Computation of Exhaust Gas Constituents of Diesel Engine

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ABSTRACT

Focus on this paper is to develop an analytical tool from first principles for free energy minimization technique to aid as a design tool for diesel engines operating on diesel fuel and oxidizer being atmospheric air. It is emphasized in this work that understanding has to be attained from first principle and computer program be developed, calibrated with experimental results/validated with literature and calibrated code be further used for conceptual design for futuristic engines or analyzing the existing engine.

Keywords - Equilibrium composition, computation, diesel, first principle, calibrated code.

1. INTRODUCTION

R & D (Research and Development) program on diesel engines has been initiated and making rapid strides in the Department of Mechanical Engineering of Christ University Faculty of Engineering. The major in-house funded research program is in progress [1]. In phase one, state-of-the-art dynamometer test facility is being established; in phase two, detailed engine testing would be carried for performance evaluation of the engine characteristics and exhaust gas analysis measurements with six gas analyzer. In phase three, engine mod is planned with zirconium oxide coating on piston top and again testing the engine to establish value addition in terms of specific fuel consumption and pollutants. Low Heat Rejection Engines research provides the existing base line engines with value addition and pros and cons of thermal carrier coating are detailed in [2].

A fast and robust tool for computing equilibrium concentrations of combustion products can greatly aid the design, development and analyses of new engine operating regimes, and engines fuelled by diesel. Chemical equilibrium of a closed reacting system at a given pressure and temperature can be computed by minimizing the Gibbs free energy of the system or by using the approach of equilibrium constants using a set of reactions. In this paper Gibbs free energy technique is used in the mathematical model. A computer program developed by Gordon and Mcbride [3] has had a worldwide acceptance for any reacting chemical system including liquid rocket engines for rocket and space applications. Even though program is available in net for use, keeping in mind our R & D objective of understanding from first principles , calibrating the code with experiment for diesel engine conceptual design, this program is modified, developed and successfully run in power Fortran on laptop platform. It has taken almost ten months of developmental efforts. The program is capable of doing the following kinds of

problems: The thermodynamic states may be specified by the assigning thermodynamic state functions (a) Temperature and Pressure (TP), (b) Enthalpy and Pressure (HP) (c) Entropy and Pressure (SP) (d) Temperature and Volume or Density (TV) (e) Internal Energy and Volume or Density (UV) (f) Entropy and Volume or Density (SV).

In the ongoing R & D program, an attempt is made to understand from first principles and a computer program is developed and literature validation is done. Convergence has been obtained in maximum of eighteen iterations on a lap top platform. A good match between the developed program and literature [3] case study results has been obtained. In this paper focus is on to elucidate the mathematical formulation and apply it to diesel engines.

2. MATHEMATICAL FORMULATION

The mathematical formulation is as in the following and based on first principles:

2.1 Equations describing chemical equilibrium

Chemical equilibrium is usually described by either of two equivalent formulations: equilibrium constants or minimization of free energy. If a generalized method of solution is used, the two formulations reduce to the same number of iteration equations. However, several disadvantages of the equilibrium constant method are: numerical difficulties with use of components and more difficulty in testing for presence of some condensed species, and much more difficulty in extending the generalized method for non-ideal equations of state. For these reasons, the free-energy minimization formulation is used. The condition for equilibrium may be stated in terms of any of several thermodynamic functions such as the minimization of the Gibbs free energy or Helmholtz free energy or the maximization of entropy. If one wishes to use temperature and pressure to

characterize a thermodynamic state, the Gibbs free energy is most easily minimized in as much as temperature and pressure are its natural variables. Similarly, the Helmholtz free energy is most easily minimized if the thermodynamic state is characterized by temperature and volume (or density).

2.2 Equation of state

We assume all gases to be ideal and that interactions among phases may be neglected. The equation of state for the mixture is:

$$PV = nRT$$
$$Or$$
$$\frac{P}{\rho} = nRT \qquad \cdots \cdots \cdots (1)$$

Where, P is pressure (N/m^2), V specific volume (m^3/kg), n moles (kg-mole/kg), T temperature (K) and ρ density (kg/m^3).

Eq. (1) is assumed to be correct even when small amounts of condensed species (up to several percent by weight) are present. In this event, the condensed species are assumed to occupy a negligible volume and exert a negligible pressure compared to the gaseous species. In the variables V, n, and p, the volume and moles refer to gases only while the mass is for the entire mixture including condensed species. The word "mixture" will be used to refer to mixtures of species as distinguished from mixtures of reactants which will be referred to as "total reactants**."** The molecular weight of the mixture M is then defined to be:

$$M = \frac{1}{n} \qquad \cdots \cdots \cdots (2)$$

Where,

$$n = \sum_{j=1}^{m} n_j \qquad \cdots \cdots \cdots (3)$$

n_j is the number of kilogram-moles of species j per kilogram of mixture. An equivalent expression for M is:

$$M = \frac{\sum_{j=1}^{n} n_j M_j}{\sum_{j=1}^{m} n_j} \qquad \cdots \cdots \cdots (4)$$

Where, M$_j$ is the molecular weight of species j. As implied in equation (4), among the n possible species which may be considered, gases are indexed from 1 to m and condensed species from m + l to n.

2.3 Minimization of Gibbs free energy

For a mixture of n species, the Gibbs free energy per kilogram of mixture (g) is given by:

$$g = \sum_{j=1}^{n} \mu_j n_j \qquad \cdots \cdots \cdots (5)$$

Where, the chemical potential per kilogram-mole of species j is defined to be:

$$\mu_j = \left(\frac{\partial g}{\partial n_j} \right)_{T,P,n\, i \neq j} \qquad \cdots \cdots \cdots (6)$$

The condition for chemical equilibrium is the minimization of free energy. This minimization is usually subject to certain constraints such as the following mass balance constraints:

$$\sum_{j=1}^{m} a_{ij} n_j - b_i^0 = 0 \qquad i = 1, \cdots \cdots, l \qquad \cdots \cdots (7)$$

$$b_i - b_i^0 = 0 \qquad i = 1, \cdots \cdots, l \qquad \cdots \cdots (7a)$$

Where, the stoichiometric coefficients a$_{ij}$ are the number of kilogram-atoms of element i per kilogram-mole of species J and b$_i^0$ is the assigned number of kilogram-atoms of element i per kilogram of total reactants and

$$b_i = \sum_{j=1}^{n} a_{ij} n_j \qquad i = 1, \cdots \cdots, l \qquad \cdots \cdots (7b)$$

is the number of kilogram-atoms of element i per kilogram of mixture.

Let us define a term G to be:

$$G = g + \sum_{i=1}^{l} \lambda_i \{ b_i - b_i^0 \} \qquad \cdots \cdots (8)$$

Where λ_i are Lagrangian multipliers.

2.4 The condition for equilibrium

The condition for equilibrium becomes:

$$\partial G = \sum_{j=1}^{n} \left\{ \mu_i + \sum_{i=1}^{l} \lambda_i a_{ij} \right\} \partial n_j + \sum_{i=1}^{l} \{ b_i - b_i^0 \} \partial \lambda_i = 0$$
$$\cdots \cdots (9)$$

Treating the variations δ_{n_j} and δ_{λ_i} as independent gives:

$$\mu_j + \sum_{i=1}^{l} \lambda_i a_{ij} = 0 \qquad j = 1, \cdots \cdots, n \qquad \cdots (10)$$

And also the mass balance Eq. (7a). Based on the assumptions in the equation of state, the chemical potential may be written as:

$$\mu_j = \mu_j^0 + RT \ln \left\{ \frac{n_j}{n} \right\} + RT \ln P_{atm} \qquad j = 1, \cdots \cdots m$$

$$= \mu_j^0 \qquad j_0 = m + 1, \cdots \cdots, n \qquad \cdots \cdots (11)$$

Where, $\mu^o{}_j$ for gases (j= 1 to m) and for condensed phases (j > m) is the chemical potential in the standard state. For a gas, the standard state is the hypothetical ideal gas at unit fugacity and for a pure solid or liquid; the standard state is the substance in the condensed phase under a pressure of one atmosphere. The numerical values of $\mu_{o\,j}$ that are generally found in the literature depend partly on a term involving units of atmospheres. Therefore, to be consistent, pressure P_{atm} in Eq. 11 must be in units of atmospheres. Eqs.(7 and 10) permit the determination of equilibrium compositions for thermodynamic states specified by an assigned temperature T_o and pressure P_0. That is, in addition to equations (7) and (10), we have the pair of trivial equations:

$$T = T_O \qquad \cdots \cdots \cdots (12a)$$

$$P = P_0 \qquad \cdots \cdots \cdots (12b)$$

However, the thermodynamic state may be specified by assigning any two state functions. For example, the thermodynamic state corresponding to constant pressure combustion is specified, instead of by equation (12), by:

$$h = h_o \qquad \cdots \cdots \cdots (13a)$$

$$P = P_0 \qquad \cdots \cdots \cdots (13b)$$

Where, h is the enthalpy of the mixture and h_o is a constant equal to the enthalpy of the reactants. The expression for h is:

$$h = \sum_{j=1}^{n} n_j \left\{ hT^o \right\}_j \cdots \cdots \cdots \cdots (14)$$

The thermodynamic state is specified by:

$$S = S_0 \ldots \ldots \ldots (15a)$$

$$P = P_0 \ldots \ldots \ldots (15b)$$

$$S = \sum_{j=1}^{n} n_j S_j \qquad \cdots \cdots (16)$$

Where,

$$S_j = \left\{ S_T^0 \right\}_j - R \ln \left\{ \frac{n_j}{n} \right\} - R \ln P_{atm} \qquad j = 1, \cdots, m$$

$$= \left\{ S_T^0 \right\}_j \qquad j = m + 1, \cdots \cdots, n \qquad \cdots \cdots (17)$$

and $\{ S_T^0 \}_j$ is the standard state entropy for species J. The equations required to obtain composition are not all linear in the composition variables and therefore an iteration procedure is generally required. In the iteration procedure described in the following section it will be convenient to treat n as an independent variable.

2.5 Gibbs iteration equations

The Newton-Raphson method is used to solve for corrections to initial estimates of compositions n_j, Lagrangian multipliers λ_i, moles n and when required temperature T. This method involves a Taylor series expansion of the appropriate equations with all terms truncated containing derivatives higher than the first. The correction variables used are $\Delta \ln n_j$ (j = 1,..., m), Δn_j (j = m + 1,. ., n), $\Delta \ln n$, $\pi_i = - \lambda_i /RT$ and $\Delta \ln T$. There is no restriction to start each iteration with the estimate for the Lagrangian multipliers equal to zero inasmuch as they appear linearly in Eq. (10). After making dimensionless those equations containing thermodynamic functions, the Newton-Raphson equations obtained from Eqs (10), (7), (3), (13a), and (15a) are:

$$\Delta \ln n_j - \sum_{i=1}^{l} a_{ij} \pi_i - \Delta \ln n - \left[\frac{\left\{ hT^o \right\}_j}{RT} \right] \Delta \ln T$$

$$= \left\{ \frac{\mu_j}{RT} \right\} \qquad \cdots \cdots j = 1, \cdots \cdots, m \qquad \cdots \cdots (18)$$

$$- \sum_{i=1}^{l} a_{ij} \pi_i - \left[\frac{\left\{ hT^o \right\}_j}{RT} \right] \Delta \ln T$$

$$= - \left\{ \frac{\mu_j}{RT} \right\} \qquad \cdots \cdots j = 1, \cdots \cdots, n \qquad \cdots (19)$$

$$\sum_{j=1}^{m} a_{kj} n_j \Delta \ln T + \sum_{j=m+1}^{n} a_{kj} \lambda n_j = b_k^o - b_k$$

$$\cdots \cdots k = 1, \cdots \cdots, l \qquad \cdots (20)$$

$$\sum_{j=1}^{m} n_j \Delta \ln n_j - n \Delta \ln n = n - \sum_{j=1}^{m} n_j \qquad \cdots \cdots (21)$$

$$\sum_{j=1}^{m} \left[\frac{n_j \left(H_T^{0} \right)_j}{RT} \right] \Delta \ln n_j + \sum_{j=m+1}^{n} \left[\frac{n_j \left(H_T^{0} \right)_j}{RT} \right] \Delta n_j +$$

$$\sum_{j=1}^{m} \left[\frac{n_j \left(C_p^{0} \right)_j}{R} \right] \Delta \ln T = \frac{h_o - h}{RT} \qquad \cdots\cdots (22)$$

$$\sum_{j=1}^{m} \frac{n_j S_j}{R} \Delta \ln n_j + \sum_{j=m+1}^{n} \frac{\left(S_T^{0} \right)_j}{R} \Delta n_j +$$

$$\sum_{j=1}^{n} \frac{n_j \left(C_p^{o} \right)_j}{R} \Delta \ln T = \frac{S_0 - S}{R} + n - \sum_{j=1}^{m} n_j \qquad \cdots (23)$$

2.6 Reduced Gibbs iteration equations

For problems with assigned thermodynamic states (T,P), (H,P) or (S,P), various combinations of Eqs. (18) to (23) could be used to obtain corrections to estimates. However, for chemical systems containing many species, it would be necessary to solve a large number of simultaneous equations. This large number of equations can be reduced quite simply to a much smaller number by algebraic substitution. This is accomplished by substituting the expression for λ in n_j obtained from Eq. (18) into Eqs. (20) to (23). Including equation (19) written with signs reversed, the resulting reduced numbers of equations are:

$$\sum_{i=1}^{l} \sum_{j=1}^{m} a_{kj} a_{ij} n_j \pi_i + \sum_{j=m+1}^{n} a_{kj} \Delta_{nj} + \sum_{j=m+1}^{m} a_{kj} n_j \Delta \ln n +$$

$$\frac{\sum_{j=1}^{m} a_{kj} n_j \left(HT^{o} \right)_j}{RT} \Delta \ln T = \left(b_k^{o} - b^{k} \right) +$$

$$\frac{\sum_{j=1}^{m} a_{kj} n_j \mu_j}{RT} \qquad \cdots k = 1, \cdots \quad \cdots\cdots (24)$$

$$\sum_{i=1}^{l} a_{ij} \pi_i + \frac{\left\{ HT^{o} \right\}_j}{RT} \Delta \ln T = \frac{\mu_j}{RT} \qquad \cdots\cdots (25)$$

$$\sum_{i=1}^{l} \sum_{j=1}^{m} a_{ij} n_j \pi_i + \sum_{j=1}^{m} \left(n_j - n \right) \Delta \ln n +$$

$$\frac{\sum_{j=1}^{m} \left\{ n_j \left(HT^{o} \right)_j \right\}}{RT} \Delta \ln T =$$

$$n - \sum_{j=1}^{m} n_j + \sum_{j=m}^{m} \frac{n_j \mu_j}{RT} \qquad \cdots\cdots (26)$$

$$\sum_{i=1}^{l} \frac{\sum_{j=1}^{m} a_{ij} n_j \left(HT^{o} \right)_j}{RT} \pi_i + \sum_{j=m+1}^{n} \frac{\left(HT^{o} \right)_j}{RT} \Delta \ln n_j +$$

$$\frac{\sum_{j=1}^{m} n_j \left(HT^{o} \right)_j}{RT} \Delta \ln n +$$

$$\left[\sum_{j=1}^{n} \frac{n_j \left(C_p^{o} \right)_j}{R} + \sum_{j=1}^{m} \frac{n_j \left(HT^{o} \right)_j^{2}}{R^{2} T^{2}} \right] \Delta \ln T =$$

$$\frac{h_0 - h}{RT} + \sum_{j=1}^{m} \frac{n_j \left(HT^{o} \right)_j T \mu_j}{R^{2} T^{2}} \qquad \cdots\cdots (27)$$

$$\sum_{i=1}^{l} \sum_{j=1}^{m} \frac{\left\{ a_{ij} n_j S_j \right\}}{R} \pi_i + \sum_{j=m+1}^{n} \frac{S_j}{R} \Delta \ln n_j +$$

$$\sum_{j=1}^{l} \frac{\left\{ n_j S_j \right\}}{R} H \ln n +$$

$$\left[\sum_{j=1}^{n} \frac{\left\{ n_j \left(C_p^{o} \right)_j \right\}}{R} + \sum_{j=1}^{m} \frac{\left\{ n_j \left(HT^{o} \right)_j S_j \right\}}{R^{2} T} \right] \Delta \ln T =$$

$$\frac{S_0 - S}{R} + n - \sum_{j=1}^{m} n_j + \sum_{j=1}^{m} \frac{n_j S_j \mu_j}{R^{2} T} \qquad \cdots\cdots (28)$$

2.7 Thermodynamic derivatives from matrix solution

All thermodynamic first derivatives can be expressed in terms of any three independent first derivatives. The Bridgman tables, as tabulated express first derivatives in terms of $(\partial V/ \partial T)_P$, $(\partial V/ \partial P)_T$, and $(\partial h,/ \partial T)_P = C_p$. We will use the logarithmic form of the volume derivatives inasmuch as in that form they give an indication of the extent of chemical reaction occurring among the reaction species. From Eq. 14:

$$C_p = \left(\frac{\partial h}{\partial T} \right)_P = \sum_{j=1}^{n} n_j \left(C_p^{o} \right)_j +$$

$$\sum_{j=1}^{m} \frac{n_j \left(H_T^{o} \right)_j}{T} \left(\frac{\partial \ln n}{\partial \ln T} \right)_P +$$

$$\sum_{j=m+1}^{n} \frac{\left(H_T^{o} \right)_j}{T} \left(\frac{\partial \ln n}{\partial \ln T} \right)_P \qquad \cdots\cdots (29)$$

From Eq. (1)

$$\left(\frac{\partial \ln V}{\partial \ln T}\right)_P = 1 + \left(\frac{\partial \ln n}{\partial \ln T}\right)_P \qquad \cdots \cdots (30)$$

$$\left(\frac{\partial \ln V}{\partial \ln P}\right)_T = -1 + \left(\frac{\partial \ln n}{\partial \ln P}\right)_T \qquad \cdots \cdots \cdots (31)$$

In principle, obtaining equilibrium compositions by means of the Newton-Raphson iteration procedure should offer no difficulties. However, there are a number of practical items which require detailed attention in order to avoid numerical difficulties. These items include initial estimates, tests for condensed phases, phase transitions and triple points, convergence, accidental singularities, special handling of ions, and consideration of trace species.

2.7.1 Initial estimates

An extremely simple procedure is used to assign initial estimates for composition. For the first iteration of the first point, we assign n = 0.1.This is equivalent to an estimate of 10 for molecular weight. Then the number of kilogram moles of each gaseous species per kilogram of mixture is set equal   to 0. 1/m, where m is the number of gaseous species being considered. The number of moles of each condensed species is set equal to zero. For HP, SP, UV, and SV problems, an arbitrary initial estimate of T = 3800 K is used by the program unless a different estimate is included with other input .Furthermore, the estimating technique is used only for the first point in any schedule of points. For all points after the first, the results of a preceding point serve as initial estimates.

2.7.2 Convergence

The iteration equations sometimes give large corrections, which, if used directly, could lead to divergence. Two situations can cause large corrections. The first situation occurs in the early stages of the calculation and is due to poor estimates. The second may occur at later stages of the calculation when the iteration process sometimes attempts to make extremely large increases in moles of species that are present in trace amounts. In both of these cases a control factor λ is used to restrict the size of the corrections to $\ln n_j$ (j = 1,..., m) and n_j (j =m+ 1,..., n) as well as to $\ln n$ and $\ln T$. The numerical value of λ is determined on the basis of two empirical rules which experience has shown to be satisfactory.

For T, n, and n_j for those gaseous species and for which

$\frac{n_j}{n} > 10^{-8} \ln\left(\frac{n_j}{n}\right) > -18.420681$ and for which $\Delta \ln n_j$

> 0, a number λ_1 is defined as:

$$\lambda_1 = \frac{2}{\max \left[\left|\Delta \ln T\right|, \left|\Delta \ln n\right|, \left|\Delta \ln n_j\right|\right]} \qquad \cdots \cdots (32)$$

This limits the change in T and n and the increase in n_j, for those species whose gas phase mole fraction exceeds 10^{-8} to a factor $e^2 = 7.3891$.For those gaseous species for which $\ln \frac{n_j}{n} \leq -18.420681$ and $\Delta \ln n_j > 0$, a number λ_2 is defined as

$$\lambda_2 = \min \frac{\ln \frac{n_j}{n} - 9.2103404}{\Delta \ln n_j - \Delta \ln n} \qquad j = 1, \cdots \cdots, m$$

$$\cdots\cdots\cdots (33)$$

This prevents a gaseous species with a mole fraction less than 10^{-8} from increasing to more than 10^{-4}. The control factor λ to be used in Eq. (35) is defined in terms of λ_1 and λ_2 as:

$$\lambda = \min (1, \lambda_1, \lambda_2) \qquad \cdots\cdots (34)$$

A value for λ is determined for each iteration. Whenever current estimates of composition and/or temperature are far from their equilibrium values, λ will be less than 1. Whenever they are close to their equilibrium values, λ will equal 1. New estimates for composition and temperature are then obtained from the following correction:

$$\ln n_j^{i+1} = \ln n_j^1 + \lambda^1 \left(\Delta \ln n_j\right) \qquad \cdots j = 1, \cdots, m$$

$$n_j^{i+1} = n_j^1 + \lambda^1 \left(\Delta n_j\right) \qquad \cdots j = m+1, \cdots, n$$

$$\ln n^{i+1} = \ln n^1 + \lambda^1 \left(\Delta n\right)$$

$$\ln T^{i+1} = \ln T^i + \lambda^1 \left(\Delta \ln T\right)^i \qquad \cdots\cdots (35)$$

Where, the superscript i represents the i[th]estimate. The iteration procedure is continued until corrections to composition satisfy the following criteria:

$$\frac{n_j \left|\Delta \ln n_j\right|}{\sum_{j=1}^{m} n_j} \leq 0.5 \times 10^{-05} \qquad j = 1,..,m$$

$$\frac{\left|\Delta \ln n_j\right|}{\sum_{j=1}^{m} n_j} \leq 0.5 \times 10^{-05} \qquad j = m+1,..,n$$

$$\left|\Delta \ln n_j\right| \leq 0.5 \times 10^{-05} \qquad ....(36)$$

For a constant entropy problem (SP, SV, or RKT) the following convergence test on entropy is also required.

$$\left| \frac{S_o - S}{R} \right| \leq 0.5 \times 10^{-04} \qquad \ldots(37)$$

The tests ensure accuracy to five places in composition when expressed as mole fractions. Convergence has always been obtained in less than the eighteen iterations permitted by the program. The developed program has provision for testing condensed phases, phase transitions and special derivatives and ions.

2.7.3 Singularities

The iteration method can successfully handle numerous chemical systems under a wide variety of thermodynamic conditions. Nevertheless, special procedures are required to take care of a few rare situations which would otherwise cause the iteration method to fail. One such situation is a occurs when two rows of the coefficient matrix are identical. This happens when the ratio of the assigned elements in these two rows is equal to the ratio of the stoichiometric coefficients of these two elements in every gaseous species for which $\frac{n_j}{n} > 10^{-8}$ and which contains both elements.

$$\frac{a_{ij}}{a_{kj}} = \frac{b_i^o}{b_k^o} \qquad \ldots\ldots (38)$$

A procedure which usually takes care of this difficulty is to assign values in the input that will make the ratio $\frac{b_i^o}{b_k^o}$ differ from the left side in the 6th or 7th figure. The program does this automatically if an equivalence ratio r = 1.0 is read in by reassigning r = 1.000005. Whenever a singular matrix occurs, the program automatically reinserts the species with $\frac{n_j}{n} < 10^{-08}$ and reassigns them values of $n_j = 10^{-06}$. If, after restart, the iteration procedure the iteration procedure still leads a singular matrix, a message is printed and a test is made for another possible cause of singularity. This singularity occurs if the program is considering several condensed species whose determinant of stoichiometric coefficients is *zero*. In this case, if two or more of the condensed species are composed of the same chemical elements, the program will remove all of these species except the one with the most negative contribution to the free energy of the mixture based on the tests already described.

2.8 Thermodynamic data

Thermodynamic data are entered in the block data subroutine and printed for reading as a file.

2.8.1 Assigned enthalpies

For each species, heats of formation (and when applicable heats of transition) are combined with sensible heats to give assigned enthalpies H_T^0 and by definition:

$$H_T^o = H_{298.15}^0 + \left(H_T^o - H_{298.15}^0 \right) \qquad \ldots\ldots (39)$$

It arbitrarily assumed:

$$H_{298.15} = \left(\Delta H_f^o \right)_{298.5} \text{ Eq. (39) then becomes}$$

$$H_T^o = \left(\Delta H_f^o \right)_{298.15} + \left(H_T^0 - H_{298.15}^0 \right) \quad \cdots (40)$$

In general, $H_T^0 \neq \left(\Delta H_f^o \right)_T H_T^0$ for T $\neq$298.15 K. For reference elements $\left(\Delta Ho_f \right)_{298.15} = H_{298.15}^0 = 0$

Assigned enthalpies for reactants are available in cal /mole (as required for program input together with some other reactant data.

2.8.2 Least square coefficients

For each reaction species, the thermodynamic functions specific heat, enthalpy, and entropy as functions of temperature are given in the form of least squares coefficients as follows:

$$\frac{C_p^o}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \quad \cdots (41)$$

$$\frac{H_T^o}{R} = a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 \quad \cdots (42)$$

$$\frac{S_T^o}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 +$$

$$\frac{a_5}{4} T^4 + a_7 \quad \cdots (43)$$

2.8.3 Chemical equilibrium for assigned thermodynamic states

A thermodynamic state is defined by specifying two parameters. Some of the problems handled by the program (the TP, HP, SP, TV, UV, SV problems) use just one combination of assigned states. For example, the TP problem consists of a schedule of one or more assigned temperatures and pressures. The TP problem might be used to construct Mollier diagrams. The HP problem gives constant pressure combustion properties

by using an assigned enthalpy equal to that of the reactants and a schedule of one or more pressures. Similarly, the UV problem gives constant volume combustion properties by using an assigned internal energy equal to that of the reactants and a schedule of one or more volumes.

3   PROBLEM SIMULATION

A computer program of 10000 lines is developed on a laptop platform in power FORTRAN and the following case studies have been computed and results are presented and discussed.

3.1   Literature validation of the code

A reacting system comprising of oxidizer F_2 (fluorine) and fuel, a mixture of N_2H_4 (hydrazine) and $N_2H_8C_2$ (unsymmetrical dimethyl hydrazine) is studied with the program, computational results obtained and compared with literature results. A good agreement has been obtained between the developed code and the literature results in terms of computed thermodynamic properties and these are illustrated in [4].

One may wonder why author has chosen this case study for literature validation. The first author has had a couple of decades of experience in liquid rocket engines [5] followed by another couple of decades on hot end technologies (combustor and after burner) of an aero gas turbine engine [6]. In view of the continued interest in the above and for validation purpose this case study is taken.

3.2.   Significance of soot and state-of-the-art methodology of soot mitigation

Particulate matter emissions are of critical importance to both global climate change and human health. Studies have shown that human exposure to carbon-based ambient aerosols increases the odds of developing pulmonary and cardiac problems which can lead to lung and heart diseases, and in the long-term may be fatal [7]. With regard to climate effects, carbon aerosols have the ability to absorb and scatter solar radiation. Recent modeling efforts have indicated the propensity for carbon particulates to increase the global mean surface air temperature by 0.2 to 0.37 K per year, and the radiative forcing is estimated to be 70% that of CO_2 in the atmosphere [8]. The largest effects occur in regions with high fossil fuel emissions and burning of biomass. Clearly, there is an urgent need to curb carbon particulate emissions. Edwards and Roberts [9] have detailed the methodology of soot formation. Within a direct injection diesel engine, soot formation occurs in regions of locally high equivalence ratios and favorable temperatures. There exist both low and high temperature limits, although a change in the combustion

strategy is required to move beyond these limits. Other R&D efforts t in the field has moved towards the direction of staying below the low temperature and this has the additional benefit of avoiding high thermal NOx production. Fig.1 as taken from [9, 10] shows a graph of equivalence ratio versus temperature, indicating how a typical diesel engine fuel jet occupies several regions. The method by which LTC (Low Temperature Combustion) is implemented usually involves the use of EGR (Exhaust Gas Recirculation). Much work within the combustion community has been done investigating the development of chemical mechanisms that can predict both nucleation and growth of condensed phase. The type of species called PAHs (Polycyclic Aromatic Hydrocarbon) has been identified experimentally as being critical to initiating soot inception.
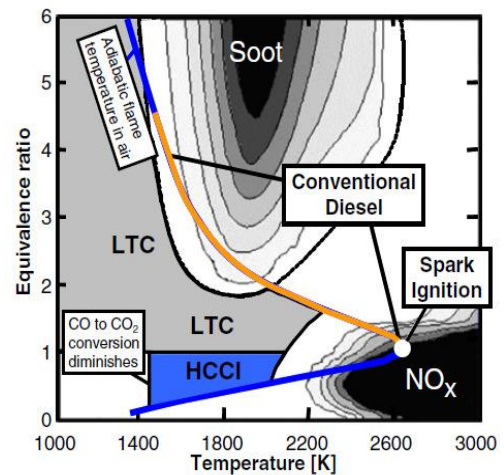

Fig. 1 Local equivalence ratio versus temperature, with reference to regions that describe a conventional Diesel fuel jet [9, 10]

A chemical mechanism has been developed by Blanquart [11] that includes up to 4 ringed aromatic species, inclusive of many aromatic radicals. It was designed to validate the combustion of large hydrocarbon fuels namely n-heptane and iso-octane, although a number of smaller hydrocarbon species have been validated against experimental data as well. It contains ~ 1650 elementary reactions and ~ 150 species and includes both transport as well as thermodynamic data. This mechanism is being used to study gas phase kinetics, in particular the temporal growth of PAH species in order to predict soot formation tendencies.

3.3. Necessity of equilibrium computations for diesel engine

Within a direct-injected jet the formation of soot is kinetically controlled; that is, there are regions within

the fuel jet where specific species are formed and given little oxygen and favorable temperature, a condensed phase is formed, in other words equilibrium is not reached. The state-of-the-art research is to both control the equilibrium state and to reach it, all within the reacting jet. It is thus informative to have a clear idea of what thermodynamic equilibrium indicates about the product composition of a particular mixture. Hence, it is very clear that equilibrium composition prediction is very important in diesel engines.

4. COMPUTER PRORAM INPUTS

The typical compression ratio is 18:1 and the computer program is run as TP = TRUE Problem. The following r (Equivalence ratio) and the corresponding T (Temperature) are selected for the runs; r = 1, T =2600 K ; r = 2, T = 2000K, r = 3, T = 1700K, r=4, T = 1600K; r = 5, T = 1500 K.

4.1 Oxidizer fuel inputs

Most of the literature studies have used diesel surrogate n heptane as fuel and oxidizer atmospheric air comprising of oxygen and nitrogen only. In the present work diesel is used as a fuel and atmospheric air comprising of nitrogen, oxygen, argon, carbon dioxide is used. Table 1 gives the oxidizer and fuel input details. It could be observed that all constituents of atmospheric air are taken into account with the corresponding properties. It could be observed that the temperature of the air constituents is ~ 647 K due to the fact that the engine compression stroke increases the pressure as well as temperature. These are processed by the program and the effective fuel and oxidizer are tabulated in Table 2.

Table 1 Oxidizer and Fuel Inputs

Chemical Formula	Weight fraction	Energy (Cal/Mole)	State	Temp (Deg K)	Density (g/cc)
OXIDIZER ATMOSPHERIC AIR					
N=2.00000	.75524	174.100	G	647.95	.0013
O= 2.00000	.23144	1630.000	G	647.15	.0014
AR=1.00000	.01286	1947.000	G	647.95	.0020
C=1.00000 O= 2.0	.00046	1538.000	G	647.95	.0014
FUEL DIESEL					
C=12.00000 H=26.0	1.00	1952.000	G	298.15	.825

Table 2 Effective Fuel and Oxidizer

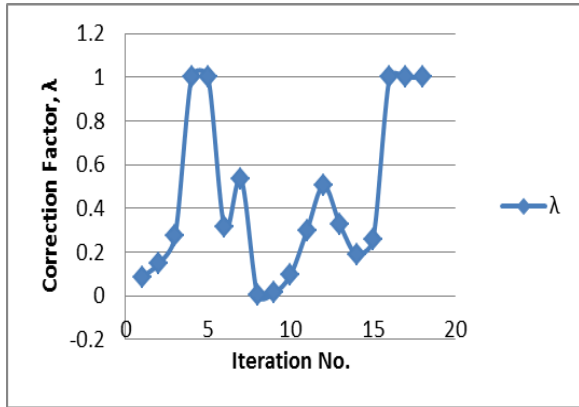| (Kg-Mol)(Deg K)/KG	Effective Fuel	Effective Oxidant	Mixture
	0.3003583E+02	0.2036590E+02	.10810000E+02
Kg-Atoms/kg	B0P(I,2)	B0P(I,2)	B0P(I,3)
N	00000000E+00	.53919910E-01	.47578230E-01
O	00000000E+00	.14486450E-01	.14486450E-01
AR	.00000000E+00	.32191850E-03	.28405670E-03
C	.70446920E-01	.10452180E-04	.82946900E-02
H	.15263500E+00	.00000000E+00	.1795186E-01

Fig. 2 Correction Factor Variation with Iteration

5. RESULTS AND DISCUSSIONS

The computer program is run for five sets of conditions of equivalence ratio and the results are presented below.

5.1 Convergence

In a mathematical development and computer program simulation the convergence criteria as already discussed is very important and the correction factor λ is defined by Eq. 34. For a typical run, this is plotted as shown in Fig. 2. It could be observed that when the correction factors are nearing or equal to unity the convergence is successfully achieved. Typically convergence is obtained in a maximum of 20 iterations, beyond which λ continues to be unity.

For different equivalence ratios, density, enthalpy, entropy, molecular weight and thermodynamic derivatives with respect to temperature and pressure,

and specific heat at constant pressure, gamma value and sonic values are obtained as computer output.

5.2 Thermodynamic properties

The program output regarding thermodynamic properties is tabulated in Table 3

5.3 Gaseous products species composition

The exhaust gas species compositions are tabulated in Table 4. The trace species that could be neglected are indicated. The pie chart gives the mole fraction distribution in Fig. 3 for unity equivalence ratio.

Additional products which were considered but whose mole fractions are less than 0.5E-05 for all assigned conditions are : C (S), C,C+, C- ,CH, CH2, CH2O, CH4, CN2, C2,C2-, C2H, C2H2, C2H4, C2N, C2N2, C2O, C3, C3O2, C4, C5, HCN, HNO, H2O(S), H2O2, N, NH, NH2, NH3
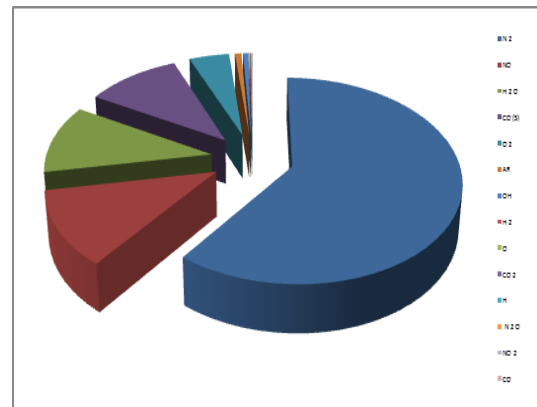

Fig. 3 Pie Chart for Mole Fractions

Table 3 Thermodynamic Properties

Equivalence Ratio	1.0	2.0	3.0	4.0	5.0
ρ, g/cc	0.0227625	.0029950	.0036436	.0039083	.00419167
H, Cal/g	382.1562	92.18266	-180.161	-259.372	-318.1989
S, Cal/(g)(K)	2.303798	2.172178	2.023167	1.974986	1.936893
M,Mol Weight	26.97925	27.30642	28.23698	28.50654	28.66255
(DLV/DLT)P	-1.0013	-1.00376	1.004866	-1.00279	-1.00125
(DLV/DLT)P	1.032887	1.131102	1.195544	1.118312	1.056148
CP, Cal/(g)	.4515143	.7011974	.8959663	.6847144	.5036045
Gamma (S)	1.208804	1.148131	1.120324	1.142244	1.179677
Acoustic vel, m/s	984.153	836.13	748.859	730.096	716.446

Table 4 Species Composition – Mole Fractions

Equivalence Ratio	1.0	2.0	3.0	4.0	5.0
AR	0.0081428	.0082416	.0085224	.0086038	.0086509
CO	0.0000220	0.0000253	0.000010	.0000051	0.000002
CO(S)	0.1185372	0.1016598	0.03738	0.018669	0.007844
CO_2	0.0003771	0.0186936	0.087090	0.106994	0.118510
H	0.0003104	0.0000024	0.000001	0.000000	0.00000
H_2	0.0011324	0.0000383	0.000005	0.000002	0.000001
H_2O	0.1237169	0.1296952	.134495	0.135813	0.136573
NO	0.1323867	0.0036857	0.000875	0.000416	0.000172
NO_2	0.0000215	0.0000124	0.000003	0.000001	0.000000
N_2	0.6752487	0.6883221	0.713271	0.720326	0.724395
N_2O	0.0000636	0.0000446	0.000023	0.000015	0.000009
O	0.0012137	0.0000344	0.000001	0.000003	0.000000
OH	0.0071086	0.000770	0.000109	0.000045	0.000016
O_2	0.0508642	0.048774	0.018215	0.009109	0.003827

6. CONCLUSION

An attempt is made to compute the diesel engine exhaust gas constituents and a computer program developed for application in diesel engines. The literature validated code, running on laptop platform, aids in the conceptual design of futuristic engine or can be used for analyzing the existing engine. An application of the literature validated code diesel engine is demonstrated. Very soon, engine would be on test bed and detailed testing planned to compare analytical and experimental results

7. ACKNOWLDEDGMENT

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NOMENCLATURE

$a_{i,j}$, Stoichiometric coefficients, kg-atoms of element i per kg-mole of species j, (kg-atom)$_i$ /(kg-mol) $_j$

$a_{i,j}{}^k$, Stoichiometric coefficients, kg-atoms of element i per kg-mole of reactant (oxidant if k=1 fuel if k=2), (kg-atom) $_i{}^k$/(kg-mole)j ^{k}

a_i (i=1,7), Least square coefficients in Eqs. (41, 42 and (43)

b_i, kg-atoms of element i per kg of mixture, (kg-atom) $_i$ /kg , Eq. (7 b)

BOP (I,1), kg-atoms of ith element per kg of total oxidant, (Table 2)

BOP (I,2) , kg-atoms of i th element per kg of total fuel, (Table 2)

$(C_p{}^0)_j$, Standard state constant pressure specific heat for species or reactant j, J/(kg-mole) $_j$ (K)

$(C_v{}^0)_j$, Standard state constant volume specific heat for species j, J/(kg-mol) $_j$ K

C_p, Constant pressure specific heat of mixture, J/kg K

C_v, Constant volume specific heat of mixture, J/kg K

f/a , Fuel to air weight (or mass) ratio or fuel to oxidant weight (or mass) ratio

G, Gibbs free energy of mixture, J/kg

$(H^o{}_T)_j$, Standard state enthalpy for species j, J/(kg-mole)

$(\Delta H_F{}^0)$ T, Heat of formation at temperature T, J/(kg-mole)

h_0, Enthalpy of total reactants, kg-mole/kg

H, Enthalpy of mixture, kg-mole/kg

M, Molecular weight of mixture, kg/kg-mole

$n_j{}^{(K)}$, kg-moles of reactant j (oxidant if k=1 and fuel if k=2), (kg-mole) $_j{}^{(K)}$

n, Moles of mixture, kg-mole/kg

n_j, kg-moles of species j per kg of mixture , (kg-mole) $_j$ /kg

o/f, oxidant to fuel weight (or mass) ratio

P, Pressure, N/m ^{2}

P_{atm}, Pressure, atm

P_0, Assigned initial pressure, N/ m ^{2}

R, Universal gas constant, 8314.3 J/(kg-mole)

r, Equivalence ratio

S_j , Entropy of species j, J/(kg-mole) $_j$ (K)

$(S^0{}_T)_j$, Standard state entropy for species j , J/(kg-mole)(k)

S, Entropy of mixture, J/(kg K)

T, Temperature, KV, Specific volume m ^{3} /kg

Ʌ, Control Factor

$Ʌ_i$, Langrangian multiplier for chemical element i, J/(kg-atom) $_i$

μ_j, Chemical potential of species j, J/(kg-mole)/(kg-atom) $_i$, (Eq.6)

$\pi_i = - Ʌ_i / RT$, Lagrangian multiplier for chemical element i, kg-mole/(kg-atom) $_i$, (Eq. 18)

ρ, Density of mixture, kg/ m ^{3}

ρ_0, Density of total reactant, kg/ m ^{3}

Subscripts

c, Combustion, condensed

g, gas

Superscripts

k, 1 Oxidant; k, 2 Fuel

0, Initial Condition