

# SDTOOLBOX

NUMERICAL TOOLS FOR SHOCK AND DETONATION WAVE MODELING

Explosion Dynamics Laboratory  
Graduate Aerospace Laboratories  
California Institute of Technology  
Pasadena, CA USA 91125

## Contributors:

S. Kao  
J. Ziegler  
N. Bitter  
B. Schmidt  
J. Lawson  
J. E. Shepherd

GALCIT Report FM2018.001  
Revised January 7, 2025

This document is in a state of continuous development and you are examining a snapshot in time. There are sections on real gas thermodynamics and vibrational-rotational-translational equilibrium but no discussion of the related software which is still under development. This version was published just as V2.5.1 of Cantera was released so there few references to the YAML format for the thermochemical database.



**Disclaimer and Copyright** The software tools described in this document are based on the Cantera software library which was originally developed at Caltech. The software is offered under the following licensing terms:

Copyright (c) 2001-2023, California Institute of Technology All rights reserved.

Redistribution and use of these programs in source and binary forms, with or without modification, are permitted provided that the following conditions are met:

- Redistributions of source code must retain the above copyright notice, this list of conditions and the following disclaimer.
- Redistributions in binary form must reproduce the above copyright notice, this list of conditions and the following disclaimer in the documentation and/or other materials provided with the distribution.
- Neither the name of the California Institute of Technology nor the names of its contributors may be used to endorse or promote products derived from this software without specific prior written permission.

THIS SOFTWARE IS PROVIDED BY THE COPYRIGHT HOLDERS AND CONTRIBUTORS "AS IS" AND ANY EXPRESS OR IMPLIED WARRANTIES, INCLUDING, BUT NOT LIMITED TO, THE IMPLIED WARRANTIES OF MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE ARE DISCLAIMED. IN NO EVENT SHALL THE COPYRIGHT OWNER OR CONTRIBUTORS BE LIABLE FOR ANY DIRECT, INDIRECT, INCIDENTAL, SPECIAL, EXEMPLARY, OR CONSEQUENTIAL DAMAGES (INCLUDING, BUT NOT LIMITED TO, PROCUREMENT OF SUBSTITUTE GOODS OR SERVICES; LOSS OF USE, DATA, OR PROFITS; OR BUSINESS INTERRUPTION) HOWEVER CAUSED AND ON ANY THEORY OF LIABILITY, WHETHER IN CONTRACT, STRICT LIABILITY, OR TORT (INCLUDING NEGLIGENCE OR OTHERWISE) ARISING IN ANY WAY OUT OF THE USE OF THIS SOFTWARE, EVEN IF ADVISED OF THE POSSIBILITY OF SUCH DAMAGE.

# Contents

<b>Contents</b>	ii
<b>List of Figures</b>	vi
<b>List of Tables</b>	ix
<b>Preface</b>	1
<b>1 Introduction</b>	<b>3</b>
1.1 Overview and Quickstart . . . . .	4
<b>I Thermodynamics</b>	<b>7</b>
<b>2 Fundamentals</b>	<b>9</b>
2.1 General Principles . . . . .	9
2.2 Ideal Gas . . . . .	13
2.3 Perfect Gases . . . . .	20
2.4 Thermochemistry . . . . .	20
<b>3 Statistical Mechanics and Thermodynamics</b>	<b>23</b>
3.1 Molecular Partition Functions and RRHO model . . . . .	24
3.2 Spectroscopic Approach for Diatomic Molecules . . . . .	28
3.3 Thermodynamic Properties from Partition Functions . . . . .	31
3.4 Estimating Heat Capacities . . . . .	36
3.5 RRHO Model Thermodynamics . . . . .	37
<b>4 Equilibrium</b>	<b>43</b>
4.1 Second Law of Thermodynamics . . . . .	43
4.2 Equilibrium at Constant Temperature and Pressure . . . . .	44
4.3 Composition Constraints . . . . .	45
4.4 Equilibrium as Constrained Minimization . . . . .	46
4.5 Reaction Coordinates . . . . .	48
4.6 Equilibrium as Unconstrained Minimization . . . . .	48
4.7 Element Potentials . . . . .	51
4.8 Equilibrium Constants . . . . .	51
4.9 Partition Function Method . . . . .	52
<b>5 Thermodynamic Property Representation</b>	<b>55</b>
5.1 Specification for Cantera input . . . . .	57
5.2 Resources for Thermodynamic Data . . . . .	59
5.3 Least Squares Fit for Piecewise Thermodynamic Representation . . . . .	60

<b>II Equilibrium and Frozen Flows</b>	<b>65</b>
<b>6 Jump Conditions</b>	<b>67</b>
6.1 Introduction . . . . .	67
6.2 Chemical Composition . . . . .	69
6.3 Rayleigh Line and Hugoniot . . . . .	69
6.4 Shock Waves - Frozen and Equilibrium . . . . .	71
6.5 Detonation Waves and the Chapman-Jouguet Condition . . . . .	73
6.6 Reflected Waves . . . . .	77
6.7 Relationship of Ideal Model parameters to Real Gas Properties . . . . .	78
6.8 Inverse Shock Relations . . . . .	80
<b>7 Applications</b>	<b>83</b>
7.1 Detonations in Tubes . . . . .	83
7.2 Approximating the TZ Wave . . . . .	86
7.3 Oblique Waves . . . . .	87
7.4 Prandtl-Meyer Expansion . . . . .	90
7.5 Isentropic Expansion Following Shock Wave . . . . .	92
7.6 Reflection of overdriven detonation waves . . . . .	93
7.7 Detonation in a compressed gas region and subsequent reflection . . . . .	93
7.8 Pressure-velocity relationship behind a detonation . . . . .	94
7.9 Ideal Rocket Motor Performance . . . . .	94
7.10 Equilibrium and Frozen Isentrope Properties . . . . .	96
7.11 Shock Tube Simulation . . . . .	108
<b>8 Numerical Methods</b>	<b>115</b>
8.1 Iterative Solution with Density . . . . .	115
8.2 Newton-Raphson Method in Temperature and Volume . . . . .	118
8.3 Chapman-Jouguet Detonation Velocity . . . . .	121
8.4 Verification and Convergence . . . . .	125
<b>III Reacting Flows</b>	<b>129</b>
<b>9 Reacting Flow Equations</b>	<b>131</b>
9.1 Reacting Compressible Flow . . . . .	131
9.2 Adiabatic Change Relation . . . . .	135
9.3 Thermicity . . . . .	136
9.4 Equilibrium and Frozen Flow . . . . .	140
9.5 Nonsteady Flow . . . . .	142
9.6 Steady flow . . . . .	143
9.7 Temperature . . . . .	144
9.8 Real Gas Modeling . . . . .	146
<b>10 Reactions and Reaction Rates</b>	<b>163</b>
10.1 Unimolecular reactions . . . . .	163
10.2 Bi-molecular or two-body reactions . . . . .	165
10.3 Ter-molecular or three-body reactions . . . . .	169
10.4 Reaction Networks . . . . .	176
10.5 Molecular Collisions and Reaction Rates . . . . .	177
10.6 One-step Reactions . . . . .	182
<b>11 Applications</b>	<b>193</b>
11.1 Steady shock waves followed by reaction zones . . . . .	193
11.2 ZND Detonation Model . . . . .	195

11.3 Constant volume and pressure explosions . . . . .	203
11.4 Unsteady Control Volume Models . . . . .	204
11.5 Reaction zones with stream tube area change . . . . .	206
11.6 Streamtube Area . . . . .	206
11.7 Formulation using thermicity . . . . .	208
11.8 Flows with Friction and Thermal Interactions . . . . .	209
11.9 Stagnation Point and Shock Tube Flows . . . . .	211
11.10 Curvature-Area Relation . . . . .	214
11.11 Shock Change Relations - Planar Waves . . . . .	215
11.12 Shock Change Relations - Curved Waves . . . . .	226
11.13 Unsteady Reaction Zone Models . . . . .	228
11.14 Shock Waves with Vibrational Relaxation . . . . .	232
11.15 Modeling Nonequilibrium Processes . . . . .	242
<b>IV Toolbox Software</b>	<b>245</b>
<b>12 Functions</b>	<b>247</b>
<b>13 Demonstration Programs</b>	<b>263</b>
<b>14 Utility Programs</b>	<b>267</b>
<b>15 Hints and Tips</b>	<b>269</b>
<b>V Acknowledgments</b>	<b>273</b>
<b>VI References</b>	<b>275</b>
<b>VII Appendices</b>	<b>287</b>
<b>A Perfect Gas Analytical Solutions</b>	<b>289</b>
A.1 Incident Shock Waves . . . . .	289
A.2 Reflected Shock Waves . . . . .	291
A.3 Detonation Waves in Perfect Gases . . . . .	294
A.4 Chapman-Jouguet Conditions . . . . .	294
A.5 Two-gamma CJ Conditions . . . . .	295
A.6 One-gamma CJ Conditions . . . . .	296
A.7 Strong detonation approximation . . . . .	296
A.8 Reflection of Detonation . . . . .	296
A.9 Oblique Shocks in Perfect Gases . . . . .	299
A.10 Prandtl-Meyer Expansion in Perfect Gas . . . . .	300
A.11 Shock Tubes . . . . .	302
<b>B Differentials on the Hugoniot</b>	<b>303</b>
B.1 Differential Relationships on the Hugoniot . . . . .	303
B.2 CJ Point Analysis . . . . .	304
B.3 Derivatives of Pressure . . . . .	305
B.4 Thermodynamic Analysis . . . . .	306
B.5 Perfect Gas Analysis . . . . .	307
<b>C Thermodynamics of the Hugoniot</b>	<b>311</b>
C.1 Jouguet's rule . . . . .	311

C.2 Entropy Extremum . . . . .	314
C.3 Temperature and Entropy on the Hugoniot . . . . .	316
<b>D Real Gas Adiabatic Change Equation</b>	<b>317</b>
D.1 Thermicity . . . . .	318
D.2 Abbott's Theorem: Derivative of Intensive Properties by Extensive Properties . . . . .	319
D.3 Application . . . . .	320
<b>E Classical Thermodynamics</b>	<b>321</b>
E.1 Thermodynamic potentials and fundamental relations . . . . .	321
E.2 Maxwell relations . . . . .	321
E.3 Various defined quantities . . . . .	322
E.4 $v(P, s)$ relation . . . . .	324
E.5 Equation of State Construction . . . . .	324
<b>F Physical Constants of Selected Molecules</b>	<b>327</b>
F.1 Diatomic Molecule Energy Levels . . . . .	327
F.2 Degeneracy, Electronic States, Bond and Ionization Energies . . . . .	330
<b>G Constants and Conversions</b>	<b>331</b>
G.1 Fundamental Physical Constants . . . . .	331
G.2 Gases . . . . .	331
G.3 Our Atmosphere . . . . .	332
G.4 Unit Conversions . . . . .	333

DRAFT

# List of Figures

3.1	Effective potential energy as a function of radial distance $r$ and rotational quantum number $J$ . This example uses the Morse potential and parameters of the NO ground state. . . . .	31
3.2	NO heat capacity computed from partition function . . . . .	34
3.3	CH heat capacity computed from partition function . . . . .	35
3.4	OH heat capacity computed from partition function . . . . .	35
3.5	Low-temperature heat capacity of CO computed using the RRHO partition function (3.120) and compared to the standard NASA-9 fit. . . . .	40
3.6	Low-temperature heat capacity of CO computed using the RRHO partition function (3.121) and compared to the standard NASA-9 fit. . . . .	41
3.7	Low-temperature heat capacity of H <sub>2</sub> computed using the RRHO partition function (3.123) assuming equilibrium between ortho and para states with comparison to the standard NASA-9 fit. . . . .	42
3.8	Low-temperature heat capacity of O <sub>2</sub> computed using the RRHO partition function (3.125) and compared to the standard NASA-9 fit. . . . .	42
5.1	Example usage of NASA-7 thermodynamic coefficients with Cantera for 2-Butenal. . . . .	57
5.2	Example usage of NASA-9 thermodynamic coefficients with Cantera for O <sub>2</sub> . . . . .	58
5.3	Polynomial fit to statistical thermodynamic data. . . . .	61
5.4	Comparision of tabulated and polynomial fit to reduced heat capacity $C_p/R$ for 2-butenal (CH <sub>3</sub> CHCHCHO). . . . .	62
5.5	Comparision of tabulated and polynomial fit to reduced enthalpy $H/RT$ for 2-butenal (CH <sub>3</sub> CHCHCHO). . . . .	62
5.6	Comparision of tabulated and polynomial fit to reduced entropy $S/R$ for 2-butenal (CH <sub>3</sub> CHCHCHO). . . . .	63
6.1	Cartoon depiction of the transformation from the laboratory to the wave fixed reference frame. . . . .	67
6.2	Hugoniots (a) Shock wave propagating in a non-exothermic mixture or a mixture with frozen composition. (b) Shock wave propagating in an exothermic mixture. . . . .	70
6.3	The Rayleigh line and Hugoniot for air with initial pressure of 1 atm and initial temperature of 300 K. . . . .	71
6.4	Frozen isentropes, Hugoniot, and a Rayleigh line for a 1000 m/s shock wave in air. . . . .	72
6.5	Equilibrium Hugoniot and two Rayleigh lines illustrating detonation and deflagration branches. . . . .	74
6.6	Hugoniot and three representative Rayleigh lines illustrating $w_1 = U_{CJ}$ as the minimum wave speed and tangency of Rayleigh line and Hugoniot at the CJ point. . . . .	75
6.7	Hugoniot, Rayleigh line, and three representative isentropes (equilibrium) illustrating the tangency conditions at the CJ point. . . . .	76
6.8	Diagrams showing the incident shock or detonation wave before (a) and after (b) reflection with a wall. States 1, 2, and 3 are shown. . . . .	77
7.1	Detonation propagation in tube with a closed end. . . . .	84
7.2	Geometry of oblique shock or detonation illustrating normal and perpendicular components . . . . .	88
7.3	Examples of shock polars for air computed with frozen composition . . . . .	89
7.4	Illustration of an expansion fan between two uniform states, 1 and 2, deflecting the flow downward $d\theta < 0$ and increasing the speed $du > 0$ . . . . .	90
7.5	Example results from numerical evaluation of Prandtl-Meyer function for equilibrium expansion of hot air (3000 K and 1 atm initial conditions). (a) Prandtl-Meyer function $\omega(M)$ . (b) Pressure-deflection $P(\theta)$ relationship within expansion fan. . . . .	91

7.6	Property variation on an isentrope (frozen) passing through the postshock state of a 1633 m/s shock wave in air. . . . .	92
7.7	Incident and reflected pressures for a detonation in H <sub>2</sub> -N <sub>2</sub> O (31% H <sub>2</sub> , 1 bar , 300 K) mixtures. . . . .	93
7.8	Ratio of reflected-to-incident pressures for data in Fig. 7.7. . . . .	94
7.9	a) CJ state and pressure velocity-relationship on reflected shock wave for H <sub>2</sub> -N <sub>2</sub> O mixtures initially at 300 K and 1 bar. b) Matching pressure and velocity for transmitting a shock wave into water. . . . .	95
7.10	Vacuum specific impulse for an ideal hydrogen-oxygen-helium rocket motor . . . . .	96
7.11	Frozen vs. equilibrium isentrope in <i>P</i> - <i>V</i> coordinates . . . . .	97
7.12	Species equilibrium composition an isentrope . . . . .	98
7.13	Frozen vs. equilibrium values of sound speed squared <i>a</i> <sup>2</sup> for isentropic expansion of combustion products of stoichiometric H <sub>2</sub> -O <sub>2</sub> constant volume explosion. . . . .	107
7.14	Frozen vs. equilibrium values of $\gamma - 1$ and $\kappa - 1$ for isentropic expansion of combustion products of stoichiometric H <sub>2</sub> -O <sub>2</sub> constant volume explosion. . . . .	108
7.15	Frozen vs. equilibrium values of $\gamma - 1$ and $\kappa - 1$ . . . . .	108
7.16	(a) Equilibrium value of the function $(\rho/P)(dP/d\rho)_T$ . (b) Equilibrium value of the function $(T/v)(dv/dT)_P$ . . . . .	109
7.17	Conventional shock tube and initial wave system generated by diaphragm rupture. . . . .	110
7.18	Equilibrium postshock properties: (a) density, (b) temperature, (c) pressure as a function of shock Mach number and (d) Pressure-velocity relationship. Air at an initial state of 1 bar and 298.15 K. . . . .	111
7.19	Wave curves and solutions for four types of drivers: (a) He ; (b) constant volume explosion of propane-oxygen; (c) reverse (propagation away from diaphragm) detonation of mixture used in case (b); (d) forward (propagation toward diaphragm) detonation of mixture used in case (b). . . . .	112
7.20	Pressure-velocity, reflected shock case . . . . .	113
8.1	The Rayleigh line and reactant (frozen) Hugoniot with the minimum (8.6) and maximum (8.7) density ratios superimposed for stoichiometric hydrogen-air. . . . .	117
8.2	$\gamma$ as a function of temperature for stoichiometric hydrogen-air at 1 atm (frozen composition). . . . .	118
8.3	Initial velocity as a function of density ratio for stoichiometric hydrogen-air with intial temperature 300 K and initial pressure 1 atm. . . . .	124
8.4	Initial velocity as a function of density ratio for stoichiometric hydrogen-oxygen with intial temperature 300 K and initial pressure 1 atm. . . . .	124
8.5	Cumulative distribution function <i>F</i> for error in fitted parameters. . . . .	125
8.6	The percent error in the exact solution and the results of PostShock.fr for one mole of Argon with initial temperature 300 K and initial pressure 1 atm. . . . .	126
8.7	The percent difference in the solutions of STANJAN and PostShock.fr for hydrogen-air at an equivalence ratio of 0.5 for varying shock speed with initial temperature 300 K and initial pressure 1 atm. . . . .	127
8.8	A contour plot of the RMS surface with the solution indicated at the minimum. . . . .	127
8.9	Convergence study for stoichiometric hydrogen-air with initial temperature 300 K and initial pressure 1 atm using PostShock.fr. . . . .	128
10.1	Measured reaction rates for H+O <sub>2</sub> → OH+O from Baulch et al. (2005). . . . .	167
10.2	Equilibrium constants <i>K<sub>p</sub></i> for the forward and reverse reactions of H+O <sub>2</sub> → OH+O. . . . .	169
10.3	Forward and reverse rates for H+O <sub>2</sub> → OH+O using the recommended values from Baulch et al. (2005) and the estimate <i>k<sub>f</sub></i> / <i>K<sub>c</sub></i> for the reverse rate. . . . .	170
10.4	Evaluation of rate constants for (R23) as a function of pressure for two temperatures using the Burke et al. (2012) rate constant parameters and an atmosphere consisting of stoichiometric hydrogen-air combustion products in equilibrium at the specified temperatures and pressures. . . . .	174
10.5	Evaluation of rate constants for (R24) as a function of pressure for two temperatures using the Burke et al. (2012) rate constant parameters and an atmosphere consisting of stoichiometric hydrogen-air combustion products in equilibrium at the specified temperatures and pressures. . . . .	175
10.6	Reduced collision integral as a function of reduced temperature for Lennard-Jones potential . . . . .	180

10.7	Equilibrium product species distribution for R27 as a function of temperature at a pressure of 1 atm.	184
10.8	Equilibrium product enthalpy for R27 as a function of temperature at pressures of 1, 10 and 100 atm.	186
10.9	Linear fits to reactant (a) and equilibrium product (b) enthalpy for R27 as a function of temperature at a pressure of 1 atm.	187
10.10	Comparison of stoichiometric pentane-air $h(T)$ for reactants and products (CJ isentrope) as well as low and high-temperature linear fits to equilibrium product enthalpy.	188
10.11	Example constant-pressure combustion simulation with two- $\gamma$ , one-step reaction model $k = A(1 - \lambda)^n \exp(-E/RT)$ , $E_a = 30 \text{ kcal} \cdot \text{mol}^{-1}$ . a) $n = 1/2$ , $A = 5.15 \times 10^6$ . b) $n = 1$ , $A = 3.6 \times 10^8$ . c) $n = 2$ , $A = 1.7 \times 10^{12}$ . The initial conditions are $P_0 = 3.49 \text{ MPa}$ ; $T_0 = 1549 \text{ K}$ , the vN state for a stoichiometric pentane-air CJ detonation.	189
10.12	Example constant-pressure combustion simulation with three reaction and thermodynamic models, same initial conditions as in Fig. 10.11. a) Detailed chemistry and thermodynamics using the JetSurf2 mechanism. b) One-step reaction of Westbrook and Dryer (1981) c) One-step reaction of Burcat and Dvinyaninov (1995).	191
11.1	Reaction zone structure behind a strong shock wave ( $U = 6000 \text{ m/s}$ ) in a mixture of $\text{N}_2/\text{CO}_2$ (4/96) initially at 13.3 Pa and 300 K.	194
11.2	Schematic of the ZND detonation model. (a) States 1, 2, and 3 (b) Reaction zone structure.	195
11.3	Path (red) between frozen Hugoniot (solid) and equilibrium Hugoniot (dashed) for a ZND detonation traveling at the Chapman-Jouget detonation velocity.	196
11.4	Reaction zone spatial profiles for the ZND model of a steady CJ detonation in a stoichiometric $\text{CH}_4$ -air mixture with initial conditions of 25°C and 1 atm.	197
11.5	Reaction zone spatial profiles for the ZND model of a steady CJ detonation in a stoichiometric $\text{H}_2\text{-O}_2\text{-Ar}$ mixture (70% Ar dilution) with initial conditions of 25°C and 0.1 atm.	198
11.6	ZND model results for (a) thermicity and (b) Mach number spatial profiles for the stoichiometric $\text{CH}_4$ -air case shown in Fig. 11.4.	199
11.7	ZND model results for (a) thermicity and (b) Mach number spatial profiles for a steady CJ detonation for the stoichiometric $\text{H}_2\text{-O}_2\text{-Ar}$ case shown in Fig. 11.5.	199
11.8	Definitions of induction and energy length based on thermicity profile for case shown in Fig. 11.4.	200
11.9	Reaction zone temporal profiles for: a) constant pressure simulation and, b) constant volume simulation with postshock conditions for CJ a detonation in a stoichiometric $\text{CH}_4$ -air mixture.	203
11.10(a)	Constant-volume explosion simulation of reaction behind a reflected shock wave for $0.1\text{H}_2 + 0.05\text{O}_2 + 99.85\text{Ar}$ at $P_1 = 64 \text{ atm}$ and $T_1 = 1585 \text{ K}$ . The induction time determined from the location of the peak in $dT/dt$ is $\tau_i = 48 \mu\text{s}$ , (Fig. 54 Schultz and Shepherd, 2000)	204
11.11	Comparison of flow properties evaluated with planar shock and stagnation point models using the transformation methodology of (11.83).	213
11.12	Explanation of relationship between wave curvature and stream tube expansion for a decaying blast wave.	215
11.13	Shock change relation function $F(M)$ for a perfect gas, $\gamma = 1.4$ .	222
11.14	Comparison of RRHO model of specific heats with equilibrium values from the NASA compilation for (a) $\text{N}_2$ , $\Theta_v = 3352.3 \text{ K}$ (b) $\text{O}_2$ , $\Theta_v = 2238.7 \text{ K}$ , and (c) $\text{NO}$ , $\Theta_v = 2697.7 \text{ K}$ .	237
11.15	Comparison of RRHO model of internal energy for the ground state ( $\Theta_v = 3352.3 \text{ K}$ ) with equilibrium values from the NASA compilation for $\text{N}_2$ .	238
11.16	Comparison of RRHO model of specific heats with equilibrium values from the NASA compilation for (a) $\text{CO}_2$ , $\Theta_v = 959.7 \text{ K}$ (bending, $g = 2$ ), 1997 K (symmetric, $g = 1$ ), 3397 K (antisymmetric, $g = 1$ ). (b) $\text{CO}$ , $\Theta_v = 3083.3 \text{ K}$	240
C.1	Grüneisen parameter, denominator of (C.6), and isentropic exponent (C.26) for the example shown in Fig. 6.7.	314

# List of Tables

2.1 Thermodynamic potentials and associated relationships. . . . .	11
4.1 Optimization problems for equilibrium processes Kondepudi and Prigogine (1998). . . . .	44
6.1 Parameters for CJ detonation in stoichiometric ethylene-oxygen computed by the Shock and Detonation Toolbox. . . . .	80
7.1 Comparison of real gas and two- $\gamma$ results for a CJ detonation in stoichiometric ethylene-oxygen. . . . .	87
9.1 Thermodynamic critical states for some common components of combustion reactants and products (Reid et al., 1987). . . . .	148
9.2 Effective thermodynamic critical parameters for stoichiometric CH <sub>4</sub> -air mixtures. . . . .	148
9.3 Pseudo-critical parameters for stoichiometric CH <sub>4</sub> -air mixtures computed using <i>a</i> and <i>b</i> values for Redlich-Kwong equation of state. . . . .	151
9.4 Correspondence between terms in the constant-pressure, adiabatic temperature evolution equation for real gas and ideal gas models. . . . .	158
9.5 Correspondence between terms in the thermicity expression for real gas and ideal gas models. .	162
10.1 Thermodynamic parameters for one-step model of R27. . . . .	188
11.1 Characteristic reaction zone length and time scales for two examples of ZND detonation structure. .	202
11.2 Comparison of three methods of computing reaction zone induction time and length for a stoichiometric stoichiometric CH <sub>4</sub> -air mixture. . . . .	204
C.1 Jouguet's rule for detonations and deflagrations . . . . .	313
F.1 Critical Constants (Rumble, 2018) and LJ parameters (Cloutman, 2000, Kee et al., 1998) for selected molecular fluids . . . . .	327
F.2 Diatomic molecular constants . . . . .	328
F.3 Diatomic molecule symmetry factor, rotation and vibration quanta and dissociation energy expressed as temperatures $\Theta = \Delta E/k_b$ . . . . .	329
F.4 Degeneracy factors, ionization, enthalpy at zero temperature and dissociation energies for selected species. . . . .	330

# Preface

These notes are a tutorial on the analysis and computation of shock and detonation waves in gases with realistic thermochemistry. A library ([SDToolbox](#)) of Python and MATLAB routines is described for computations of post-shock conditions and Chapman-Jouguet detonation velocity. Notes and demonstration programs are provided for using this library to compute examples of normal and oblique shocks and detonations, shock and detonation tube operations, expansion waves, nozzle flows, ideal detonation and wave structure, propulsion systems and selected wave interaction problems.

The toolbox modules, demonstration scripts and instructions for installation are available on the SD-Toolbox [website](#). In order to use these scripts, the reader must install the Cantera software and Python or MATLAB. This revision of the document links to programs that are compatible with the most recent release of Cantera, V2.5; MATLAB, R2020; and Python 3.8. The programs were tested on earlier versions (2.3 and 2.4) of Cantera, MATLAB (2017,2018 and Python (3.5,3.6). The documentation and software for Cantera [Goodwin et al. \(2017\)](#) is open source and available at [www.cantera.org](http://www.cantera.org).

DRAFT



# Chapter 1

## Introduction

These notes are a tutorial on the analysis and computation of shock and detonation waves with selected applications to explosion and propulsion. Numerical solution methods are necessary for solving the conservation equations or jump conditions that determine the properties of shock and detonation waves in a multi-component, reacting gas mixture. Only the idealized situations of perfect (constant heat-capacity) gases with fixed chemical energy release can be treated analytically (Appendix A). Although widely used for simple estimates and mathematical analysis, the results of perfect gas models are not suitable for analysis of laboratory experiments and carrying out numerical simulations based on realistic thermochemical properties.

The science of shock and detonation waves began in the 19th century and continues to be an ongoing activity. Technological applications such as chemical propulsion (rockets, gas turbines and gaseous detonation concepts) and high explosives motivated the development of numerical solution methods and software for modeling chemical equilibrium in multi-species and multi-phase mixtures. These efforts began in the 1950s and some of these software packages are still in use today, however there are issues with using the older software including limited availability due to national security or proprietary concerns, lack of support for legacy software, and challenges of integration into modern software environments. In response to this situation, we have developed a library of software tools, the **Shock and Detonation Toolbox**, that we are making openly available for academic research. The Toolbox and associated demonstration programs are based on the [Cantera](#) software library to evaluate gas thermodynamic and transport properties, chemical reaction rates and carry out chemical equilibrium computations.

This document is divided into four parts. These parts describe the underlying scientific principles, the functionality of the Toolbox, numerical methods, applications to a variety of combustion problems with links to the programs, graphical and tabular results of program outputs.

In Part I, the fundamentals of thermodynamics, the ideal gas mixture formalism, and the concepts underlying chemical equilibrium are presented. In Part II of the report, we describe the algorithms used in the toolbox for the numerical solution of shock and detonation jump conditions in ideal gas mixtures with realistic thermochemical properties. An iterative technique based on a two-variable Newton's method is selected as being the most robust method for both reactive and nonreactive flows. A library of routines is described for Python and MATLAB computations of post-shock conditions and Chapman-Jouguet detonation velocity. Notes and demonstration programs are provided to illustrate how to use these routines to solve a range of problems. In addition to numerical methods for realistic thermochemistry, perfect gas analytical solutions are also provided.

In Part III of the report, we describe steady flows and some simple unsteady flows which not in equilibrium or frozen and chemical reaction must be considered. The steady flows treated are the reaction zones behind shock and detonation waves moving at constant speed, the reaction zone along the stagnation streamline in supersonic blunt body flows, flow through a converging-diverging nozzle and quasi-one dimensional flows with friction and heat transfer modeled as wall functions. The unsteady flows modeled include reaction occurring

under constant temperature, pressure and volume conditions or with prescribed volume or pressure time dependence.

In Part IV, the software components of the Toolbox and the application programs are described.

## 1.1 Overview and Quickstart

This overview describes situations that are commonly encountered and links to the associated toolbox routines and demonstration programs. For more details on the input and output parameters for these routines, see Chapter 12. For a listing and links to demonstration programs that illustrate various applications of the toolbox, see Chapter 13. In order to use these scripts, the reader must first install the Cantera software and have previously installed Python or MATLAB. The toolbox modules, demonstration scripts and instructions for installation are available on the SDToolbox [website](#).

1. Non-reactive shock wave. If the chemical reactions occur sufficiently slowly compared to translational, rotational, and vibrational equilibrium,<sup>1</sup> then a short distance behind a shock wave flow can be considered to be in thermal equilibrium but chemical nonequilibrium. This is often referred to as a “frozen shock” since the chemical composition is considered to be fixed through the shock wave. Computations of post-shock conditions are used as initial conditions for the subsequent reaction zone and are therefore a necessary part of computing shock or detonation structure. Usually, these computations proceed from specified upstream conditions and shock speed; the aim of the computation is to determine the downstream thermodynamic state and fluid velocity. On occasion, we consider the inverse problem of starting from a specified downstream state and computing the upstream state.

**Function PostShock.fr:** Demos - MATLAB: `demo_PSfr.m` Python: `demo_PSfr.py`

2. Reactive shock wave. The region sufficiently far downstream from the shock wave is considered in thermodynamic equilibrium. Thermodynamics can be used to determine the chemical composition, but this is coupled to the conservation equation solutions since the entropy and enthalpy of each species is a function of temperature. As a consequence, the solution of the conservation equations and chemical equilibrium must be self-consistent, requiring an iterative solution for the general case. In the case of endothermic reactions (i.e., dissociation of air behind the bow shock on re-entry vehicle), there are no limits on the specified shock velocity and the computation of the downstream state for specified upstream conditions is straightforward. For exothermic reactions, solutions are possible only for a range of wave speeds separated by a forbidden region. The admissible solutions are detonation (high velocity, i.e., supersonic) and deflagration (low velocity, i.e., subsonic) waves, and there are usually two solutions possible for each case.

**Function PostShock\_eq:** Demos - MATLAB: `demo_PSeq.m` Python: `demo_PSeq.py`

3. Chapman-Jouguet (CJ) detonation. This is the limiting case of the minimum wave speed for the supersonic solutions to the jump conditions with exothermic reactions. The Chapman-Jouguet solution is often used to approximate the properties of an ideal steady detonation wave. In particular, detonation waves are often observed to propagate at speeds within 5-10% of their theoretical CJ speeds in experimental situations where the waves are far from failure.

**Function CJSpeed:** Demos - MATLAB: `demo_CJ.m` Python: `demo_CJ.py`

4. Reflected shock wave. When a detonation or shock wave is incident on a hard surface, the flow behind the incident wave is suddenly stopped, creating a reflected shock wave that propagates in the opposite direction of the original wave. If we approximate the reflecting surface as rigid, then we can compute the speed of the reflected shock wave given the incident shock strength. This computation is frequently carried out in connection with estimating structural loads from shock or detonation waves.

**Function reflected\_eq and reflected\_fr:**

Demos - MATLAB: `demo_reflected_eq.m` and `demo_reflected_fr.m`

Python: `demo_reflected_eq.py` and `demo_reflected_fr.py`

---

<sup>1</sup>The structure of shock waves with vibration non-equilibrium is discussed at length by Clarke and McChesney (1964) and Vincenti and Kruger (1965)

5. ZND Model Detonation Structure Computation. The idealized reaction zone behind a steady shock or detonation wave is one-dimensional reactive flow. The model equations and properties were first explored by [Zel'dovich \(1940\)](#), [von Neumann \(1942\)](#), and [Doering \(1943\)](#). The solution method used in the toolbox is to convert the differential-algebraic equations representing the conservation of mass, momentum, energy and species evolution to a fully differential system of ODE and integrate these with a method suitable for stiff equations.

**Function ZND:**

Demos - MATLAB: [demo\\_ZNDCJ.m](#), [demo\\_ZNDshk.m](#) and [demo\\_ZND\\_CJ\\_cell.m](#)

Python: [demo\\_ZNDCJ.py](#), [demo\\_ZNDshk.py](#) and [demo\\_ZND\\_CJ\\_cell.py](#)

6. CV Model Explosion Structure Computation. The time-evolution of a mass of fluid reacting at constant volume is frequently used as a surrogate for the reaction process behind incident and reflected shock waves, as well as detonations. The model equations are based on the first law of thermodynamics for an adiabatic, constant-volume system. The ordinary differential equations for energy conservation and species evolution are integrated with a stiff ODE solver.

**Function CV:**

Demos - MATLAB: [demo\\_cv.m](#), [demo\\_cv\\_comp.m](#), [demo\\_cvCJ.m](#), [demo\\_cvshk.m](#)

Python: [demo\\_cvCJ.py](#), [demo\\_cvshk.py](#)

DRAFT



# **Part I**

## **Thermodynamics**

Shock waves and detonation computations for reacting gases are based on the fundamental concepts of combining pure species properties to obtain mixture properties and the methods of chemical equilibrium to compute composition. This part of the notes presents the essential background and a brief introduction to chemical equilibrium computations.



# Chapter 2

## Fundamentals

Thermodynamics is fundamental to all the computations and analysis in this version of the SDT. The principles can be found in many textbooks, for example, [Kondapudi and Prigogine \(1998\)](#). Classical references with a emphasis on chemical reactions and chemical equilibrium include [Denbigh \(1981\)](#) and [Smith and Missen \(1991\)](#). This chapter focuses on the definitions and relationships between properties that are essential in the reacting flows of gases.

### 2.1 General Principles

A fluid substance such as a gas can be subdivided into elements or volumes that are transported and deformed during motion but retain their identity as a fixed quantity of material if we neglect diffusive transport. The elements can be considered as thermodynamic systems with an internal energy  $E$ , temperature  $T$ , pressure  $P$ , and volume  $V$ . The internal energy<sup>1</sup> changes  $dE$  of the element are determined by the First Law of Thermodynamics

$$dE = dQ + dW \quad (2.1)$$

and the energy added in the form of heat  $dQ$ , and the mechanical work  $dW$ . For *reversible changes*, we can define an entropy function  $S$  related to the heat interaction

$$dS = \frac{dQ}{T} \quad (2.2)$$

and the work interaction can be defined in terms of pressure and volume changes

$$dW = -PdV \quad (2.3)$$

The evolution of an isolated (no heat or work interactions, fixed quantity of material) system is determined by the Second Law of Thermodynamics

$$dS \geq 0 \quad (2.4)$$

If the element is made up of  $K$  distinct molecular species each in amounts  $N_1, N_2, \dots, N_K$  that can react with each other, the internal energy can be written as

$$E = E(S, V, N_1, N_2, \dots, N_K) \quad (2.5)$$

and the changes in energy for a fixed mass of reacting material can be computed as

$$dE = TdS - PdV + \sum_{i=1}^K \mu_i dN_i \quad (2.6)$$

<sup>1</sup>The internal energy is the thermodynamic contribution to the total energy of a moving parcel of fluid and is usually denoted with the symbol  $U$ . Because we often use  $U$  for velocity in fluid mechanics, we use the symbol  $E$  instead. Equation (2.1) only applies in the frame of reference of the moving fluid and in the absence of any external forces. In general, the left-hand side should be the total energy of the system,  $U + \text{kinetic energy} + \text{potential energy} + \dots$