with assigned area, over a prescribed time or distance interval. The flow area profile is given by a function that corrects for frictional losses: These corrections are included for both laminar and turbulent boundary layers.[2,39–41]

PSR

Steady-state PSR computations can be performed for either a specified mass flow rate or a specified reactor temperature. In the former case, the code solves for the mixture composition and temperature at the reactor exit. In the latter case, the mass flow rate through the reactor and exit mixture composition are computed. The problem type is identified by examining the input parameters required for problem solution. For steady operation of the PSR and both problem types outlined earlier, the governing algebraic equations are obtained from the conservation equations for species concentrations and energy:

$$\dot{m}\left(\sigma_i - \sigma_i^*\right) = W_i \mathcal{V}, \qquad i = 1, \ldots, N_{\mathrm{RS}} \tag{28}$$

$$\dot{m}(h - h^*) = -\dot{Q} \tag{29}$$

In these equations, $\dot{m}$ is the mass flow rate through the reactor, W_i is the molar rate of production of species i per unit volume, $\mathcal{V}$ is the reactor volume, N_{RS} is the total number of reacting species, $\dot{Q}$ is the heat loss rate from the reactor, and the asterisk denotes inlet conditions. The heat loss rate can be specified as a polynomial function of up to fourth degree in reactor temperature. [See Eq. (10).]

To solve the system of nonlinear algebraic equations, LSENS uses essentially the same Newton–Raphson iteration technique that is built into CEA[28] for computing the equilibrium state. In particular, to reduce convergence difficulties, the method automatically limits the size of the corrections. Also, to avoid negative results, the code solves for the logarithm of the variables. Starting with conditions close to the equilibrium state, a series of PSR computations is performed until the desired mass flow rate or reactor temperature is reached. This technique is used to minimize the possibility of convergence to a false solution, one that is mathematically correct but physically unrealistic. The routine includes several tests and, when necessary, restarts of the calculation, to ensure that the solution is physically meaningful. Finally, LSENS includes tests for possible blowout of the chemical reaction within the reactor.

Combined PSR and Plug Flow Problem

A plug flow calculation can be performed after a PSR problem in a single computer run. Such a two-step process is sometimes used as a simplified model of a gas-turbine combustor. To solve the combined PSR and plug flow problem, the code first performs a PSR calculation, using the necessary input information for this problem type, and then solves the ODEs governing one-dimensional inviscid flow. For the flow problem, and sensitivity analysis computations, the code uses the PSR solution as the initial, that is, inflow, conditions.

Code Usage

Two input data files are normally required to execute the code. The first one, referred to as the standard thermodynamic data file, must contain the chemical symbol and composition, molecular weight, and thermodynamic data for each species. The second file, the problem data file, must give information about, and data required by, the problem(s) to be solved. A third input file, the transport properties data file, which contains transport property data, is required for certain computations. Standard thermodynamic and transport properties data files, containing data from the most recent database of the code CEA[28] for many species in the C–H–N–O system, are supplied with LSENS. However, the user has the option of specifying thermodynamic data for some (or all) species by including them in the problem data file. Thus, the user has a convenient means of temporarily changing any thermodynamic data or adding new species without modifying the standard file.

The problem data file must specify the problem type and provide the data needed to solve the problem. This information includes the chemical reaction mechanism, rate coefficient parameters, third-body collisional efficiencies, and inert species (if any). The user must also provide details of the problem, including the independent variable for a flow problem; assigned-variable, that is, density, pressure, or area profile; temperature data, if a temperature profile is to be specified; heat transfer data, if heat transfer is to be calculated; optional information such as the input units and output units (cgs, SI, or U.S. customary); and output controls. For a PSR problem, the desired reactor conditions (mass flow rate or temperature) should be specified and data given that tell the code when intermediate solutions are needed. The latter option provides a convenient method of obtaining reactor operating conditions as a function of residence time in a single computer run.

The preceding information must be followed by the initial (or inlet) conditions, including mixture composition, which may be specified by means of mole fractions, mass fractions, fuel–oxidant equivalence ratio, or fuel–oxidant mass ratio. For static and flow problems, the required integration controls must also be specified. Finally, if sensitivity analysis is required, the problem data file must include lists of the parameters with respect to which sensitivity coefficients are to be computed and of the dependent variables of interest.

For normal code usage, the user will set only two integration controls: the local relative error tolerance for all variables (EMAX) and the local absolute error tolerance for all reacting species (ATOLSP). It is clear from Eq. (17) that the magnitudes of the two error tolerances control the accuracy of the numerical solution. In addition, LSODE controls only the estimated local error, the error committed on a single step, starting with data regarded as exact, whereas the quantity of general interest is the global error, which is the deviation of the numerical solution from the exact solution. The latter error is neither measured nor controlled by the code. The user is, therefore, advised to be conservative in selecting EMAX and ATOLSP, especially if performing sensitivity analysis during late heat release or equilibration; for example, formation of nitrogen oxides (NO_x) becomes significant only during these regimes. (See Ref. 1 for details.) In particular, the ATOLSP/EMAX ratio must be sufficiently small to ensure accuracy in the concentration of trace species such as NO_x (Refs. 1, 18, and 21). However, the computational cost generally increases with increased accuracy requirements. Some experimentation may be necessary to optimize the local error tolerances.[1,2]

If multiple problems are to be solved during a single execution of the code, the required data for the second and subsequent cases depend on the information, if any, that can be used from the preceding case(s). The code was designed to minimize the amount of input data, especially when they are the same for two or more consecutive cases. Thus, for example, the user need not provide the reaction mechanism when it is either identical to that used on the preceding case, or can be obtained from it by adding reactions or modifying rate coefficient parameters.

Illustrative Test Problems

In addition to the thermodynamic and transport properties data files, two problem data files are provided with LSENS, to illustrate the problem types that can be solved by the code and the options built into it. These data files also help elucidate construction of the problem data file required to execute the code. To demonstrate the capability of solving multiple problems in a single run, both problem files contain many test cases, as discussed hereafter.

The first data file contains 16 kinetics-only, that is, no sensitivity analysis, test cases, which are summarized in Table 2. In Table 2, N_R is the total number of elementary reactions in the reaction mechanism, N_S the total number of species, N the total number of ODEs solved, and CPU the execution time (i.e., not including the CPU time required for preprocessing and input/output) in seconds on an SGI Octane$^{\text{TM}}$ computer with the MIPS R12000$^{\text{TM}}$ processor. It is clear from Table 2 that the problem size varies from a simple case involving one reaction among three species (problem 1) to one involving 42 species participating in 143 reactions (problem 10). In addition to the CPU times given in Table 2, detailed accuracy and efficiency comparisons with other methods and codes for kinetics-only calculations are available in Ref. 1.

Table 2 also illustrates the variety of problem types that can solved by LSENS and the different options built into it. For example, problem 1 shows use of the shock-kinetics option and boundary-layer correction for area. Different types of static and one-dimensional flow reactions are also considered: constant-density static (problems 10, 13, and 14), assigned-pressure static (problem 5), constant-pressure flow (problems 6 and 9), constant-area flow (problems 2, 3, and 12), assigned-pressure flow (problem 4), and assigned-area flow (problems 1, 7, 8, 11, 15, and 16). Problem 11 demonstrates a PSR calculation. The various options for specifying temperature are also illustrated (problems 8, 9, and 13), as are the different heat transfer models (problems 2–5 and 11). Finally, the use of other options built into LSENS is shown by these test cases. (Details are not included in Table 2.) For example, the equilibrium option for the different assigned states is demonstrated in cases 6, 9, 13, and 14 and calculation of rocket performance parameters in case 11.

The second data file contains nine sensitivity analysis test cases, which are summarized in Table 3. Here, N_P is the total number of sensitivity parameters, that is, initial conditions and rate coefficient parameters. The first six cases are isothermal problems, for which sensitivity analysis results obtained with different methods and codes and the required execution times are available. (See Ref. 1 for details.) For cases 1 and 2, analytical solutions have also been derived. Thus, these six problems serve as useful test cases for assessing accuracy and efficiency. Excellent agreement was obtained

Table 2 Description of kinetics-only test problems supplied with LSENS

		Problem parameters			
Test problem	Description of problem	N_R	N_S	N	CPU, s
1	Dissociation of bromine in a shock tube	1	3	5	<0.01
2	Hydrogen–air combustion in constant-area supersonic flow with heat transfer	36	18	19	0.013
3	Same problem as case 2, but with a larger reaction mechanism, obtained by adding reactions to mechanism of case 2	37	18	19	0.013
4	Hydrogen–oxygen combustion in subsonic flow at assigned pressure with heat transfer	18	8	11	0.015
5	Static, rich methane–air combustion at assigned pressure with heat transfer	133	39	41	0.12
6	Lean methane–air adiabatic combustion in supersonic flow at constant pressure	133	39	41	0.11
7	Same problem as case 6, except that the area obtained from case 6 is assigned as input	133	39	42	0.18
8	Same problem as case 6, except that the area and temperature obtained from case 6 are assigned as input	133	39	41	0.11
9	Constant-temperature, constant-pressure, methane–air reaction in supersonic flow	133	39	40	0.050
10	Constant-density, static methanol–air adiabatic combustion	143	42	42	0.090
11	PSR combustion of a rich propane–air mixture, followed by supersonic expansion of the combustion products through a diverging nozzle with heat loss	136	42	44	0.050, 0.084[a]
12	High-temperature, adiabatic air ionization reaction in constant-area subsonic flow	12	12	15	<0.01
13	High-temperature, high-pressure, static reaction of carbon monoxide–hydrogen mixture at constant density and constant temperature	23	13	13	<0.01
14	Constant-density, adiabatic, static problem involving photolytic ignition of hydrogen–oxygen mixture at low initial temperature	20	8	9	0.015
15	Methane–air adiabatic combustion in supersonic flow, with assigned duct area and output required at axial locations corresponding to specified values of duct area	133	39	42	0.13
16	Same problem as case 15, except here output is required at specified axial positions	133	39	42	0.13

[a] For problem 11, the first execution time given is for the perfectly stirred reactor problem, and the second for the flow problem.

Table 3 Description of sensitivity test problems supplied with LSENS

		Problem parameters				
Test problem	Description of problem	N_R	N_S	N	N_P	CPU, s
1	Constant-volume, isothermal reaction, $A = B$	2	2	2	4	<0.01
2	Constant-volume, isothermal reaction, $A = B = C$	4	3	3	4	<0.01
3	Constant-volume, isothermal pyrolysis of ethane, using a simplified mechanism	5	7	8	4	<0.01
4	Constant-volume, isothermal reaction of a methane–oxygen–argon mixture containing trace concentrations of carbon dioxide and hydrogen	44	14	13	44	0.058
5	Constant-volume, isothermal oxidation of a formaldehyde–carbon monoxide mixture	25	15	14	25	<0.01
6	Constant-volume, isothermal reaction of a wet carbon monoxide–oxygen–nitrogen mixture	52	12	11	58	0.12
7	Adiabatic, constant-pressure isomerization reaction with simplified rate coefficient expression that permits analytical solution	1	2	4	7	<0.01
8	Constant-pressure, adiabatic, static ignition of a stoichiometric hydrogen–air mixture, seeded with 0.45% nitric oxide	40	19	20	20	0.19
9	Adiabatic, constant-density, static combustion of a shock-heated, near-stoichiometric benzene–oxygen–argon mixture	120	40	42	51	0.90

for all six cases between the LSENS and literature results.[1] The last three cases are nonisothermal problems, which illustrate the application of sensitivity analysis to combustion kinetics. Case 7 describes a simple nonisothermal problem whose analytical solution is known.[1,13,26] For cases 8 and 9, which use more realistic combustion chemistry, sensitivity coefficients were generated by using finite difference approximations.[1] The results produced by LSENS showed excellent agreement with the analytical solutions for both the model problem and the sensitivity coefficients with respect to all four initial conditions and the three rate coefficient parameters of the reaction (case 7) and with the finite difference solutions (cases 8 and 9).[1]

Extensive accuracy and efficiency comparisons of the sensitivity analysis method built into LSENS with other methods and computer codes have also been performed for both isothermal and nonisothermal reactions.[1,13,26] In particular, comparisons of the computational work required by a systemic sensitivity analysis method, such as the DDM used here, with those required by the brute force method of varying one parameter at a time, show the significant savings in computational time that can be realized by use of the former method. For example, case 9, which describes the ignition and subsequent combustion of a benzene–oxygen–argon mixture, consists of 120 reversible reactions among 39 reacting species and the inert species argon. To solve for the dependent variables required 6.3 s of execution time on the Amdahl 5870™ computer. To solve for the dependent variables and sensitivity coefficients with respect to all of the 402 possible problem parameters, that is, all 42 initial conditions (40 species mass-specific mole numbers, density, and temperature) and all 360 rate coefficient parameters, required 246 s. This execution time may be compared to the more than 2500 s that would be required by a finite difference method wherein parameters are varied one at a time.

Conclusions

The multipurpose kinetics and sensitivity analysis code LSENS, which has been developed for complex, homogeneous, gas-phase reactions, was described. The code has been designed for a variety of reaction models: static system; steady, one-dimensional, inviscid flow; reaction initiated by an incident shock; PSR; and PSR followed by a plug flow reactor. In addition, the equilibrium state can be computed for several assigned states and systematic sensitivity analysis performed for both static and flow problems. The different capabilities and computational procedures built into the code and its usage were described briefly. Standard thermodynamic and transport properties data are provided with the code, as are two problem data files that illustrate the different problem types that can be solved by, and options built into, the code.

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