

usually obtained as primitive variables  $Q_p$  ( $Q_p = [p, u, v, w, T, Y_j]^T$ ). Transformation of the conservation equations to this set of variables leads to Jacobians,

$$\Gamma = \frac{\partial Q}{\partial Q_p}, \quad A = \frac{\partial (E_i)}{\partial Q_p}, \quad B = \frac{\partial F_{vi}}{\partial Q_p} \quad D = \frac{\partial \dot{\Omega}}{\partial Q_p}. \quad (2.5)$$

These Jacobians contain derivatives of density  $\rho$  and enthalpy  $h$ , which can be determined using equation of state and caloric equation defined above.

The last vector,  $\dot{\Omega}$ , in equation 2.1 contains source terms for species conservation equations. Calculation of the source terms is described in section 2.2 with an emphasis on the types of reactions involved in the kinetics mechanisms used for this work.

### Homogeneous Liquid-Gas Model using Amagat's Law

It is postulated that ignition of hypergolic propellants is critically influenced by liquid phase phenomena as evidenced from the fact that hypergolic propellants neither require to be pre-vaporized nor need an external source of ignition. The liquid phase is therefore an essential part of the overall ignition process and needs to be included in the modeling efforts.

The homogeneous liquid-gas model presents an attractive option for modeling liquid-gas mixtures, without the complexities of interface tracking and accompanying spatial resolution requirements. This model uses Amagat's law, which states that the total volume of a fluid is the sum of partial volumes of its components. It is well suited for mixtures containing liquids, enabling treatment of the liquids and gases in the same framework. In order to understand the difference between the Gibbs-Dalton law and Amagat's law, consider the mathematical statement of Amagat's law,

$$V = \sum_j^N v_j \quad (2.6)$$

where  $V$  is the total volume occupied by a mixture and  $v_j$  is the volume of  $j^{th}$  component of the mixture of  $N$  fluids. Writing in terms of mass and density,

$$\frac{M}{\rho} = \sum_j^N \frac{m_j}{\rho_j} \quad (2.7)$$

which gives,

$$\frac{1}{\rho} = \sum_j^N \frac{m_j}{M} \frac{1}{\rho_j} = \sum_j^N \frac{Y_j}{\rho_j} \quad (2.8)$$

where  $M$  is the total mass of the system,  $m_j$  is the mass of  $j^{th}$  species and  $Y_j$  is the mass fraction of  $j^{th}$  species in the mixture. It is important to note that this relation between mass fraction and mixture density does not depend on equation of state for any individual species. Definition of partial density is given for the Gibbs-Dalton law as, Gibbs-Dalton:

$$\rho_j = \frac{m_j}{V} \quad (2.9a)$$

and for Amagat's law as,

$$\rho_j = \frac{m_j}{v_j} \quad (2.9b)$$

where  $m_j$  is the mass of  $j^{th}$  species,  $V$  is the total volume of the mixture and  $v_j$  is the volume occupied by each component of the mixture. In actual calculation procedure, mixture density and appropriate derivatives are required, which can be calculated from equation 2.8. Volume fractions are not determined unless of interest. Thus, Amagat's law allows fluid mixtures to include arbitrary liquids for which the equation of state and the caloric equation are known. Details of various mixture property derivatives required for the Jacobians can be found in [66, 67].

A straightforward way of obtaining an equation of state for a liquid is to treat the liquid as a low compressibility fluid so that,

$$\rho = \rho_0 + \frac{Zp}{RT} \quad (2.10)$$

where  $\rho_0$  is the incompressible density and  $Z$  is the compressibility factor, determined as the smallest positive root of the Peng-Robinson equation of state [71], given as,

$$Z^3 - (1 - B_z)Z^2 + (A_z - 3B_z^2 - 2B_z)Z - (A_zB_z - B_z^2 - B_z^3) = 0 \quad (2.11)$$

where the terms  $Z$ ,  $A_z$  and  $B_z$  are given as,

$$Z = \frac{\rho RT}{p} \quad (2.12a)$$

$$A_z = \frac{ap}{R^2T^2} \quad (2.12b)$$

$$B_z = \frac{bp}{RT} \quad (2.12c)$$

where  $a$  and  $b$  can be determined from critical pressure and temperature as,

$$a_c = 0.45724 \frac{R^2T_c^2}{p_c} \quad (2.13a)$$

$$b = 0.07780 \frac{RT_c}{p_c} \quad (2.13b)$$

where  $p_c$  and  $T_c$  are critical pressure and temperature of the substance. Parameter  $a$  scales with  $\alpha$ , which is a function of acentric factor  $\omega$  and reduced temperature  $T_r = T/T_c$  as,

$$a = a_c \times \alpha \quad (2.14)$$

where  $\alpha$  is,

$$\alpha = \left(1 + \kappa \left(1 - \sqrt{T_r}\right)\right)^2 \quad (2.15)$$

and  $\kappa$  is the property of a substance given by,

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2. \quad (2.16)$$

For an ideal gas,  $\rho_0$  is zero and the compressibility factor is unity. Thus for all fluids,

$$\frac{\partial \rho}{\partial p} = \rho_p = \frac{Z}{RT} \quad (2.17a)$$

$$\frac{\partial \rho}{\partial T} = \rho_T = -\frac{Zp}{RT^2}. \quad (2.17b)$$

Specific enthalpy,  $h$  of fluids is given as,

$$h = h_{ref} + h(T) \quad (2.18)$$

where  $h_{ref}$  is the specific enthalpy at the reference state and  $h(T)$  is sensible enthalpy which is a function of the temperature  $T$ . In case of liquids, the enthalpy for compressed liquid is also added. Thus the liquid enthalpy is given as,

$$h = h_{ref} + \frac{p}{\rho} + h(T) \quad (2.19)$$

which gives the necessary derivatives for the gas species as,

$$\frac{\partial h}{\partial p} = h_p = 0 \quad (2.20a)$$

$$\frac{\partial h}{\partial T} = h_T = C_p \quad (2.20b)$$

where  $C_p$  is the specific heat at constant pressure. For liquids, the same are,

$$h_p = \frac{1}{\rho} \quad (2.21a)$$

$$h_T = C. \quad (2.21b)$$

Properties of liquids such as the constant density  $\rho_0$ , specific heat capacity  $C$  and transport properties viscosity, and thermal conductivity are given in Table 2.1. Mass diffusivities of liquids are determined from a Schmidt number of 600, which is a representative value for liquids [72].

Table 2.1. Liquid properties.

Liquid	Density $\rho_0$ ( $kg/m^3$ )	Dynamic viscosity $\mu$ ( $Pa - s$ )	Specific heat capacity C ( $J/kg - K$ )	Thermal conductivity $\lambda$ ( $W/m - K$ )
MMH	875	$8.55 \times 10^{-4}$	2928.7	0.24
RFNA	1570	$9 \times 10^{-4}$	1760	0.28

### 2.1.2 Axisymmetric Opposed Jets

Axisymmetric formulation is a subset of the multi-dimensional governing equations described previously, expressed in cylindrical coordinates instead of Cartesian. In a similar form as before, the governing equations are given by,

$$r \frac{\partial Q}{\partial t} + r \frac{\partial E_i}{\partial x_i} - r \frac{\partial F_{vi}}{\partial x_i} = H + r \dot{\Omega} \quad (2.22)$$

where the vector  $Q$  contains conserved variables in axial and radial directions. The source term corresponding to radial direction is modified as,

$$H = \begin{pmatrix} 0 \\ 0 \\ p + \mu \left( \frac{2v}{r} - \frac{2}{3} \frac{\partial u_i}{\partial x_i} \right) \\ 0 \\ 0 \end{pmatrix} \quad (2.23)$$

where it is assumed that  $y$  direction is the radial direction.

These governing equations can be simplified assuming a self-similar solution with the similarity variable  $v/r$ , as a function of axial coordinate  $x$ . Further details of the transformation can be found in [64].

### 2.1.3 Homogeneous Reactor Model

A common observation from experiments involving MMH and RFNA is that there is a finite delay between liquid contact and gas phase ignition. Experimental studies by Lecourt et al., [16], Farmer et al. [38], Smith [39], Wang and Thynell [11] and by Forness et al. [36] have shown, during this delay there is continued evolution of gaseous species comprising products of liquid reaction and vapors of the propellants. A typical ignition delay from drop on pool experiments by Smith [39] showed that the time delay between gas evolution and ignition is less than a millisecond while the overall delay from liquid contact to ignition is at least an order of magnitude higher. During this intermediate time, propellant vapors mix and in the limiting case, form a homogeneous mixture before acquiring the superheat necessary for ignition. The process of ignition after acquiring the necessary energy can be modeled assuming a homogeneous reactor, which decouples heat and mass transfer effects from reaction kinetics. The governing equations are therefore conservation of energy and species, forming a set of non-linear ODEs. An additional constraint is necessary for complete description of the problem and two straightforward options are: constant pressure and constant volume. For the constant pressure case, conservation equations are given by,

$$\frac{\partial \rho h}{\partial t} = 0 \quad (2.24a)$$

$$\frac{\partial \rho Y_i}{\partial t} = \dot{\omega}_i \quad (2.24b)$$

where  $Y_i$  are conserved mass fractions of the species and specific enthalpy  $h$  is related to specific energy  $e$  as

$$h = e + \frac{p}{\rho} \quad (2.25)$$

and  $\dot{\omega}_i$  are the species source terms, calculated as described in section 2.2. In the case of a constant volume homogeneous reactor, the specific energy is conserved instead of the enthalpy as,

$$\frac{\partial \rho e}{\partial t} = 0. \quad (2.26)$$

These equations are augmented by state relations,

$$\rho = \rho(p, T) \quad (2.27a)$$

$$h = h(p, T) \quad (2.27b)$$

to provide closure.

## 2.2 Gas Phase Reaction Kinetics

It is known that the majority of the hypergolic heat release occurs in the gas phase. It is thus a logical place to begin our modeling efforts. Based on prior works described in section 1.3 and as stated in section 1.2, ignition depends upon state of the mixture and gas phase reactions considered. The reacting gas phase model is therefore instrumental in accurately capturing ignition and subsequent combustion.

### 2.2.1 Reduced Kinetic Mechanisms

Recent efforts on fundamental modeling of gas phase kinetics of hydrazine based fuels with nitric acid based oxidizers have developed large scale mechanisms as described by Catoire et al. [51, 52], Anderson et al. [59] and Labbe [70]. Reduction of these mechanisms is necessary for their effective use in fluid dynamic simulations. Three such reductions by Prof. Westmoreland's group at N.C. State University [60–62] are used in the present work. Following are the details of the three mechanisms.

The first two of the three mechanisms, henceforth referred to as RChem1 and RChem2, are developed from the mechanism assembled by Anderson et al. [59] (referred to as ARL mechanism), containing 81 species and 513 reactions. These two mechanisms contain 25 and 29 species and have 98 and 120 reactions respectively. The third mechanism is developed from a combination of the ARL mechanism and the detailed mechanism of morpholine chemistry by Lucassen [73] and contains 200 reactions of 41 species. Table 2.2 gives a summary of the three mechanisms more detailed characteristics are evaluated in section 3.1.

Table 2.2. Details of the reduced mechanisms.

	RChem1	RChem2	RChem3
Species	25	29	41
Reactions	98	120	200

### 2.2.2 Determination of Reaction Rates and Species Source Terms

An important part of the present work deals with reacting gaseous flows, which requires solving multiple species equations and capturing the correct interactions. In a fundamental form, these reactions are given by a set of elementary chemical reactions, that can be compactly written [74] as,



where  $\chi_j$  is  $j^{th}$  species participating in the  $k^{th}$  reaction,  $K_f$  and  $K_b$  are forward and reverse rates of reaction, while  $\nu'_{j,k}$  and  $\nu''_{j,k}$  are forward and reverse stoichiometric coefficients of  $j^{th}$  species in the reaction. The forward rate is given by an Arrhenius expression,

$$K_f = AT^b e^{\frac{-E_a}{R_u T}} \quad (2.29)$$



where  $A$  and  $b$  are constants,  $T$  is temperature,  $E_a$  is activation energy and  $R_u$  is universal gas constant. Many elementary reactions require additional parameters for determining the forward reaction rates. These parameters are discussed next, followed by the procedure to get the backward rate  $K_b$ .

### Third Body Efficiency

Some of the uni-molecular dissociation reactions require excitation via collisions with other molecules. These can be considered to have two steps,



where, the first step is collision with a molecule of species M, to acquire necessary energy and form the radical  $A \cdot$ . This step is reversible and can lead back to species A. Species M can be any species, including A itself. Similarly, recombination reactions may also require a third species M.



In this case, species M is required to carry away excess energy and prevent a possible dissociation of  $AB \cdot$ . In both these cases, species M acts as an energy carrier, for which some species are better suited than others. In order to capture this effectiveness of a species to carry energy, the parameter third body efficiency,  $\eta$ , is defined and specified for a reaction amongst the rate parameters. Instead of writing such reactions in multiple steps, they may equivalently be written as,



For  $N$  species system, the concentration of the third body is given by,

$$[M] = \sum_{i=1}^N [\chi_i] \eta_i \quad (2.33)$$

where the third body efficiencies  $\eta_i$  are unity unless specified otherwise.

### Pressure Dependence

Some reactions behave differently for low pressure and/or temperature conditions, called the low pressure limit [75, 76]. Often reactions require presence of a third body at the low pressure limit alone. Such reactions are written with  $(+M)$  to indicate third body dependence at the low pressure limit. Rate calculation for such a reaction can be better illustrated with an example. Consider the reaction,



Rate parameters for this reaction include two sets of Arrhenius constants given in Tables 2.3, 2.4 and 2.5. The rate at the low pressure limit is  $k_0$  while  $k_\infty$  corresponds to the rate at normal conditions. For intermediate states of the mixture (“fall-off” region), a smooth transition is desirable and can be obtained by,

$$k = k_\infty \left( \frac{P_r}{1 + P_r} \right) F \quad (2.35)$$

where  $P_r$  is called the reduced pressure, given by

$$\frac{k_0 [M]}{k_\infty} \quad (2.36)$$

and  $F$  is the broadening factor, introduced to better represent reaction rate in this region. It is either assumed to be unity or calculated from the Troe parameters [75] or the Tsang and Herron [77] linear fits, that are provided with the reaction parameters.

The broadening factor  $F$  incorporated to account for complex energy transfers between colliding molecules for unimolecular and recombination reactions. The simplest approximation,  $F = 1$ , known as the Lindemann form, neglects energy transfers due to weak collisions, leading to an earlier transition of reaction rate to the high pressure limit. The broadening factor due to Troe [75] provides a better approximation of this transition to the high pressure limit. The Troe form employs four parameters and three exponential terms, calculation of which can be simplified using Tsang and Herron linear fits. These are two parameter expressions, determined by comparing theoretically calculated reaction rates and the Lindemann form at various temperatures. In Table 2.5, a Tsang and Herron fit for reaction in equation 2.34 is provided, giving  $F$  as

$$F = tsa_1 + tsa_2 \times T. \quad (2.37)$$

If the Troe parameters are given,  $F$  can be calculated as,

$$\log F = \left[ 1 + \left[ \frac{\log(P_r) + c}{n - d(\log P_r + c)} \right]^2 \right]^{-1} \log(F_{cent}) \quad (2.38)$$

where  $F_{cent}$  is given as,

$$F_{cent} = (1 - \alpha) e^{(-T/t_1)} + \alpha e^{(-T/t_2)} + e^{(-t_3/T)} \quad (2.39)$$

where  $t_1$ ,  $t_2$  and  $t_3$  are Troe parameters. Other constants in the calculation of  $F_{cent}$  are,

$$\begin{aligned} c &= -0.4 - 0.67 \log(F_{cent}), \\ n &= 0.75 - 1.27 \log(F_{cent}) \\ d &= 0.14 \end{aligned} \quad (2.40)$$

Table 2.3. Arrhenius rate parameters for reaction in equation 2.34.

Condition	A	b	$E_a$
Normal ( $k_\infty$ )	$7.6 \times 10^{18}$	-1.27	73290
Low pressure ( $k_0$ )	$2.47 \times 10^{28}$	-3.37	74800

Table 2.4. Third body efficiencies for reaction in equation 2.34.

Species	$\eta_{third}$
N <sub>2</sub> O	1.5
H <sub>2</sub> O	4.4
N <sub>2</sub>	1.0
CO <sub>2</sub>	2.3

Table 2.5. Tsang and Herron fit for broadening factor, reaction in equation 2.34.

$tsa_1$	$tsa_2$
0.94	$-1 \times 10^{-4}$

Once we have determined the forward rate, the reverse reaction rate can be obtained from equilibrium constant  $K_{eq}$ . The equilibrium constant in terms of concentrations can be given as,

$$\begin{aligned}
 K_{eq} &= \frac{\prod_{j=1}^{N_{spc}} [\chi_j]^{\nu_j''}}{\prod_{j=1}^{N_{spc}} [\chi_j]^{\nu_j'}} \left( \frac{R_u T_{ref}}{P_{ref}} \right)^{\sum \nu_j'' - \sum \nu_j'} \\
 &= \frac{K_f}{K_b} \left( \frac{R_u T_{ref}}{P_{ref}} \right)^{\sum \nu_j'' - \sum \nu_j'}
 \end{aligned} \tag{2.41}$$

where  $R_u$  is the universal gas constant in molar units and  $[\chi_i]$  are species concentrations in  $Kmol/m^3$ . The equilibrium constant is also given as,

$$K_{eq} = e^{-\frac{\Delta G^0}{R_u T}} \tag{2.42}$$

where  $G^0$  is the Gibbs energy of formation at a reference condition,

$$G^0 = (h^0 - Ts^0)_{ref} \quad (2.43)$$

leading to, for  $k^{th}$  reaction,

$$\Delta G_k^0 = \sum_{j=1}^N (\nu''_{j,k} G_j^0 - \nu'_{j,k} G_j^0). \quad (2.44)$$

Thus backward reaction rate  $K_b$  is then determined from equations 2.42 and 2.41.

### Species Sources

For species conservation equations, we need to calculate source terms arising from chemical reactions.

For  $k^{th}$  reaction in the mechanism 2.28 [74] ,

$$q_{\text{progf-k}} = k_f \prod_i [\chi]_i^{\nu'_{ik}} \quad (2.45a)$$

$$q_{\text{progb-k}} = k_b \prod_i [\chi]_i^{\nu''_{ik}} \quad (2.45b)$$

where  $q_{\text{prog}}$  refers to progress of the reaction k. Depending on forward and reverse rates, the net reaction rate,  $[NRR]$  is,

$$[NRR] = q_{\text{progf}} - q_{\text{progb}}. \quad (2.46)$$

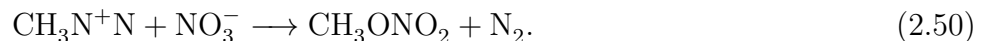
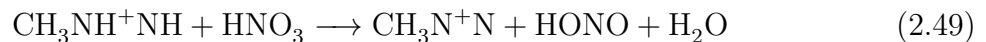
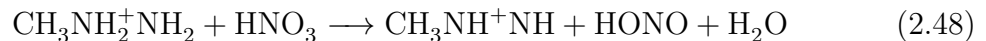
Finally, the species production (destruction) vector is,

$$\dot{\Omega} = [\dot{\omega}_1, \dot{\omega}_2 \dots \dot{\omega}_j]^T = [\nu'' - \nu']^T \cdot ([NRR] \cdot [MW_j]^T) \quad (2.47)$$

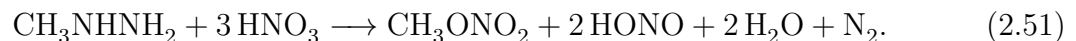
where  $MW_j$  is molar mass of species “j”.

### 2.3 Liquid Reaction and Vaporization

Upon contact of hypergolic propellants, liquid reactions supersede other phenomena and hence need to be included in the model. Reactions for liquid MMH and RFNA, identified in literature [22, 59] give products that are either liquid complexes (MMHN) or solids such as ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). In contrast, measurements from a recent study, [11] show that the resulting products of liquid phase reactions are gases. While the understanding of liquid complexes or solid intermediate pathways is poor for MMH and RFNA, their inclusion also presents difficulties due to escalating computational cost. An alternative is to consider observed products as resulting from a global reaction. A multi-step mechanism for pre-ignition liquid reactions is proposed by Wang and Thynell [11]. Three steps which are a part of that mechanism are:



A global reaction based on these three steps is shown below.



In this reaction, all the products are gaseous and contain water and nitrogen, which are final combustion products, indicating that this global reaction represents a parallel path to gas phase chemistry. The product species methyl nitrate ( $\text{CH}_3\text{ONO}_2$ ) is known to be a mono-propellant as well as an explosive, which is particularly affected by the presence of oxygen [78]. The heat of this reaction, calculated from enthalpies of the species involved ( $6.4 \text{ MJ/kg}$ ), is 12% of that resulting from complete combustion of methane ( $55 \text{ MJ/kg}$ ) and has an adiabatic flame temperature of  $1030 \text{ K}$ .

Hence incorporating this liquid phase reaction can release the energy necessary for vaporization and gas phase ignition.

While the liquid phase reaction is essential, including a liquid phase requires an adequate model for vaporization. The simplest model for this purpose is to consider vaporization as a chemical reaction, with each of the liquids as a reactant and corresponding vapor as the product. The well known Langmuir model can be used to estimate the rate of vaporization [79] as,

$$\dot{m}_v = \frac{Sp_{vref}}{\sqrt{2\pi MW RT}} e^{\frac{\Delta H_v}{2.303R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right)} \quad (2.52)$$

where  $S$  is the surface area of the liquid,  $p_{vref}$  is reference vapor pressure at temperature  $T_{ref}$ ,  $T$  is the current liquid temperature,  $MW$  is molecular mass,  $R$  is universal gas constant and  $\Delta H_v$  is the heat of vaporization. This expression can be cast into an equivalent Arrhenius rate form as,

$$\dot{m}_v = A \times T^b \exp\left(\frac{-E_a}{RT}\right) \quad (2.53)$$

$$A = \frac{Sp_{vref} \exp\left(\frac{\Delta H_v}{2.303RT_{ref}}\right)}{\sqrt{2\pi MW R}} \quad (2.54)$$

$$b = -0.5 \quad (2.55)$$

$$E_a = \frac{\Delta H_v}{2.303}. \quad (2.56)$$

In this model, the surface area  $S$  of the liquid can be approximated from homogeneous equilibrium model as it relates to gradient of the volume fraction of the liquid, which in turn varies as the inverse of the cell size,  $1/\Delta x$ . Also, the difference in the enthalpy of the phases provides the expected endothermic behavior.

Liquid reaction and vaporization models introduced here, are calibrated in chapter 3 and premixed liquids in a homogeneous reactor are modeled using these. Gas phase chemistry calculations are also a part of the homogeneous reactor modeling and comparison with Cosilab results is used for validating their implementation. Additionally,

transport properties need to be calculated, details of which are provided in Appendix A. Opposed diffusion flames of vapors are used for validation of transport properties and determine required grid resolution by comparing with CHEMKIN results. Subsequent two-dimensional calculations adhere to the cell size, found to accurately predict the species profiles within the flame.

## 2.4 Adaptive Time Stepping for Homogeneous Reactor Modeling

The governing equations described above for a homogeneous reactor constitute a system of non-linear ODEs, which depending on the kinetics mechanism, can be a stiff problem. According to Cash [80], such a stiff problem is a combination of smooth and transient problems, where the stiffness is usually associated with the transient. The time step for solving such problems is therefore dependent on the transient, which is a non-linear region, (whose location is unknown) that needs high resolution. In such regions, the limiting time scale depends upon two factors, namely rate of the fastest reaction and the levels of trace species. Both these factors play an important role at ignition, which has a steep temperature gradient that influences reaction rates, as well as the highest concentrations of many trace species. Employing the smallest time scale associated with ignition for the entire calculation can insure accuracy, but the computational cost would be prohibitive even for a single point calculation.

Significant non-linear behavior of a reaction mechanism is typically observed in three regions: initiation transient, ignition transient and near equilibrium transient. During initiation transient, as intermediate species are created in trace amounts, their destruction through reverse reactions is responsible for non-linearity and requires good temporal resolution. The same is true for the final stage of the reactions near equilibrium. During the ignition transient, both the reaction rate and trace species dictate the required resolution, although for larger mechanisms usually the trace species play the critical role. These limitations on the time scale can be imposed by estimating change in the solution for a given time step and restricting it to a pre-