

HyNECC: Hypersonic NonEquilibrium Comparison Cases LeMANS results for Phase 1: N₂/N, O₂/O and 5-species air in 0-D adiabatic bath

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I. LeMANS Physical Model

LeMANS is a CFD code, which was originally developed at the University of Michigan in 2007 by Leonardo Scalabrin and Iain Boyd [1, 2]. Since then numerous researchers have developed, advanced, and utilized the code to investigate phenomena relevant to hypersonic flight and re-entry. The code has been verified against similar NASA codes and validated against numerous flight and experimental data. The following are details of the physical models within LeMANS and has been adapted from Ref. [1]. More details of LeMANS can be found in Refs. [1, 2]. It should be noted that the following sections are for a general LeMANS simulation (e.g., multi-dimensional). The governing equations and physical models are greatly simplified for the adiabatic heat bath case and will be similar to that provided in the SU2-NEMO documentation.

A. Bulk Flow Transport Equations: Mass Conservation Equation, Momentum Transport Equation, and Energies Transport Equations

The fluid conservation equations solved by LeMANS to simulate flows with thermal nonequilibrium and finite-rate chemical reactions can be written as,

Conservation of Mass

$$\frac{\partial \rho_s}{\partial t} + \nabla \cdot (\rho_s \mathbf{u} + \mathbf{J}_s) = \dot{w}_s \quad (1a)$$

Conservation of Momentum

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u} + p \bar{\bar{I}} - \bar{\bar{\tau}}) = 0 \quad (1b)$$

Conservation of Energy

$$\frac{\partial E_t}{\partial t} + \nabla \cdot \left((E_t + p) \mathbf{u} - \bar{\bar{\tau}} \cdot \mathbf{u} + (\mathbf{q}_{tr} + \mathbf{q}_{ve}) + \sum_s (\mathbf{J}_s h_s) \right) = 0 \quad (1c)$$

$$\frac{\partial E_{ve}}{\partial t} + \nabla \cdot \left(E_{ve} \mathbf{u} + \mathbf{q}_{ve} + \sum_s (\mathbf{J}_s e_{ve,s}) \right) = \dot{w}_{ve} \quad (1d)$$

where ρ_s is the density of species s , \mathbf{u} is the bulk velocity, p is the pressure, $\bar{\bar{I}}$ is the identity matrix, $\bar{\bar{\tau}}$ is the viscous stress tensor, h_s is the species enthalpy, and \mathbf{J}_s is the diffusion flux of species s modeled using a modified form of Fick's law [3]. E and E_{ve} are the total and vibrational-electron-electronic energies per unit volume of mixture, respectively, while $e_{ve,s}$ is the vibrational-electron-electronic energy per unit mass. The source term \dot{w}_s in Equation 1a is the species

mass production and recombination (i.e. destruction) rate due to chemical reactions. The source term \dot{w}_{ve} includes the energy transfer between nonequilibrium modes, the change of vibrational energy due to chemical reactions, and an approximation to the work done on the electrons by the electric field induced by the electron pressure gradient [1]. For the current work, LeMANS is run as a two-temperature (2T) code. This assumes that the rotational and translational energy modes of all species can be described by a single temperature T_{tr} because the rotational energy equilibrates with the translational energy in just a few collisions. Furthermore, this assumes that the vibrational and electronic energy modes of all species and the electron translational energy mode can be described by a single temperature T_{ve} . This assumption is based on three postulates:

- 1) The energy transfer between the translational mode of electrons and the vibrational mode of molecules is very fast in air [4].
- 2) The vibrational temperature of different molecules are very similar [5] due to highly efficient vibrational-vibrational energy transfer [6].
- 3) The electron translational energy can be modeled by a single Maxwell-Boltzmann distribution because the electronic mode is excited by the translational mode of electrons [6].

Although not used in this work, LeMANS has the capability to run additional nonequilibrium energy modes such as rotational [7] and electron [8]. These assumptions regarding energy transfer simplify the system of equations considerably by eliminating translational and vibrational energy equations for each polyatomic species and an energy equation for the electrons. This is considered a large simplification of the problem but the energy transfer models are not accurate enough to warrant extra complexity in the equations [1]. While these simplifications may not be adequate for some problems, such as plasma properties in hypersonic boundary layers, they provide accurate results for aerodynamic coefficients and convective heat transfer rates of reentry configurations [4]. The heat fluxes in the energy conservation equations, $q_{t,ve}$, are modeled according to Fourier's law as,

$$\mathbf{q}_{tr,ve} = -\kappa_{tr,ve} \nabla T_{tr,ve}. \quad (2)$$

and the viscous stresses are modeled assuming the flow is a Newtonian fluid and Stokes' hypothesis is applicable [9].

The source terms in the species conservation equations are determined by the finite-rate chemistry model. The reactions considered for this work is listed in Table 1 and correspond to 5-species air (no ionization). For *TCIA.1*, reactions 1 and 3 are used. For *TCIA.2*, reactions 2 and 4 are used. For *TCIA.3*, all 17 reactions are used. The reactions can be classified as dissociative, exchange, recombination, ionization, charge exchange and impact ionization reactions. All reactions for the three models can be represented generically as:



where $[S]$ represents one of the species of the reaction set and α and β are the stoichiometric coefficients. The reactions are typically written such that the right arrow represents an exothermic reaction. The chemical production rate of species s in reaction k is given by [4]:

$$\dot{w}_{sk} = (\beta_{sk} - \alpha_{sk}) \left[k_{fk} \prod_j \left(\frac{\rho_j}{M_j} \right)^{\alpha_{jk}} - k_{bk} \prod_j \left(\frac{\rho_j}{M_j} \right)^{\beta_{jk}} \right] \quad (4)$$

where k_{fk} and k_{bk} are the forward and backward reaction rates, respectively. The source terms in the species conservation equations can be then determined by:

$$\dot{w}_s = M_s \sum_s \dot{w}_{sk}. \quad (5)$$

The forward and backward reaction rates are affected by the level of non-equilibrium in the flow. To account for that effect, Park's two-temperature model [10] is utilized.*. In that model the dissociation reactions are controlled by a combination of the translational-rotational and the vibrational-electron-electronic temperature:

$$T_c = T_{tr}^a T_{ve}^b \quad (6)$$

to account for the fact that vibrationally excited molecules are more likely to dissociate. This work sets the values of a and b to 0.5. Exchange reactions are controlled by the translational-rotational temperature. The controlling temperatures used in this work is summarized in Table 1. Note that the backward controlling temperature, T_{bc} , is not necessarily the same as for the forward reaction controlling temperature, T_{fc} [12]. The forward reaction rates are calculated using Arrhenius curve fits on the controlling temperature, T_{fc} , as:

$$k_{fk} = C_{fk} T_c^{n_k} \exp(-\theta_k/T_c) \quad (7)$$

where C_{fk} , n_k , and θ_k are constants for each reaction and are provided in Table 1. The backward reaction rate is obtained from the equilibrium constant, K_{eq} [10, 12]:

$$k_{bk}(T_{bc}) = \frac{k_{fk}(T_{bc})}{K_{eq}(T_{bc})} \quad (8)$$

LeMANS can utilize two different approaches for determining the equilibrium constant. The first one, denoted *Park*,

*Also included results for *TCIA.3* using the MMT 2T model [11].

determines the equilibrium constants for each reaction by curve fits of the form:

$$K_e(T) = \exp \left[A_1 \left(\frac{T}{10,000} \right) + A_2 + A_3 \ln \left(\frac{10,000}{T} \right) + A_4 \left(\frac{T}{10,000} \right) + A_5 \left(\frac{T}{10,000} \right)^2 \right] \quad (9)$$

where the coefficients A_i are a function of the local number density and provided in the literature for common air reactions [10]. The second approach, denoted Gibbs, is to calculate the equilibrium constants using Gibb's free energy as:

$$K_r = \left(\frac{p_0}{RT_{tr}} \right)^{\nu_r} \exp \left[- \sum_s (\beta_{s,r} - \alpha_{s,r}) \left(\frac{\hat{h}_s}{RT_{tr}} - \frac{\hat{s}_s}{R} \right) \right] \quad (10)$$

where p_0 is a reference temperature set to 1 bar and

$$\nu_r = \sum_s (\beta_{s,r} - \alpha_{s,r}) \quad (11)$$

Finally, the normalized enthalpy, $\frac{\hat{h}_s}{RT_{tr}}$, and entropy, $\frac{\hat{s}_s}{R}$, are obtained from curve fits of the form:

$$\frac{\hat{h}_s}{RT_{tr}} = -\frac{a_{1s}}{T^2} + a_{2s} \frac{\ln T}{T} + a_{3s} + a_{4s} \frac{T}{2} + a_{5s} \frac{T^2}{3} + a_{6s} \frac{T^3}{4} + a_{7s} \frac{T^4}{5} + \frac{a_{8s}}{T} \quad (12)$$

$$\frac{\hat{s}_s}{R} = -\frac{a_{1s}}{2T^2} - \frac{a_{2s}}{T} + a_{3s} \ln T + a_{4s} T + a_{5s} \frac{T^2}{2} + a_{6s} \frac{T^3}{3} + a_{7s} \frac{T^4}{4} + a_{9s} \quad (13)$$

where the values of a_i are provided for different species for corresponding temperature ranges [13]. This is the approach used for this work because data is available for over 2000 species, including cesium relevant species, [13] and this is a common approach for calculating the back reaction rates [14].

The vibrational energy source term is given by:

$$\dot{w}_v = S_{epg} + S_{c,v} + S_{t-v} + S_{h-e} + S_{e,i}, \quad (14)$$

where

$$S_{epg} = -p_e \cdot \vec{u}, \quad (15)$$

which is an approximation to the work done on electrons by the electric field induced by the electron pressure gradient [4, 5]. $S_{c,v}$ is the vibrational-electron-electronic energy added or removed by chemical reactions, S_{t-v} is the energy transferred between the translational-rotational and the vibrational-electron-electronic modes, S_{h-e} is the energy transfer between heavy particles and electrons, and $S_{e,i}$ is the energy removed from free electrons during impact ionization

reactions.[†]

The vibrational energy added or removed by reactions can be modeled using a preferential or non-preferential model where in the non-preferential model it is assumed that molecules are created or destroyed at the average vibrational energy while in the preferential model it is assumed that the molecules are created or destroyed at higher vibrational energy levels. Results are included for both the preferential and non-preferential models. In the preferential model, it is assumed the value of energy added or removed is a fraction of the dissociation energy of the molecules. This fraction is set to 0.3 for this work. Both the preferential and non-preferential models are phenomenological simplifications to a complicated physical process for which there are no definitive models in a 2T framework, which state-to-state (STS) modeling is typically used to capture the physical processes involved [15]. However, recent work has been done to implement models based on *ab-initio* quantum chemistry data into LeMANS [16, 17], which is included for the *TCIA.3* case.

The term S_{tv} is the energy exchange rate between the vibrational-electronic and the translational-rotational energy modes. It is assumed that these multi energy mode exchange rates can be modeled by a single exchange rate due to the fast energy transfer between translational-rotational modes and between the vibrational-electronic modes. The single energy exchange rate is modeled using the Beth-Teller (also commonly referred to as Landau-Teller) model [18, 19] as:

$$S_{tv} = \sum_s \rho_s \frac{e_{vs}^* - e_{vs}}{\tau_s} \quad (16)$$

where

$$\tau_s = \langle \tau_s \rangle + \tau_{ps} \quad (17)$$

and where the molar averaged Landau-Teller relaxation time is written as [6]:

$$\langle \tau_s \rangle = \frac{\sum_r X_r}{\sum_r X_r / \tau_{sr}} \quad (18)$$

where X_r is the molar fraction of species r . The Landau-Teller inter-species relaxation time, τ_{sr} , is modeled using curve fits developed by Millikan and White [20] for vibrational relaxation as:

$$p\tau_{sr} = \exp[A_{sr}(T^{-1/3} - B_{sr}) - 18.42] \quad [\text{atm-sec}] \quad (19)$$

[†] No ionization reactions considered for this work.

where:

$$A_{sr} = 1.16 \times 10^{-3} \mu_{sr}^{1/2} \theta_{vs}^{4/3} \quad (20)$$

$$B_{sr} = 0.015 \mu_{sr}^{1/4} \quad (21)$$

$$\mu_{sr} = \frac{M_s M_r}{M_s + M_r} \quad (22)$$

The values needed to tabulate A_{sr} and B_{sr} can be calculated using the previous generic expressions or using tabulated data [14]. The values used for this work are provided in Table 2. It is known that Millikan and White curve fits underpredict the relaxation time at high temperatures. This is addressed by limiting the collision cross section and adding the corresponding limiting relaxation time to Eq. 18 [10]:

$$\tau_{ps} = \frac{1}{\sigma_s c_s N} \quad (23)$$

where N is the number density of the mixture, c_s is the average molecular speed of the species given by:

$$c_s = \sqrt{\frac{8R_u T}{\pi M_s}} \quad (24)$$

and σ_s is the limiting cross section given by:

$$\sigma_s = 10^{-20} \left(\frac{50,000}{T} \right)^2 \text{ m}^2 \quad (25)$$

Eq. 16 can be simplified as [4]:

$$S_{tv} = \sum_s \rho_s \frac{e_{vs}^* - e_{vs}}{\tau_s} = \frac{\rho C_{v,ve}}{\tau} (T_{tr} - T_{vib}) \quad (26)$$

where

$$\tau = \frac{\sum_{mol} \rho_s / M_s}{\sum_{mol} \rho_s / (M_s \tau_s)}. \quad (27)$$

B. Real Gas Thermodynamics

The mixture pressure p is obtained using Dalton's law of partial pressures and the perfect gas law for each species:

$$p = \sum_{s \neq e} \rho_s \frac{R_u}{M_s} T_{tr} + \rho_e \frac{R_u}{M_e} T_e \quad (28)$$

where T_e is assumed to equal T_{ve} in this work. The total energy per unit volume of mixture is given by:

$$E = \sum_{s \neq e} \rho_s C_{v,tr,s} T_{tr} + \frac{1}{2} (u^2 + v^2 + w^2) + \sum_{s \neq e} \rho_s h_s^o + E_{ve}, \quad (29)$$

where h_s^o is the species enthalpy of formation. The translational-rotational specific heat at constant volume, $C_{v,tr,s}$, is given by:

$$C_{v,tr,s} = C_{v,t,s} + C_{v,r,s}. \quad (30)$$

This work assumes that the translational and the rotational specific heats at constant volume are constant and given by:

$$C_{v,t,s} = \frac{3}{2} \frac{R_u}{M_s} \quad (31)$$

and

$$C_{v,r,s} = \begin{cases} \frac{R_u}{M_s} & \text{for molecules,} \\ 0 & \text{for atoms and electrons.} \end{cases} \quad (32)$$

This is a good approximation because the translational and the rotational energy modes are fully excited even at low temperatures. The species vibrational energy per unit mass is modeled using a harmonic oscillator as:

$$e_{v,s} = \begin{cases} \frac{R_u}{M_s} \frac{\theta_{v,s}}{\exp(\theta_{v,s}/T_{v,e}) - 1} & \text{for molecules,} \\ 0 & \text{for atoms and electrons.} \end{cases} \quad (33)$$

where $\theta_{v,s}$ is the species characteristic vibrational temperature. This harmonic oscillator model is adequate because it is accurate for the low vibrational energy levels and because the energy contribution of the higher levels, where the model loses accuracy, is negligible [6]. The vibrational specific heat at constant volume is calculated by:

$$C_{v,v,s} = \begin{cases} \frac{R_u}{M_s} \frac{(\theta_{v,s}/T_{v,e})^2 \exp(\theta_{v,s}/T_{v,e})}{[\exp(\theta_{v,s}/T_{v,e}) - 1]^2} & \text{for molecules,} \\ 0 & \text{for atoms and electrons.} \end{cases} \quad (34)$$

The species electronic energy, $e_{el,s}$ is modeled by:

$$e_{el,s} = \begin{cases} \frac{R_u}{M_s} \frac{\sum_{i=1}^{\infty} g_{i,s} \theta_{el,i,s} \exp(-\theta_{el,i,s}/T_{ve})}{\sum_{i=1}^{\infty} g_{i,s} \exp(-\theta_{el,i,s}/T_{ve})} & \text{for molecules and atoms,} \\ 0 & \text{for electrons} \end{cases} \quad (35)$$

where $\theta_{el,i,s}$ and $g_{i,s}$ are the characteristic electronic temperature and the degeneracy of the i -th energy level, respectively, which are available in NIST [21]. This model is adequate because it is accurate for the low electronic energy levels and because the energy contribution of the higher levels, where the model loses accuracy, is negligible [6]. The species electronic specific heat at constant volume is given by:

$$C_{v,el,s} = \begin{cases} \frac{\partial e_{el,s}}{\partial T_{ve}} & \text{for atoms and molecules,} \\ 0 & \text{for electrons.} \end{cases} \quad (36)$$

The vibrational-electron-electronic energy per unit mass of the species is given by:

$$e_{ve,s} = \begin{cases} e_{v,s} + e_{el,s} & \text{for molecules and atoms,} \\ C_{v,t,e} T_{ve} & \text{for electrons.} \end{cases} \quad (37)$$

and the species vibrational-electron-electronic specific heat at constant volume, $C_{v,ve,s}$, is given by

$$C_{v,ve,s} = \begin{cases} C_{v,v,s} + C_{v,el,s} & \text{for atoms and molecules,} \\ C_{v,t,e} & \text{for electrons.} \end{cases} \quad (38)$$

Finally, the mixture vibrational-electron-electronic energy per unit volume is given by:

$$E_{ve} = \sum_s \rho_s e_{ve,s} \quad (39)$$

and the internal energy per unit mass of the species is given by:

$$e_s = \begin{cases} C_{v,tr,s} T_{tr} + h_s^l + e_{ve,s} & \text{for atoms and molecules,} \\ e_{ve,e} & \text{for electrons} \end{cases} \quad (40)$$

and the species enthalpies are given by:

$$h_s = \begin{cases} R_s T_{tr} + e_s & \text{for atoms and molecules,} \\ R_e T_{ve} + e_e & \text{for electrons} \end{cases} \quad (41)$$

The values for characteristic vibrational temperature (θ_v), characteristic electronic temperature (θ_{el}), and the degeneracies can be found in the Appendix of Ref. [1].

C. Viscosity, Mass Diffusion Coefficient, Thermal Conductivity

For this work, LeMANS calculates the transport properties of the flow using Wilke's mixing rule [22], which is a simplification of the full first-order Chapman-Enskog relation:

$$\mu = \sum_s \frac{X_s \mu_s}{\phi_s} \quad (42)$$

$$\kappa = \sum_s \frac{X_s \kappa_s}{\phi_s} \quad (43)$$

where X_s is the species molar fraction, μ is the mixture viscosity, κ is the mixture thermal conductivity, μ_s is the viscosity of species s , and κ_s is the thermal conductivity of each energy mode for species s . The term ϕ_s is a dimensionless constant given by the equation for each species s in the mixture of r species/collision partners:

$$\phi_s = \sum_r X_r \left[1 + \sqrt{\frac{\mu_s}{\mu_r}} \left(\frac{M_r}{M_s} \right)^{1/4} \right]^2 \left[\sqrt{8 \left(1 + \frac{M_s}{M_r} \right)} \right]^{-1} \quad (44)$$

where M_s is the molecular weight of species s . The species viscosities, μ_s , are calculated using Blottner's curve fits [23]:

$$\mu_s = 0.1 \exp[(A_s \ln T + B_s) \ln T + C_s] \quad (45)$$

where A_s , B_s , and C_s are constants determined for each species and can be found in Ref. [23] for common air species.

The species thermal conductivities are determined from the species viscosities using Eucken's relation [19]:

$$\kappa_{tr} = \frac{5}{2} \mu_s C_{v,t,s} + \mu_s C_{v,r,s} \quad (46)$$

$$\kappa_{ve} = \mu C_{v,ve,s}. \quad (47)$$

where κ_{tr} and κ_{ve} is the thermal conductivity for the translation/rotational and vibration/electronic/electron energy mode, respectively. The mass diffusion coefficient for each species, D_s , is replaced by a single binary coefficient, D , as

a simple way to ensure that the sum of diffusion fluxes is zero. The diffusion coefficient can be determined assuming a constant Lewis number, Le :

$$D_s \approx D = \frac{Le\kappa}{\rho C_p}. \quad (48)$$

For this study, the Lewis number is assumed to equal 1.4. The single binary coefficient approximation is suitable for velocities below 10 km/s [24]. This overall approach is not designed for ionized flows even though it can be modified to handle a weakly ionized gas [25].

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Appendices

Table 1 Reaction rate coefficients currently implemented in LeMANS for this work.^a

No.	Reaction	M	T_f	T_b	C [cm ³ /mol/s]	n	E [K]	Refs.
Dissociation Reactions								
1-2	$N_2 + M \rightarrow N + N + M$	M_1	$\sqrt{T_{tr}T_{vib}}$	T_{tr}	3.0^{22}	-1.60	113,200	[10]
3-5		M_2			7.0^{21}			
6-7	$O_2 + M \rightarrow O + O + M$	M_1	$\sqrt{T_{tr}T_{vib}}$	T_{tr}	1.0^{22}	-1.50	59,500	[10]
8-10		M_2			2.0^{21}			
11-13	$NO + M \rightarrow N + O + M$	M_3	$\sqrt{T_{tr}T_{vib}}$	T_{tr}	1.1^{17}	0.00	75,500	[10]
14-15		M_4			5.0^{15}			
NO Exchange Reactions								
16	$N_2 + O \rightarrow NO + N$		T_{tr}	T_{tr}	5.7^{12}	0.42	42,938	[26]
17	$NO + O \rightarrow N + O_2$		T_{tr}	T_{tr}	8.4^{12}	0.00	19,400	[27]

^a $M_1 = N, O$

$M_2 = N_2, O_2, NO$

$M_3 = N, O, NO$

$M_4 = N_2, O_2$

Table 2 Millikan and White model coefficients.

N ₂	N ₂	221.53	0.0290
	N	180.88	0.0262
	O ₂	228.76	0.0295
	O	72.40	0.0150
	NO	225.30	0.0293
O ₂	N ₂	131.32	0.0295
	N	72.40	0.0150
	O ₂	135.91	0.0300
	O	47.70	0.0590
	NO	133.71	0.0298
NO	N ₂	149.50	0.0420
	N	149.50	0.0420
	O ₂	149.50	0.0420
	O	149.50	0.0420
	NO	149.50	0.0420