LECTURE NOTES ON FUNDAMENTALS OF COMBUSTION

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Contents

Preface

These are lecture notes for AME 60636, Fundamentals of Combustion, a course taught since 1994 in the Department of Aerospace and Mechanical Engineering of the University of Notre Dame. Most of the students in this course are graduate students; the course is also suitable for interested undergraduates. The objective of the course is to provide background in theoretical combustion science. Most of the material in the notes is covered in one semester; some extra material is also included.

The goal of the notes is to provide a solid mathematical foundation in the physical chemistry, thermodynamics, and fluid mechanics of combustion. The notes attempt to fill gaps in the existing literature in providing enhanced discussion of detailed kinetics models which are in common use for real physical systems. In addition, some model problems for paradigm systems are addressed for pedagogical purposes. Many of the unique aspects of these notes, which focus on some fundamental issues involving the thermodynamics of reactive gases with detailed finite rate kinetics, have arisen due to the author's involvement in a research project supported by the US National Science Foundation, under Grant No. CBET-0650843. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author and do not necessarily reflect the views of the National Science Foundation. The author is grateful for this public support. Thanks are also extended to my former student Dr. Ashraf al-Khateeb, who generated the steady laminar flame plots for detailed hydrogen-air combustion. General thanks are due to students in the course over the years whose interest has motivated me to find ways to improve the material.

The notes, along with information on the course itself, can be found on the world wide web at `http://www.nd.edu/~powers/ame.60636`. At this stage, anyone is free to make copies for their own use. I would be happy to hear from you about errors or suggestions for improvement.

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Chapter 1

Introduction to kinetics

Poca favilla gran fiamma seconda.[1] (A great flame follows a little spark.).

Dante Alighieri (1265-1321), *Paradiso*, Canto I, l. 34.

————————————-

Let us consider the reaction of N molecular chemical species composed of L elements via J chemical reactions. Let us assume the gas is an ideal mixture of ideal gases that satisfies Dalton's[2] law of partial pressures. The reaction will be considered to be driven by *molecular collisions*. We will not model individual collisions, but instead attempt to capture their collective effect.

An example of a model of such a reaction is listed in Table 1.1. There we find a $N = 9$ species, $J = 37$ step irreversible reaction mechanism for an $L = 3$ hydrogen-oxygen-argon mixture from Maas and Warnatz,[3] with corrected f_{H_2} from Maas and Pope.[4] The model has also been utilized by Fedkiw, *et al.*[5] The symbol M represents an arbitrary *third body* and is an inert participant in the reaction. We need not worry yet about f_{H_2}, which is known as a *collision efficiency factor*. The one-sided arrows indicate that each individual reaction is considered to be irreversible. Note that for nearly each reaction, a separate reverse reaction is listed; thus, pairs of irreversible reactions can in some sense be considered to model reversible reactions. In this model a set of elementary reactions are hypothesized. For the jth reaction we have the collision frequency factor a_j, the temperature-dependency exponent β_j, and the activation energy $\overline{\mathcal{E}}_j$. These will be explained in short order.

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[1]This verse from *La Divina Commedia* was selected in a spirit of optimism that the poet's better known entreaty from that opus's more topical *Inferno*: *Lasciate ogne speranza, voi ch'entrate.* (All hope abandon, ye who enter in.), Canto III, l. 1, will prove to be irrelevant.

[2]John Dalton, 1766-1844, English chemist.

[3]Maas, U., and Warnatz, J., 1988, "Ignition Processes in Hydrogen-Oxygen Mixtures," *Combustion and Flame*, 74(1): 53-69.

[4]Maas, U., and Pope, S. B., 1992, "Simplifying Chemical Kinetics: Intrinsic Low-Dimensional Manifolds in Composition Space," *Combustion and Flame*, 88(3-4): 239-264.

[5]Fedkiw, R. P., Merriman, B., and Osher, S., 1997, "High Accuracy Numerical Methods for Thermally Perfect Gas Flows with Chemistry," *Journal of Computational Physics*, 132(2): 175-190.

j	Reaction	$a_j \left(\dfrac{\left(mole/cm^3\right)^{\left(1-\nu'_{M,j}-\Sigma_{i=1}^{N} \nu'_{ij}\right)}}{s \cdot K^{\beta_j}} \right)$	β_j	$\overline{\mathcal{E}}_j \left(\frac{kJ}{mole}\right)$
1	$O_2 + H \rightarrow OH + O$	2.00×10^{14}	0.00	70.30
2	$OH + O \rightarrow O_2 + H$	1.46×10^{13}	0.00	2.08
3	$H_2 + O \rightarrow OH + H$	5.06×10^{4}	2.67	26.30
4	$OH + H \rightarrow H_2 + O$	2.24×10^{4}	2.67	18.40
5	$H_2 + OH \rightarrow H_2O + H$	1.00×10^{8}	1.60	13.80
6	$H_2O + H \rightarrow H_2 + OH$	4.45×10^{8}	1.60	77.13
7	$OH + OH \rightarrow H_2O + O$	1.50×10^{9}	1.14	0.42
8	$H_2O + O \rightarrow OH + OH$	1.51×10^{10}	1.14	71.64
9	$H + H + M \rightarrow H_2 + M$	1.80×10^{18}	-1.00	0.00
10	$H_2 + M \rightarrow H + H + M$	6.99×10^{18}	-1.00	436.08
11	$H + OH + M \rightarrow H_2O + M$	2.20×10^{22}	-2.00	0.00
12	$H_2O + M \rightarrow H + OH + M$	3.80×10^{23}	-2.00	499.41
13	$O + O + M \rightarrow O_2 + M$	2.90×10^{17}	-1.00	0.00
14	$O_2 + M \rightarrow O + O + M$	6.81×10^{18}	-1.00	496.41
15	$H + O_2 + M \rightarrow HO_2 + M$	2.30×10^{18}	-0.80	0.00
16	$HO_2 + M \rightarrow H + O_2 + M$	3.26×10^{18}	-0.80	195.88
17	$HO_2 + H \rightarrow OH + OH$	1.50×10^{14}	0.00	4.20
18	$OH + OH \rightarrow HO_2 + H$	1.33×10^{13}	0.00	168.30
19	$HO_2 + H \rightarrow H_2 + O_2$	2.50×10^{13}	0.00	2.90
20	$H_2 + O_2 \rightarrow HO_2 + H$	6.84×10^{13}	0.00	243.10
21	$HO_2 + H \rightarrow H_2O + O$	3.00×10^{13}	0.00	7.20
22	$H_2O + O \rightarrow HO_2 + H$	2.67×10^{13}	0.00	242.52
23	$HO_2 + O \rightarrow OH + O_2$	1.80×10^{13}	0.00	-1.70
24	$OH + O_2 \rightarrow HO_2 + O$	2.18×10^{13}	0.00	230.61
25	$HO_2 + OH \rightarrow H_2O + O_2$	6.00×10^{13}	0.00	0.00
26	$H_2O + O_2 \rightarrow HO_2 + OH$	7.31×10^{14}	0.00	303.53
27	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.50×10^{11}	0.00	-5.20
28	$OH + OH + M \rightarrow H_2O_2 + M$	3.25×10^{22}	-2.00	0.00
29	$H_2O_2 + M \rightarrow OH + OH + M$	2.10×10^{24}	-2.00	206.80
30	$H_2O_2 + H \rightarrow H_2 + HO_2$	1.70×10^{12}	0.00	15.70
31	$H_2 + HO_2 \rightarrow H_2O_2 + H$	1.15×10^{12}	0.00	80.88
32	$H_2O_2 + H \rightarrow H_2O + OH$	1.00×10^{13}	0.00	15.00
33	$H_2O + OH \rightarrow H_2O_2 + H$	2.67×10^{12}	0.00	307.51
34	$H_2O_2 + O \rightarrow OH + HO_2$	2.80×10^{13}	0.00	26.80
35	$OH + HO_2 \rightarrow H_2O_2 + O$	8.40×10^{12}	0.00	84.09
36	$H_2O_2 + OH \rightarrow H_2O + HO_2$	5.40×10^{12}	0.00	4.20
37	$H_2O + HO_2 \rightarrow H_2O_2 + OH$	1.63×10^{13}	0.00	132.71

Table 1.1:   Third body collision efficiencies with M are $f_{H_2} = 1.00$, $f_{O_2} = 0.35$, and $f_{H_2O} = 6.5$.

j	Reaction	$a_j \left(\dfrac{\left(mole/cm^3\right)^{\left(1-\nu'_{M,j}-\Sigma_{i=1}^{N}\nu'_{ij}\right)}}{s\cdot K^{\beta_j}} \right)$	β_j	$\overline{\mathcal{E}}_j \left(\frac{cal}{mole}\right)$
1	$H_2 + O_2 \rightleftharpoons OH + OH$	1.70×10^{13}	0.00	47780
2	$OH + H_2 \rightleftharpoons H_2O + H$	1.17×10^{9}	1.30	3626
3	$H + O_2 \rightleftharpoons OH + O$	5.13×10^{16}	-0.82	16507
4	$O + H_2 \rightleftharpoons OH + H$	1.80×10^{10}	1.00	8826
5	$H + O_2 + M \rightleftharpoons HO_2 + M$	2.10×10^{18}	-1.00	0
6	$H + O_2 + O_2 \rightleftharpoons HO_2 + O_2$	6.70×10^{19}	-1.42	0
7	$H + O_2 + N_2 \rightleftharpoons HO_2 + N_2$	6.70×10^{19}	-1.42	0
8	$OH + HO_2 \rightleftharpoons H_2O + O_2$	5.00×10^{13}	0.00	1000
9	$H + HO_2 \rightleftharpoons OH + OH$	2.50×10^{14}	0.00	1900
10	$O + HO_2 \rightleftharpoons O_2 + OH$	4.80×10^{13}	0.00	1000
11	$OH + OH \rightleftharpoons O + H_2O$	6.00×10^{8}	1.30	0
12	$H_2 + M \rightleftharpoons H + H + M$	2.23×10^{12}	0.50	92600
13	$O_2 + M \rightleftharpoons O + O + M$	1.85×10^{11}	0.50	95560
14	$H + OH + M \rightleftharpoons H_2O + M$	7.50×10^{23}	-2.60	0
15	$H + HO_2 \rightleftharpoons H_2 + O_2$	2.50×10^{13}	0.00	700
16	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	2.00×10^{12}	0.00	0
17	$H_2O_2 + M \rightleftharpoons OH + OH + M$	1.30×10^{17}	0.00	45500
18	$H_2O_2 + H \rightleftharpoons HO_2 + H_2$	1.60×10^{12}	0.00	3800
19	$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	1.00×10^{13}	0.00	1800

Table 1.2: Nine species, nineteen step reversible reaction mechanism for a hydrogen/oxygen/nitrogen mixture. Third body collision efficiencies with M are $f_5(H_2O) = 21$, $f_5(H_2) = 3.3$, $f_{12}(H_2O) = 6$, $f_{12}(H) = 2$, $f_{12}(H_2) = 3$, $f_{14}(H_2O) = 20$.

Other common forms exist. Often reactions systems are described as being composed of reversible reactions. Such reactions are usually notated by two sided arrows. One such system is reported by Powers and Paolucci[6] and is listed here in Table 1.2. Both overall models are complicated.

1.1 Isothermal, isochoric kinetics

For simplicity, we will first focus attention on cases in which the temperature T and volume V are both constant. Such assumptions are known as *isothermal* and *isochoric*, respectively. A good fundamental treatment of elementary reactions of this type is given by Vincenti and Kruger in their detailed monograph.[7]

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[6]Powers, J. M., and Paolucci, S., 2005, "Accurate Spatial Resolution Estimates for Reactive Supersonic Flow with Detailed Chemistry," *AIAA Journal*, 43(5): 1088-1099.

[7]Vincenti, W. G., and Kruger, C. H., 1965, *Introduction to Physical Gas Dynamics*, Wiley, New York.

1.1.1 $O - O_2$ dissociation

One of the simplest physical examples is provided by the dissociation of O_2 into its atomic component O.

1.1.1.1   Pair of irreversible reactions

To get started, let us focus for now only on reactions $j = 13$ and $j = 14$ from Table 1.1 in the limiting case in which temperature T and volume V are constant.

1.1.1.1.1   Mathematical model   The reactions describe oxygen dissociation and recombination in a pair of *irreversible* reactions:

$$13 : O + O + M \quad \rightarrow \quad O_2 + M, \tag{1.1}$$

$$14 : O_2 + M \quad \rightarrow \quad O + O + M, \tag{1.2}$$
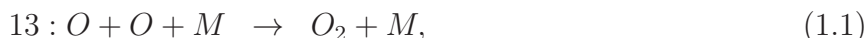
with

$$a_{13} = 2.90 \times 10^{17} \left(\frac{mole}{cm^3}\right)^{-2} \frac{K}{s}, \quad \beta_{13} = -1.00, \quad \overline{\mathcal{E}}_{13} = 0 \, \frac{kJ}{mole}, \tag{1.3}$$

$$a_{14} = 6.81 \times 10^{18} \left(\frac{mole}{cm^3}\right)^{-1} \frac{K}{s}, \quad \beta_{14} = -1.00, \quad \overline{\mathcal{E}}_{14} = 496.41 \, \frac{kJ}{mole}. \tag{1.4}$$

The irreversibility is indicated by the one-sided arrow. Though they participate in the overall hydrogen oxidation problem, these two reactions are in fact self-contained as well. So, let us just consider that we have only oxygen in our box with $N = 2$ species, O and O_2, $J = 2$ reactions (those being 13 and 14), and $L = 1$ element, that being O. We will take $i = 1$ to correspond to O and $i = 2$ to correspond to O_2.

The units of a_j are unusual. For reaction $j = 13$, we have the forward stoichiometric coefficient for species O, $i = 1$, as $\nu'_{ij} = \nu'_{1,13} = 2$, and for species O_2, $i = 2$, as $\nu'_{ij} = \nu'_{2,13} = 0$. And since an inert third body participates in reaction 13, we have $\nu'_{M,13} = 1$. So, for reaction $j = 13$, we find the exponent for the $(mole/cm^3)$ portion of the units for a_{14} to be

$$1 - \nu'_{M,j} - \sum_{i=1}^{N} \nu'_{ij} = 1 - \nu'_{M,13} - \left(\nu'_{1,13} + \nu'_{2,13}\right) = 1 - 1 - (2 + 0) = -2. \tag{1.5}$$

Similarly for reaction $j = 14$, we have the forward stoichiometric coefficient for species O, $i = 1$, as $\nu'_{ij} = \nu'_{1,14} = 0$, and for species O_2, $i = 2$, as $\nu'_{ij} = \nu'_{2,14} = 1$. And since an inert third body participates in reaction 13, we have $\nu'_{M,14} = 1$. So, for reaction $j = 14$, we find the exponent for the $(mole/cm^3)$ portion of the units for a_{14} to be

$$1 - \nu'_{M,j} - \sum_{i=1}^{N} \nu'_{ij} = 1 - \nu'_{M,14} - \left(\nu'_{1,14} + \nu'_{2,14}\right) = 1 - 1 - (0 + 1) = -1. \tag{1.6}$$

Recall that in the *cgs* system, common in thermochemistry, that $1\ erg = 1\ dyne\ cm = 10^{-7}\ J = 10^{-10}\ kJ$. Recall also that the *cgs* unit of force is the *dyne* and that $1\ dyne = 1\ g\ cm/s^2 = 10^{-5}\ N$. So, for *cgs* we have

$$\overline{\mathcal{E}}_{13} = 0\ \frac{erg}{mole}, \qquad \overline{\mathcal{E}}_{14} = 496.41\ \frac{kJ}{mole}\left(\frac{10^{10}\ erg}{kJ}\right) = 4.96 \times 10^{12}\ \frac{erg}{mole}. \qquad (1.7)$$

The standard model for chemical reaction, which will be generalized and discussed in more detail in Chapters 4 and 5, induces the following two ordinary differential equations for the evolution of O and O_2 molar concentrations:

$$\frac{d\overline{\rho}_O}{dt} = \underbrace{-2\underbrace{a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right)}_{=k_{13}(T)}\overline{\rho}_O\overline{\rho}_O\overline{\rho}_M}_{=r_{13}} + \underbrace{2\underbrace{a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{\mathcal{E}}_{14}}{\overline{R}T}\right)}_{=k_{14}(T)}\overline{\rho}_{O_2}\overline{\rho}_M}_{=r_{14}}, \qquad (1.8)$$

$$\frac{d\overline{\rho}_{O_2}}{dt} = \underbrace{\underbrace{a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right)}_{=k_{13}(T)}\overline{\rho}_O\overline{\rho}_O\overline{\rho}_M}_{=r_{13}} - \underbrace{\underbrace{a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{\mathcal{E}}_{14}}{\overline{R}T}\right)}_{=k_{14}(T)}\overline{\rho}_{O_2}\overline{\rho}_M}_{=r_{14}}. \qquad (1.9)$$

Here, we use the notation $\overline{\rho}_i$ as the molar concentration of species i. Also, a common usage for molar concentration is given by square brackets, e.g. $\overline{\rho}_{O_2} = [O_2]$. The symbol $\overline{R}$ is the universal gas constant, for which

$$\overline{R} = 8.31441\ \frac{J}{mole\ K}\left(\frac{10^7\ erg}{J}\right) = 8.31441 \times 10^7 \frac{erg}{mole\ K}. \qquad (1.10)$$

We also use the common notation of a temperature-dependent portion of the reaction rate for reaction j, $k_j(T)$, where

$$k_j(T) = a_j T^{\beta_j}\exp\left(\frac{\overline{\mathcal{E}}_j}{\overline{R}T}\right). \qquad (1.11)$$

Note that $j = 1, \ldots, J$. The reaction rates for reactions 13 and 14 are defined as

$$r_{13} = k_{13}\overline{\rho}_O\overline{\rho}_O\overline{\rho}_M, \qquad (1.12)$$
$$r_{14} = k_{14}\overline{\rho}_{O_2}\overline{\rho}_M. \qquad (1.13)$$

We will give details of how to generalize this form later in Chapters 4 and 5. The system Eq. (1.8-1.9) can be written simply as

$$\frac{d\overline{\rho}_O}{dt} = -2r_{13} + 2r_{14}, \qquad (1.14)$$
$$\frac{d\overline{\rho}_{O_2}}{dt} = r_{13} - r_{14}. \qquad (1.15)$$

Even more simply, in vector form, Eqs. (1.14-1.15) can be written as

$$\frac{d\overline{\boldsymbol{\rho}}}{dt} = \boldsymbol{\nu} \cdot \mathbf{r}. \tag{1.16}$$

Here, we have taken

$$\overline{\boldsymbol{\rho}} = \begin{pmatrix} \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix}, \tag{1.17}$$

$$\boldsymbol{\nu} = \begin{pmatrix} -2 & 2 \\ 1 & -1 \end{pmatrix}, \tag{1.18}$$

$$\mathbf{r} = \begin{pmatrix} r_{13} \\ r_{14} \end{pmatrix}. \tag{1.19}$$

In general, we will have $\overline{\boldsymbol{\rho}}$ be a column vector of dimension $N \times 1$, $\boldsymbol{\nu}$ will be a rectangular matrix of dimension $N \times J$ of rank R, and $\mathbf{r}$ will be a column vector of length $J \times 1$. So, Eqs. (1.14-1.15) take the form

$$\frac{d}{dt} \begin{pmatrix} \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} -2 & 2 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} r_{13} \\ r_{14} \end{pmatrix}. \tag{1.20}$$

Note here that the rank R of $\boldsymbol{\nu}$ is $R = L = 1$, since $\det \boldsymbol{\nu} = 0$, and $\boldsymbol{\nu}$ has at least one non-zero element. Let us also define a stoichiometric matrix $\boldsymbol{\phi}$ of dimension $L \times N$. The component of $\boldsymbol{\phi}$, ϕ_{li} represents the number of element l in species i. Generally $\boldsymbol{\phi}$ will be full rank, which will vary, since we can have $L < N$, $L = N$, or $L > N$. Here, we have $L < N$ and $\boldsymbol{\phi}$ is of dimension 1×2:

$$\boldsymbol{\phi} = \begin{pmatrix} 1 & 2 \end{pmatrix}. \tag{1.21}$$

Element conservation is guaranteed by insisting that $\boldsymbol{\nu}$ be constructed such that

$$\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \mathbf{0}. \tag{1.22}$$

So, we can say that each of the column vectors of $\boldsymbol{\nu}$ lies in the right null space of $\boldsymbol{\phi}$. For our example, we see that Eq. (1.22) holds:

$$\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \begin{pmatrix} 1 & 2 \end{pmatrix} \cdot \begin{pmatrix} -2 & 2 \\ 1 & -1 \end{pmatrix} = \begin{pmatrix} 0 & 0 \end{pmatrix}. \tag{1.23}$$

Let us take as initial conditions

$$\overline{\rho}_O(t = 0) = \widehat{\overline{\rho}}_O, \qquad \overline{\rho}_{O_2}(t = 0) = \widehat{\overline{\rho}}_{O_2}. \tag{1.24}$$

Now, M represents an arbitrary third body, so here

$$\overline{\rho}_M = \overline{\rho}_{O_2} + \overline{\rho}_O. \tag{1.25}$$

Thus, the ordinary differential equations of the reaction dynamics, Eqs. (1.8, 1.9), reduce to

$$
\begin{aligned}
\frac{d\overline{\rho}_O}{dt} &= -2a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right)\overline{\rho}_O\overline{\rho}_O\left(\overline{\rho}_{O_2}+\overline{\rho}_O\right) \\
&\quad +2a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{\mathcal{E}}_{14}}{\overline{R}T}\right)\overline{\rho}_{O_2}\left(\overline{\rho}_{O_2}+\overline{\rho}_O\right),
\end{aligned}
\tag{1.26}
$$

$$
\begin{aligned}
\frac{d\overline{\rho}_{O_2}}{dt} &= a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right)\overline{\rho}_O\overline{\rho}_O\left(\overline{\rho}_{O_2}+\overline{\rho}_O\right) \\
&\quad -a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{\mathcal{E}}_{14}}{\overline{R}T}\right)\overline{\rho}_{O_2}\left(\overline{\rho}_{O_2}+\overline{\rho}_O\right).
\end{aligned}
\tag{1.27}
$$

Equations (1.26-1.27) with Eqs. (1.24) represent two non-linear ordinary differential equations with initial conditions in two unknowns $\overline{\rho}_O$ and $\overline{\rho}_{O_2}$. We seek the behavior of these two species concentrations as a function of time.

Systems of non-linear equations are generally difficult to integrate analytically and generally require numerical solution. Before embarking on a numerical solution, we simplify as much as we can. Note that

$$
\frac{d\overline{\rho}_O}{dt}+2\frac{d\overline{\rho}_{O_2}}{dt} = 0,
\tag{1.28}
$$

$$
\frac{d}{dt}\left(\overline{\rho}_O+2\overline{\rho}_{O_2}\right) = 0.
\tag{1.29}
$$

We can integrate and apply the initial conditions (1.24) to get

$$
\overline{\rho}_O+2\overline{\rho}_{O_2}=\widehat{\overline{\rho}}_O+2\widehat{\overline{\rho}}_{O_2}=constant.
\tag{1.30}
$$

The fact that this algebraic constraint exists for all time is a consequence of the conservation of mass of each O element. It can also be thought of as the conservation of number of O atoms. Such notions always hold for chemical reactions. They do not hold for nuclear reactions.

Standard linear algebra provides a robust way to find the constraint of Eq. (1.30). We can use elementary row operations to cast Eq. (1.20) into a row-echelon form. Here, our goal is to get a linear combination which on the right side has an upper triangular form. To achieve this add twice the second equation with the first to form a new equation to replace the second equation. This gives

$$
\frac{d}{dt}\begin{pmatrix}\overline{\rho}_O \\ \overline{\rho}_O+2\overline{\rho}_{O_2}\end{pmatrix}=\begin{pmatrix}-2 & 2 \\ 0 & 0\end{pmatrix}\begin{pmatrix}r_{13} \\ r_{14}\end{pmatrix}.
\tag{1.31}
$$

Obviously the second equation is one we obtained earlier, $d/dt(\overline{\rho}_O+2\overline{\rho}_{O_2})=0$, and this induces our algebraic constraint. We also note Eq. (1.31) can be recast as

$$
\underbrace{\begin{pmatrix}1 & 0 \\ 1 & 2\end{pmatrix}}_{\mathbf{L}^{-1}}\frac{d}{dt}\begin{pmatrix}\overline{\rho}_O \\ \overline{\rho}_{O_2}\end{pmatrix}=\underbrace{\begin{pmatrix}-2 & 2 \\ 0 & 0\end{pmatrix}}_{\mathbf{U}}\begin{pmatrix}r_{13} \\ r_{14}\end{pmatrix}.
\tag{1.32}
$$

This is of the matrix form

$$\mathbf{L}^{-1} \cdot \mathbf{P} \cdot \frac{d\overline{\boldsymbol{\rho}}}{dt} = \mathbf{U} \cdot \mathbf{r}. \tag{1.33}$$

Here, $\mathbf{L}$ and $\mathbf{L}^{-1}$ are $N \times N$ lower triangular matrices of full rank N, and thus invertible. The matrix $\mathbf{U}$ is upper triangular of dimension $N \times J$ and with the same rank as $\boldsymbol{\nu}$, $R \geq L$. The matrix $\mathbf{P}$ is a permutation matrix of dimension $N \times N$. It is never singular and thus always invertable. It is used to effect possible row exchanges to achieve the desired form; often row exchanges are not necessary, in which case $\mathbf{P} = \mathbf{I}$, the $N \times N$ identity matrix. Equation (1.33) can be manipulated to form the original equation via

$$\frac{d\overline{\boldsymbol{\rho}}}{dt} = \underbrace{\mathbf{P}^{-1} \cdot \mathbf{L} \cdot \mathbf{U}}_{=\boldsymbol{\nu}} \cdot \mathbf{r}. \tag{1.34}$$

What we have done is the standard linear algebra decomposition of $\boldsymbol{\nu} = \mathbf{P}^{-1} \cdot \mathbf{L} \cdot \mathbf{U}$.

We can also decompose the algebraic constraint, Eq. (1.30), in a non-obvious way that is more readily useful for larger systems. We can write

$$\overline{\rho}_{O_2} = \widehat{\overline{\rho}}_{O_2} - \frac{1}{2}\left(\overline{\rho}_O - \widehat{\overline{\rho}}_O\right). \tag{1.35}$$

Defining now $\overline{\xi}_O = \overline{\rho}_O - \widehat{\overline{\rho}}_O$, we can say

$$\underbrace{\begin{pmatrix} \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix}}_{=\overline{\boldsymbol{\rho}}} = \underbrace{\begin{pmatrix} \widehat{\overline{\rho}}_O \\ \widehat{\overline{\rho}}_{O_2} \end{pmatrix}}_{=\widehat{\overline{\boldsymbol{\rho}}}} + \underbrace{\begin{pmatrix} 1 \\ -\frac{1}{2} \end{pmatrix}}_{=\mathbf{D}} \underbrace{(\overline{\xi}_O)}_{=\overline{\boldsymbol{\xi}}}. \tag{1.36}$$

This gives the dependent variables in terms of a smaller number of transformed dependent variables in a way which satisfies the linear constraints. In vector form, Eq. (1.36) becomes

$$\overline{\boldsymbol{\rho}} = \widehat{\overline{\boldsymbol{\rho}}} + \mathbf{D} \cdot \overline{\boldsymbol{\xi}}. \tag{1.37}$$

Here, $\mathbf{D}$ is a full rank matrix which spans the same column space as does $\boldsymbol{\nu}$. Note that $\boldsymbol{\nu}$ may or may not be full rank. Since $\mathbf{D}$ spans the same column space as does $\boldsymbol{\nu}$, we must also have in general

$$\boldsymbol{\phi} \cdot \mathbf{D} = \mathbf{0}. \tag{1.38}$$

We see here this is true:

$$\underbrace{\begin{pmatrix} 1 & 2 \end{pmatrix}}_{\boldsymbol{\phi}} \cdot \underbrace{\begin{pmatrix} 1 \\ -\frac{1}{2} \end{pmatrix}}_{\mathbf{D}} = (0). \tag{1.39}$$
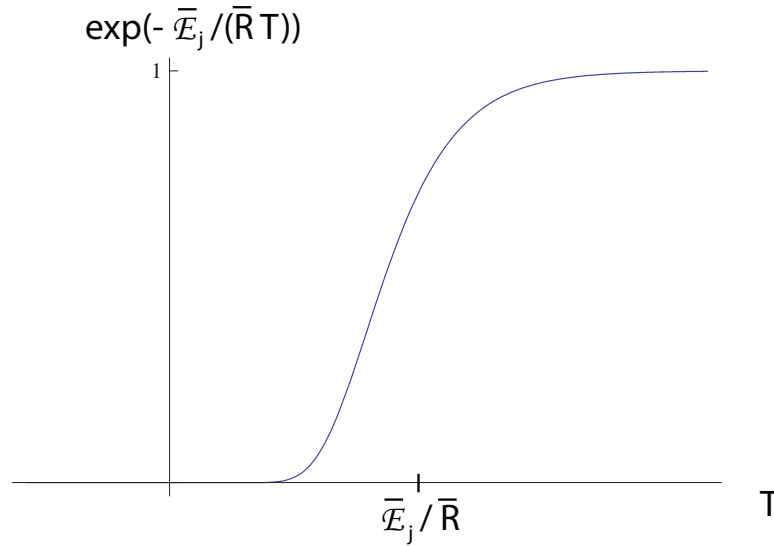
$$\exp(-\,\overline{\mathcal{E}}_j\,/(\overline{R}\,T))$$

Figure 1.1: Plot of $\exp(-\overline{\mathcal{E}}_j/\overline{R}/T)$ versus T; transition occurs at $T \sim \overline{\mathcal{E}}_j/\overline{R}$.

We also note that the term $\exp(-\overline{\mathcal{E}}_j/\overline{R}T)$ is a modulating factor to the dynamics. Let us see how this behaves for high and low temperatures. First, for low temperature, we have

$$\lim_{T \to 0} \exp\left(\frac{-\overline{\mathcal{E}}_j}{\overline{R}T}\right) = 0. \qquad (1.40)$$

At high temperature, we have

$$\lim_{T \to \infty} \exp\left(\frac{-\overline{\mathcal{E}}_j}{\overline{R}T}\right) = 1. \qquad (1.41)$$

And lastly, at intermediate temperature, we have

$$\exp\left(\frac{-\overline{\mathcal{E}}_j}{\overline{R}T}\right) \sim \mathcal{O}(1), \qquad \text{when} \qquad T = \mathcal{O}\left(\frac{\overline{\mathcal{E}}_j}{\overline{R}}\right). \qquad (1.42)$$

A sketch of this modulating factor is given in Figure 1.1. Note

- for small T, the modulation is extreme, and the reaction rate is *very* small,

- for $T \sim \overline{\mathcal{E}}_j/\overline{R}$, the reaction rate is extremely sensitive to temperature, and

- for $T \to \infty$, the modulation is unity, and the reaction rate is limited only by molecular collision frequency.

Now, $\overline{\rho}_O$ and $\overline{\rho}_{O_2}$ represent molar concentrations which have standard units of $mole/cm^3$. So, the reaction rates

$$\frac{d\overline{\rho}_O}{dt} \qquad \text{and} \qquad \frac{d\overline{\rho}_{O_2}}{dt}$$

have units of $mole/cm^3/s$.

Note that the argument of the exponential to be dimensionless. That is

$$\left[\frac{\overline{\mathcal{E}}_j}{\overline{R}T}\right] = \frac{erg}{mole}\frac{mole\ K}{erg}\frac{1}{K} \Rightarrow \qquad \text{dimensionless.} \tag{1.43}$$

Here, the brackets denote the units of a quantity, and not molar concentration. Let us use a more informal method than that presented on p. 16 to arrive at units for the collision frequency factor of reaction 13, a_{13}. We know the units of the rate ($mole/cm^3/s$). Reaction 13 involves three molar species. Since $\beta_{13} = -1$, it also has an extra temperature dependency. The exponential of a unitless number is unitless, so we need not worry about that. For units to match, we must have

$$\left(\frac{mole}{cm^3\ s}\right) = [a_{13}]\left(\frac{mole}{cm^3}\right)\left(\frac{mole}{cm^3}\right)\left(\frac{mole}{cm^3}\right)K^{-1}. \tag{1.44}$$

So, the units of a_{13} are

$$[a_{13}] = \left(\frac{mole}{cm^3}\right)^{-2}\frac{K}{s}. \tag{1.45}$$

For a_{14} we find a different set of units! Following the same procedure, we get

$$\left(\frac{mole}{cm^3\ s}\right) = [a_{14}]\left(\frac{mole}{cm^3}\right)\left(\frac{mole}{cm^3}\right)K^{-1}. \tag{1.46}$$

So, the units of a_{14} are

$$[a_{14}] = \left(\frac{mole}{cm^3}\right)^{-1}\frac{K}{s}. \tag{1.47}$$

This discrepancy in the units of a_j the molecular collision frequency factor is a burden of traditional chemical kinetics, and causes many difficulties when classical non-dimensionalization is performed. With much effort, a cleaner theory could be formulated; however, this would require significant work to re-cast the now-standard a_j values for literally thousands of reactions which are well established in the literature.

1.1.1.1.2   Example calculation   Let us consider an example problem. Let us take $T = 5000\ K$, and initial conditions $\widehat{\overline{\rho}}_O = 0.001\ mole/cm^3$ and $\widehat{\overline{\rho}}_{O_2} = 0.001\ mole/cm^3$. The initial temperature is very hot, and is near the temperature of the surface of the sun. This is also realizable in laboratory conditions, but uncommon in most combustion engineering environments.

We can solve these in a variety of ways. I chose here to solve both Eqs. (1.26-1.27) without the reduction provided by Eq. (1.30). However, we can check after numerical solution to see

if Eq. (1.30) is actually satisfied. Substituting numerical values for all the constants to get

$$-2a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right) = -2\left(2.9\times10^7\ \left(\frac{mole}{cm^3}\right)^{-2}\frac{K}{s}\right)(5000\ K)^{-1}\exp(0),$$

$$= -1.16\times10^{14}\ \left(\frac{mole}{cm^3}\right)^{-2}\frac{1}{s}, \tag{1.48}$$

$$2a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{\mathcal{E}}_{14}}{\overline{R}T}\right) = 2\left(6.81\times10^{18}\ \left(\frac{mole}{cm^3}\right)^{-1}\frac{K}{s}\right)(5000\ K)^{-1}$$

$$\times\exp\left(\frac{-4.96\times10^{12}\ \frac{erg}{mole}}{8.31441\times10^7\ \frac{erg}{mole\ K}(5000\ K)}\right),$$

$$= 1.77548\times10^{10}\ \left(\frac{mole}{cm^3}\right)^{-1}\frac{1}{s}, \tag{1.49}$$

$$a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right) = 5.80\times10^{13}\ \left(\frac{mole}{cm^3}\right)^{-2}\frac{1}{s}, \tag{1.50}$$

$$-a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{\mathcal{E}}_{14}}{\overline{R}T}\right) = -8.8774\times10^9\ \left(\frac{mole}{cm^3}\right)^{-1}\frac{1}{s}. \tag{1.51}$$

Then, the differential equation system, Eqs. (1.8,1.9), becomes

$$\frac{d\overline{\rho}_O}{dt} = -(1.16\times10^{14})\overline{\rho}_O^2(\overline{\rho}_O+\overline{\rho}_{O_2})+(1.77548\times10^{10})\overline{\rho}_{O_2}(\overline{\rho}_O+\overline{\rho}_{O_2}), \tag{1.52}$$

$$\frac{d\overline{\rho}_{O_2}}{dt} = (5.80\times10^{13})\overline{\rho}_O^2(\overline{\rho}_O+\overline{\rho}_{O_2})-(8.8774\times10^9)\overline{\rho}_{O_2}(\overline{\rho}_O+\overline{\rho}_{O_2}), \tag{1.53}$$

$$\overline{\rho}_O(0) = 0.001\ \frac{mole}{cm^3}, \tag{1.54}$$

$$\overline{\rho}_{O_2}(0) = 0.001\ \frac{mole}{cm^3}. \tag{1.55}$$

These non-linear ordinary differential equations are in a standard form for a wide variety of numerical software tools. Numerical solution techniques of such equations are not the topic of these notes, and it will be assumed the reader has access to such tools.

1.1.1.1.2.1 Species concentration versus time A solution was obtained numerically, and a plot of $\overline{\rho}_O(t)$ and $\overline{\rho}_{O_2}(t)$ is given in Figure 1.2. Note that significant reaction does not commence until $t\sim10^{-10}$ s. This can be shown to be very close to the time between molecular collisions. For 10^{-9} s $< t < 10^{-8}$ s, there is a vigorous reaction. For $t > 10^{-7}$ s, the reaction appears to be equilibrated. The calculation gives the equilibrium values $\overline{\rho}_O^{eq}$ and $\overline{\rho}_{O_2}^{eq}$, as

$$\lim_{t\to\infty}\overline{\rho}_O = \overline{\rho}_O^{eq} = 0.0004424\ \frac{mole}{cm^3}, \tag{1.56}$$

$$\lim_{t\to\infty}\overline{\rho}_{O_2} = \overline{\rho}_{O_2}^{eq} = 0.00127\ \frac{mole}{cm^3}. \tag{1.57}$$
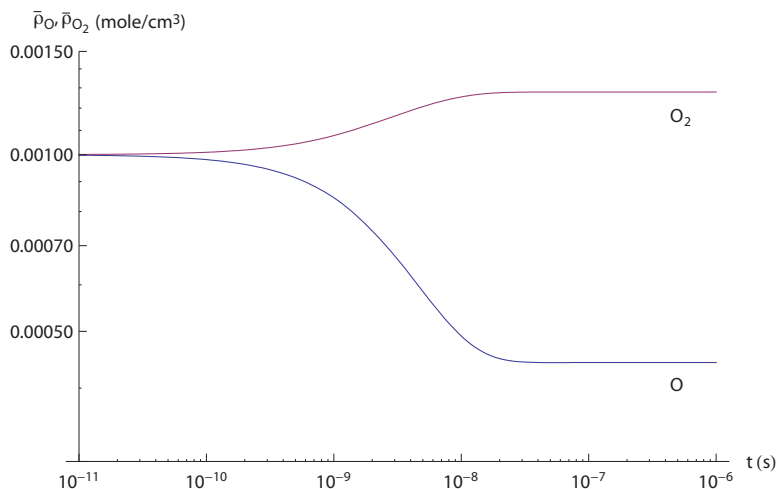
Figure 1.2: Molar concentrations versus time for oxygen dissociation problem.

Here, the superscript eq denotes an equilibrium value. Note that at this high temperature, O_2 is preferred over O, but there are definitely O molecules present at equilibrium.

We can check how well the numerical solution satisfied the algebraic constraint of element conservation by plotting the dimensionless residual error r

$$r = \left| \frac{\overline{\rho}_O + 2\overline{\rho}_{O_2} - \widehat{\overline{\rho}}_O - 2\widehat{\overline{\rho}}_{O_2}}{\widehat{\overline{\rho}}_O + 2\widehat{\overline{\rho}}_{O_2}} \right|, \tag{1.58}$$

as a function of time. If the constraint is exactly satisfied, we will have $r = 0$. Any non-zero r will be related to the numerical method we have chosen. It may contain roundoff error and have a sporadic nature. A plot of $r(t)$ is given in Figure 1.3. Clearly, the error is small and has the character of a roundoff error in that it is small and discontinuous. In fact it is possible to drive r to be smaller by controlling the error tolerance in the numerical method.

1.1.1.1.2.2 Pressure versus time We can use the ideal gas law to calculate the pressure. Recall that the ideal gas law for molecular species i is

$$P_i V = n_i \overline{R} T. \tag{1.59}$$

Here, P_i is the partial pressure of molecular species i, and n_i is the number of moles of molecular species i. Note that we also have

$$P_i = \frac{n_i}{V} \overline{R} T. \tag{1.60}$$

Note that by our definition of molecular species concentration that

$$\overline{\rho}_i = \frac{n_i}{V}. \tag{1.61}$$
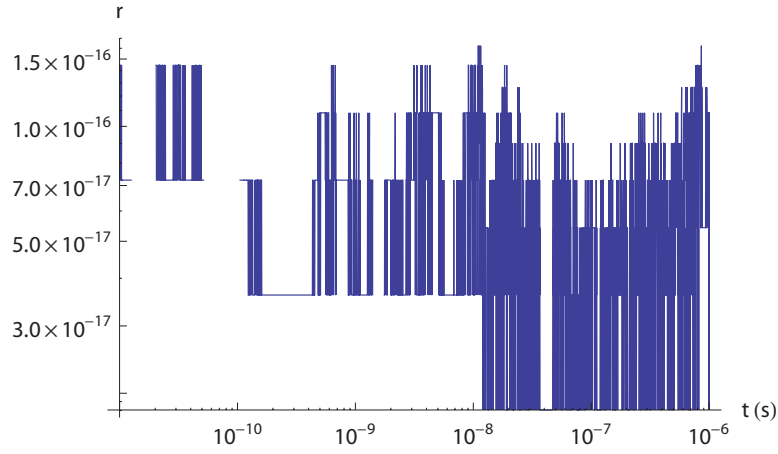
Figure 1.3: Dimensionless residual numerical error r in satisfying the element conservation constraint in the oxygen dissociation example.

So, we also have the ideal gas law as

$$P_i = \overline{\rho}_i \overline{R} T. \tag{1.62}$$

Now, in the Dalton mixture model, all species share the same T and V. So, the mixture temperature and volume are the same for each species $V_i = V$, $T_i = T$. But the mixture pressure is taken to be the sum of the partial pressures:

$$P = \sum_{i=1}^{N} P_i. \tag{1.63}$$

Substituting from Eq. (1.62) into Eq. (1.63), we get

$$P = \sum_{i=1}^{N} \overline{\rho}_i \overline{R} T = \overline{R} T \sum_{i=1}^{N} \overline{\rho}_i. \tag{1.64}$$

For our example, we only have two species, so

$$P = \overline{R} T (\overline{\rho}_O + \overline{\rho}_{O_2}). \tag{1.65}$$

The pressure at the initial state $t = 0$ is

$$
\begin{aligned}
P(t = 0) &= \overline{R} T (\widehat{\overline{\rho}}_O + \widehat{\overline{\rho}}_{O_2}), &&\text{(1.66)} \\
&= \left(8.31441 \times 10^7 \frac{erg}{mole\ K} \right) (5000\ K) \left(0.001 \frac{mole}{cm^3} + 0.001 \frac{mole}{cm^3} \right), &&\text{(1.67)} \\
&= 8.31441 \times 10^8 \frac{dyne}{cm^2}, &&\text{(1.68)} \\
&= 8.31441 \times 10^2\ bar. &&\text{(1.69)}
\end{aligned}
$$
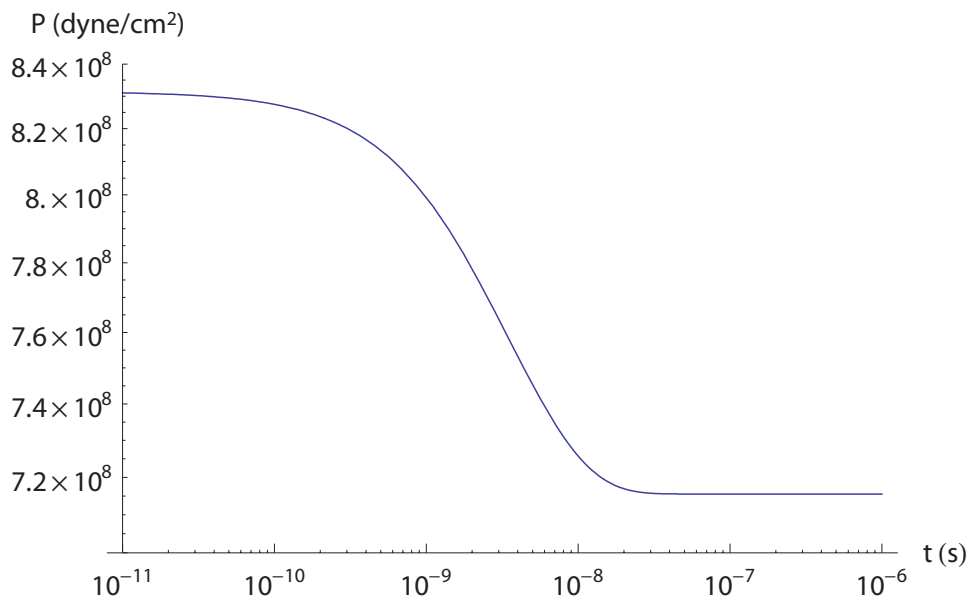
Figure 1.4: Pressure versus time for oxygen dissociation example.

This pressure is over 800 atmospheres. It is actually a little too high for good experimental correlation with the underlying data, but we will neglect that for this exercise.

At the equilibrium state we have more O_2 and less O. And we have a different number of molecules, so we expect the pressure to be different. At equilibrium, the pressure is

$$P(t \to \infty) = \lim_{t \to \infty} \overline{R}T(\overline{\rho}_O + \overline{\rho}_{O_2}), \tag{1.70}$$

$$= \left(8.31441 \times 10^7 \frac{erg}{mole\ K}\right)(5000\ K)\left(0.0004424\ \frac{mole}{cm^3} + 0.00127\ \frac{mole}{cm^3}\right), \tag{1.71}$$

$$= 7.15 \times 10^8\ \frac{dyne}{cm^2}, \tag{1.72}$$

$$= 7.15 \times 10^2\ bar. \tag{1.73}$$

The pressure has dropped because much of the O has recombined to form O_2. Thus, there are fewer molecules at equilibrium. The temperature and volume have remained the same. A plot of $P(t)$ is given in Figure 1.4.

1.1.1.1.2.3 Dynamical system form Now, Eqs. (1.52-1.53) are of the standard form for an autonomous dynamical system:

$$\frac{d\mathbf{y}}{dt} = \mathbf{f}(\mathbf{y}). \tag{1.74}$$

Here, $\mathbf{y}$ is the vector of state variables $(\overline{\rho}_O, \overline{\rho}_{O_2})^T$. And $\mathbf{f}$ is an algebraic function of the state variables. For the isothermal system, the algebraic function is in fact a polynomial.

Equilibrium

The dynamical system is in equilibrium when

$$\mathbf{f}(\mathbf{y}) = \mathbf{0}. \tag{1.75}$$

This non-linear set of algebraic equations can be difficult to solve for large systems. We will later see in Sec. 5.2.3 that for common chemical kinetics systems, such as the one we are dealing with, there is a guarantee of a unique equilibrium for which all state variables are physical. There are certainly other equilibria for which at least one of the state variables is non-physical. Such equilibria can be mathematically complicated.

Solving Eq. (1.75) for our oxygen dissociation problem gives us from Eq. (1.8-1.9)

$$-2a_{13} \exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right) \overline{\rho}_O^{eq} \overline{\rho}_O^{eq} \overline{\rho}_M^{eq} T^{\beta_{13}} + 2a_{14} \exp\left(\frac{-\overline{\mathcal{E}}_{14}}{\overline{R}T}\right) \overline{\rho}_{O_2}^{eq} \overline{\rho}_M^{eq} T^{\beta_{14}} = 0, \tag{1.76}$$

$$a_{13} T^{\beta_{13}} \exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right) \overline{\rho}_O^{eq} \overline{\rho}_O^{eq} \overline{\rho}_M^{eq} - a_{14} T^{\beta_{14}} \exp\left(\frac{-\overline{\mathcal{E}}_{14}}{\overline{R}T}\right) \overline{\rho}_{O_2}^{eq} \overline{\rho}_M^{eq} = 0. \tag{1.77}$$

We notice that $\overline{\rho}_M^{eq}$ cancels. This so-called third body will in fact never affect the equilibrium state. It will however influence the dynamics. Removing $\overline{\rho}_M^{eq}$ and slightly rearranging Eqs. (1.76-1.77) gives

$$a_{13} T^{\beta_{13}} \exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right) \overline{\rho}_O^{eq} \overline{\rho}_O^{eq} = a_{14} T^{\beta_{14}} \exp\left(\frac{-\overline{\mathcal{E}}_{14}}{\overline{R}T}\right) \overline{\rho}_{O_2}^{eq}, \tag{1.78}$$

$$a_{13} T^{\beta_{13}} \exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right) \overline{\rho}_O^{eq} \overline{\rho}_O^{eq} = a_{14} T^{\beta_{14}} \exp\left(\frac{-\overline{\mathcal{E}}_{14}}{\overline{R}T}\right) \overline{\rho}_{O_2}^{eq}. \tag{1.79}$$

These are the same equations! So, we really have two unknowns for the equilibrium state $\overline{\rho}_O^{eq}$ and $\overline{\rho}_{O_2}^{eq}$ but seemingly only one equation. Note that rearranging either Eq. (1.78) or (1.79) gives the result

$$\frac{\overline{\rho}_O^{eq} \overline{\rho}_O^{eq}}{\overline{\rho}_{O_2}^{eq}} = \frac{a_{14} T^{\beta_{14}} \exp\left(\frac{-\overline{\mathcal{E}}_{14}}{\overline{R}T}\right)}{a_{13} T^{\beta_{13}} \exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right)} = K(T). \tag{1.80}$$

That is, for the net reaction (excluding the inert third body), $O_2 \rightarrow O+O$, at equilibrium the product of the concentrations of the products divided by the product of the concentrations of the reactants is a function of temperature T. And for constant T, this is the so-called equilibrium constant. This is a famous result from basic chemistry. It is actually not complete yet, as we have not taken advantage of a connection with thermodynamics. But for now, it will suffice. A more complete discussion will be given in Sec. 4.4.

We still have a problem: Eq. (1.78), or equivalently, Eq. (1.80), is still one equation for two unknowns. We resolve this be recalling we have not yet taken advantage of our algebraic constraint of element conservation, Eq. (1.30). Let us use this to eliminate $\overline{\rho}_{O_2}^{eq}$ in favor of $\overline{\rho}_O^{eq}$:

$$\overline{\rho}_{O_2}^{eq} = \frac{1}{2}\left(\widehat{\overline{\rho}}_O - \overline{\rho}_O^{eq}\right) + \widehat{\overline{\rho}}_{O_2}. \tag{1.81}$$

So, with Eq. (1.81), Eq. (1.78) reduces to

$$a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right)\overline{\rho}_O^{eq}\overline{\rho}_O^{eq} = a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{\mathcal{E}}_{14}}{\overline{R}T}\right)\underbrace{\left(\frac{1}{2}\left(\widehat{\overline{\rho}}_O - \overline{\rho}_O^{eq}\right) + \widehat{\overline{\rho}}_{O_2}\right)}_{=\overline{\rho}_{O_2}^{eq}}. \tag{1.82}$$

Equation (1.82) is one algebraic equation in one unknown. Its solution gives the equilibrium value $\overline{\rho}_O^{eq}$. It is a quadratic equation for $\overline{\rho}_O^{eq}$. Of its two roots, one will be physical. *We note that the equilibrium state will be a function of the initial conditions.* Mathematically this is because our system is really best posed as a system of differential-algebraic equations. Systems which are purely differential equations will have equilibria which are independent of their initial conditions. Most of the literature of mathematical physics focuses on such systems of those. One of the foundational complications of chemical dynamics is the equilibria is a function of the initial conditions, and this renders many common mathematical notions from traditional dynamic system theory to be invalid. Fortunately, after one accounts for the linear constraints of element conservation, one can return to classical notions from traditional dynamic systems theory.

Consider the dynamics of Eq. (1.26) for the evolution of $\overline{\rho}_O$. Equilibrating the right hand side of this equation gives Eq. (1.76). Eliminating $\overline{\rho}_M$ and then $\overline{\rho}_{O_2}$ in Eq. (1.76) then substituting in numerical parameters gives the cubic algebraic equation

$$33948.3 - (1.78439 \times 10^{11})(\overline{\rho}_O)^2 - (5.8 \times 10^{13})(\overline{\rho}_O)^3 = f(\overline{\rho}_O) = 0. \tag{1.83}$$

This equation is cubic because we did not remove the effect of $\overline{\rho}_M$. This will not affect the equilibrium, but will affect the dynamics. We can get an idea of where the roots are by plotting $f(\overline{\rho}_O)$ as seen in Figure 1.5. Zero crossings of $f(\overline{\rho}_O)$ in Figure 1.5 represent equilibria of the system, $\overline{\rho}_O^{eq}$, $f(\overline{\rho}_O^{eq}) = 0$. The cubic equation has three roots

$$\overline{\rho}_O^{eq} = -0.003\,\frac{mole}{cm^3}, \qquad \text{non-physical}, \tag{1.84}$$

$$\overline{\rho}_O^{eq} = -0.000518944\,\frac{mole}{cm^3}, \qquad \text{non-physical}, \tag{1.85}$$

$$\overline{\rho}_O^{eq} = 0.000442414\,\frac{mole}{cm^3}, \qquad \text{physical}. \tag{1.86}$$

Note the physical root found by our algebraic analysis is identical to that which was identified by our numerical integration of the ordinary differential equations of reaction kinetics.
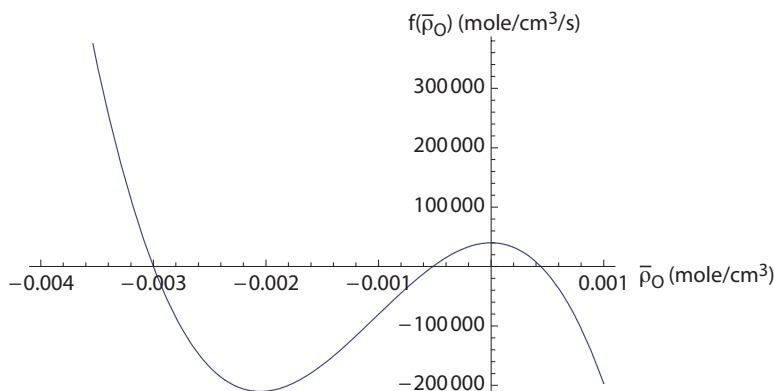
Figure 1.5: Equilibria for oxygen dissociation example.

Stability of equilibria

We can get a simple estimate of the stability of the equilibria by considering the slope of f near $f = 0$. Our dynamic system is of the form

$$\frac{d\overline{\rho}_O}{dt} = f(\overline{\rho}_O). \tag{1.87}$$

- Near the first non-physical root at $\overline{\rho}_O^{eq} = -0.003 \; mole/cm^3$, a positive perturbation from equilibrium induces $f < 0$, which induces $d\overline{\rho}_O/dt < 0$, so $\overline{\rho}_O$ returns to its equilibrium. Similarly, a negative perturbation from equilibrium induces $d\overline{\rho}_O/dt > 0$, so the system returns to equilibrium. This non-physical equilibrium point is *stable*. Note stability does not imply physicality!

- Perform the same exercise for the non-physical root at $\overline{\rho}_O^{eq} = -0.000518944 \; mole/cm^3$. We find this root is *unstable*.

- Perform the same exercise for the physical root at $\overline{\rho}_O^{eq} = 0.000442414 \; mole/cm^3$. We find this root is *stable*.

In general if f crosses zero with a positive slope, the equilibrium is unstable. Otherwise, it is stable.

Consider a formal Taylor[8] series expansion of Eq. (1.87) in the neighborhood of an equilibrium point $\overline{\rho}_O^{eq}$:

$$\frac{d}{dt}\left(\overline{\rho}_O - \overline{\rho}_O^{eq}\right) = \underbrace{f(\overline{\rho}_O^{eq})}_{=0} + \left.\frac{df}{d\overline{\rho}_O}\right|_{\overline{\rho}_O = \overline{\rho}_O^{eq}} \left(\overline{\rho}_O - \overline{\rho}_O^{eq}\right) + \ldots \tag{1.88}$$

We find $df/d\overline{\rho}_O$ by differentiating Eq. (1.83) to get

$$\frac{df}{d\overline{\rho}_O} = -(3.56877 \times 10^{11})\overline{\rho}_O - (1.74 \times 10^{14})\overline{\rho}_O^2. \tag{1.89}$$

---

[8]Brook Taylor, 1685-1731, English mathematician.

We evaluate $df/d\overline{\rho}_O$ near the physical equilibrium point at $\overline{\rho}_O = 0.0004442414 \; mole/cm^3$ to get

$$
\begin{aligned}
\frac{df}{d\overline{\rho}_O} &= -(3.56877 \times 10^{11})(0.0004442414) - (1.74 \times 10^{14})(0.0004442414)^2, \\
&= -1.91945 \times 10^8 \; \frac{1}{s}.
\end{aligned} \tag{1.90}
$$

Thus, the Taylor series expansion of Eq. (1.26) in the neighborhood of the physical equilibrium gives the local kinetics to be driven by

$$
\frac{d}{dt}\left(\overline{\rho}_O - 0.000442414\right) = -(1.91945 \times 10^8)\left(\overline{\rho}_O - 0.0004442414\right) + \dots. \tag{1.91}
$$

So, in the neighborhood of the physical equilibrium we have

$$
\overline{\rho}_O = 0.0004442414 + A \exp\left(-1.91945 \times 10^8 t\right). \tag{1.92}
$$

Here, A is an arbitrary constant of integration. The local time constant which governs the times scales of local evolution is τ where

$$
\tau = \frac{1}{1.91945 \times 10^8} = 5.20983 \times 10^{-9} \; s. \tag{1.93}
$$

This nano-second time scale is very fast. It can be shown to be correlated with the mean time between collisions of molecules.

1.1.1.1.3 Effect of temperature Let us perform four case studies to see the effect of T on the system's equilibria and its dynamics near equilibrium.

- $T = 3000 \; K$. Here, we have significantly reduced the temperature, but it is still higher than typically found in ordinary combustion engineering environments. Here, we find

$$
\begin{aligned}
\overline{\rho}_O^{eq} &= 8.9371 \times 10^{-6} \; \frac{mole}{cm^3}, \tag{1.94} \\
\tau &= 1.92059 \times 10^{-7} \; s. \tag{1.95}
\end{aligned}
$$

  The equilibrium concentration of O dropped by two orders of magnitude relative to $T = 5000 \; K$, and the time scale of the dynamics near equilibrium slowed by two orders of magnitude.

- $T = 1000 \; K$. Here, we reduce the temperature more. This temperature is common in combustion engineering environments. We find

$$
\begin{aligned}
\overline{\rho}_O^{eq} &= 2.0356 \times 10^{-14} \; \frac{mole}{cm^3}, \tag{1.96} \\
\tau &= 2.82331 \times 10^1 \; s. \tag{1.97}
\end{aligned}
$$

  The O concentration at equilibrium is greatly diminished to the point of being difficult to detect by standard measurement techniques. And the time scale of combustion has significantly slowed.

- $T = 300 \ K$. This is obviously near room temperature. We find

$$\overline{\rho}_O^{eq} = 1.14199 \times 10^{-44} \ \frac{mole}{cm^3}, \tag{1.98}$$

$$\tau = 1.50977 \times 10^{31} \ s. \tag{1.99}$$

The O concentration is effectively zero at room temperature, and the relaxation time is effectively infinite. As the oldest star in our galaxy has an age of $4.4 \times 10^{17} \ s$ ($\sim 13.75 \times 10^9 \ years$[9]), we see that at this temperature, our mathematical model cannot be experimentally validated, so it loses its meaning. At such a low temperature, the theory becomes qualitatively correct, but not quantitatively predictive.

- $T = 10000 \ K$. Such high temperature could be achieved in an atmospheric re-entry environment.

$$\overline{\rho}_O^{eq} = 2.74807 \times 10^{-3} \ \frac{mole}{cm^3}, \tag{1.100}$$

$$\tau = 1.69119 \times 10^{-10} \ s. \tag{1.101}$$

At this high temperature, O become preferred over O_2, and the time scales of reaction become extremely small, under a nanosecond.

1.1.1.2 Single reversible reaction

The two irreversible reactions studied in the previous section are of a class that is common in combustion modelling. However, the model suffers a defect in that its link to classical equilibrium thermodynamics is missing. A better way to model essentially the same physics and guarantee consistency with classical equilibrium thermodynamics is to model the process as a single *reversible* reaction, with a suitably modified reaction rate term.

1.1.1.2.1 Mathematical model

1.1.1.2.1.1 Kinetics For the reversible $O - O_2$ reaction, let us only consider reaction 13 from Table 1.2 for which

$$13 : O_2 + M \rightleftharpoons O + O + M. \tag{1.102}$$

For this system, we have $N = 2$ molecular species in $L = 1$ element reacting in $J = 1$ reaction. Here

$$a_{13} = 1.85 \times 10^{11} \ \left(\frac{mole}{cm^3} \right)^{-1} (K)^{-0.5}, \qquad \beta_{13} = 0.5, \qquad \overline{\mathcal{E}}_{13} = 95560 \ \frac{cal}{mole}. \tag{1.103}$$

---

[9]NASA, `http://map.gsfc.nasa.gov/universe/uni_age.html`, retrieved 2 January 2012.

Units of *cal* are common in chemistry, but we need to convert to *erg*, which is achieved via

$$\overline{\mathcal{E}}_{13} = \left(95560 \; \frac{cal}{mole}\right)\left(\frac{4.186 \; J}{cal}\right)\left(\frac{10^7 \; erg}{J}\right) = 4.00014 \times 10^{12} \; \frac{erg}{mole}. \tag{1.104}$$

For this reversible reaction, we slightly modify the kinetics equations to

$$\frac{d\overline{\rho}_O}{dt} = 2 \underbrace{\underbrace{a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right)}_{=k_{13}(T)}\left(\overline{\rho}_{O_2}\overline{\rho}_M - \frac{1}{K_{c,13}}\overline{\rho}_O\overline{\rho}_O\overline{\rho}_M\right)}_{=r_{13}}, \tag{1.105}$$

$$\frac{d\overline{\rho}_{O_2}}{dt} = -\underbrace{\underbrace{a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right)}_{=k_{13}(T)}\left(\overline{\rho}_{O_2}\overline{\rho}_M - \frac{1}{K_{c,13}}\overline{\rho}_O\overline{\rho}_O\overline{\rho}_M\right)}_{=r_{13}}. \tag{1.106}$$

Here, we have used equivalent definitions for $k_{13}(T)$ and r_{13}, so that Eqs. (1.105-1.106) can be written compactly as

$$\frac{d\overline{\rho}_O}{dt} = 2r_{13}, \tag{1.107}$$

$$\frac{d\overline{\rho}_{O_2}}{dt} = -r_{13}. \tag{1.108}$$

In matrix form, we can simplify to

$$\frac{d}{dt}\left(\begin{array}{c}\overline{\rho}_O \\ \overline{\rho}_{O_2}\end{array}\right) = \underbrace{\left(\begin{array}{c}2 \\ -1\end{array}\right)}_{\boldsymbol{\nu}}(r_{13}). \tag{1.109}$$

Here, the $N \times J = 2 \times 1$ matrix $\boldsymbol{\nu}$ is

$$\boldsymbol{\nu} = \left(\begin{array}{c}2 \\ -1\end{array}\right). \tag{1.110}$$

Performing row operations, Eq. (1.109) reduces to

$$\frac{d}{dt}\left(\begin{array}{c}\overline{\rho}_O \\ \overline{\rho}_O + 2\overline{\rho}_{O_2}\end{array}\right) = \left(\begin{array}{c}2 \\ 0\end{array}\right)(r_{13}), \tag{1.111}$$

or

$$\underbrace{\left(\begin{array}{cc}1 & 0 \\ 1 & 2\end{array}\right)}_{\mathbf{L}^{-1}}\frac{d}{dt}\left(\begin{array}{c}\overline{\rho}_O \\ \overline{\rho}_{O_2}\end{array}\right) = \underbrace{\left(\begin{array}{c}2 \\ 0\end{array}\right)}_{\mathbf{U}}(r_{13}). \tag{1.112}$$

So, here the $N \times N = 2 \times 2$ matrix $\mathbf{L}^{-1}$ is

$$\mathbf{L}^{-1} = \begin{pmatrix} 1 & 0 \\ 1 & 2 \end{pmatrix}. \tag{1.113}$$

The $N \times N = 2 \times 2$ permutation matrix $\mathbf{P}$ is the identity matrix. And the $N \times J = 2 \times 1$ upper triangular matrix $\mathbf{U}$ is

$$\mathbf{U} = \begin{pmatrix} 2 \\ 0 \end{pmatrix}. \tag{1.114}$$

Note that $\boldsymbol{\nu} = \mathbf{L} \cdot \mathbf{U}$ or equivalently $\mathbf{L}^{-1} \cdot \boldsymbol{\nu} = \mathbf{U}$:

$$\underbrace{\begin{pmatrix} 1 & 0 \\ 1 & 2 \end{pmatrix}}_{=\mathbf{L}^{-1}} \cdot \underbrace{\begin{pmatrix} 2 \\ -1 \end{pmatrix}}_{=\boldsymbol{\nu}} = \underbrace{\begin{pmatrix} 2 \\ 0 \end{pmatrix}}_{=\mathbf{U}}. \tag{1.115}$$

Once again the stoichiometric matrix $\boldsymbol{\phi}$ is

$$\boldsymbol{\phi} = \begin{pmatrix} 1 & 2 \end{pmatrix}. \tag{1.116}$$

And we see that $\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \mathbf{0}$ is satisfied:

$$\underbrace{\begin{pmatrix} 1 & 2 \end{pmatrix}}_{\boldsymbol{\phi}} \cdot \underbrace{\begin{pmatrix} 2 \\ -1 \end{pmatrix}}_{\boldsymbol{\nu}} = \begin{pmatrix} 0 \end{pmatrix}. \tag{1.117}$$

As for the irreversible reactions, the reversible reaction rates are constructed to conserve O atoms. We have

$$\frac{d}{dt} \left(\overline{\rho}_O + 2\overline{\rho}_{O_2} \right) = 0. \tag{1.118}$$

Thus, by integrating Eq. (1.118) and applying the initial conditions, we once again find

$$\overline{\rho}_O + 2\overline{\rho}_{O_2} = \widehat{\overline{\rho}}_O + 2\widehat{\overline{\rho}}_{O_2} = constant. \tag{1.119}$$

As before, we can say

$$\underbrace{\begin{pmatrix} \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix}}_{\overline{\boldsymbol{\rho}}} = \underbrace{\begin{pmatrix} \widehat{\overline{\rho}}_O \\ \widehat{\overline{\rho}}_{O_2} \end{pmatrix}}_{\widehat{\overline{\boldsymbol{\rho}}}} + \underbrace{\begin{pmatrix} 1 \\ -\frac{1}{2} \end{pmatrix}}_{\mathbf{D}} \underbrace{(\overline{\xi}_O)}_{\overline{\boldsymbol{\xi}}}. \tag{1.120}$$

This gives the dependent variables in terms of a smaller number of transformed dependent variables in a way which satisfies the linear constraints. In vector form, Eq. (1.120) becomes

$$\overline{\boldsymbol{\rho}} = \widehat{\overline{\boldsymbol{\rho}}} + \mathbf{D} \cdot \overline{\boldsymbol{\xi}}. \tag{1.121}$$

Once again, $\boldsymbol{\phi} \cdot \mathbf{D} = \mathbf{0}$.

1.1.1.2.1.2   Thermodynamics   Equations (1.105-1.106) are supplemented by an expression for the thermodynamics-based equilibrium constant $K_{c,13}$ which is:

$$K_{c,13} = \frac{P_o}{\overline{R}T} \exp\left(\frac{-\Delta G_{13}^o}{\overline{R}T}\right).$$ (1.122)

Here, $P_o = 1.01326 \times 10^6 \ dyne/cm^2 = 1 \ atm$ is the reference pressure. The net change of Gibbs[10] free energy at the reference pressure for reaction 13, ΔG_{13}^o, is defined as

$$\Delta G_{13}^o = 2\overline{g}_O^o - \overline{g}_{O_2}^o.$$ (1.123)

This is the special case of the more general vector form

$$\Delta \mathbf{G}^{oT} = \overline{\mathbf{g}}^{oT} \cdot \boldsymbol{\nu}.$$ (1.124)

Here, $\Delta \mathbf{G}^o$ is a $J \times 1$ vector with the net change of Gibbs free energy for each reaction, and $\overline{\mathbf{g}}^o$ is a $N \times 1$ vector of the Gibbs free energy of each species. Both are evaluated at the reference pressure. For reaction 13, we have

$$\Delta G_{13}^o = \underbrace{(\ \overline{g}_O^o \quad \overline{g}_{O_2}^o\ )}_{\overline{\mathbf{g}}^{oT}} \cdot \underbrace{\begin{pmatrix} 2 \\ -1 \end{pmatrix}}_{\boldsymbol{\nu}}.$$ (1.125)

We further recall that the Gibbs free energy for species i at the reference pressure is defined in terms of the enthalpy and entropy as

$$\overline{g}_i^o = \overline{h}_i^o - T\overline{s}_i^o.$$ (1.126)

It is common to find $\overline{h}_i^o$ and $\overline{s}_i^o$ in thermodynamic tables tabulated as functions of T.

We further note that both Eqs. (1.105) and (1.106) are in equilibrium when

$$\overline{\rho}_{O_2}^{eq} \overline{\rho}_M^{eq} = \frac{1}{K_{c,13}} \overline{\rho}_O^{eq} \overline{\rho}_O^{eq} \overline{\rho}_M^{eq}.$$ (1.127)

We rearrange Eq. (1.127) to find the familiar

$$K_{c,13} = \frac{\overline{\rho}_O^{eq} \overline{\rho}_O^{eq}}{\overline{\rho}_{O_2}^{eq}} = \frac{\prod [products]}{\prod [reactants]}.$$ (1.128)

If $K_{c,13} > 1$, the products are preferred. If $K_{c,13} < 1$, the reactants are preferred.

Now, $K_{c,13}$ is a function of T only, so it is known. But Eq. (1.128) once again is one equation in two unknowns. We can use the element conservation constraint, Eq. (1.119) to reduce to one equation and one unknown, valid at equilibrium:

$$K_{c,13} = \frac{\overline{\rho}_O^{eq} \overline{\rho}_O^{eq}}{\widehat{\overline{\rho}}_{O_2} + \frac{1}{2}(\widehat{\overline{\rho}}_O - \overline{\rho}_O^{eq})}.$$ (1.129)

[10]Josiah Willard Gibbs, 1839-1903, American mechanical engineer and the pre-eminent American scientist of the 19th century.

Using the element constraint, Eq. (1.119), we can recast the dynamics of our system by modifying Eq. (1.105) into one equation in one unknown:

$$
\frac{d\overline{\rho}_O}{dt} = 2a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{\mathcal{E}}_{13}}{\overline{R}T}\right)
$$

$$
\times\left(\underbrace{(\widehat{\overline{\rho}}_{O_2}+\frac{1}{2}(\widehat{\overline{\rho}}_O-\overline{\rho}_O))}_{=\overline{\rho}_{O_2}}\underbrace{(\widehat{\overline{\rho}}_{O_2}+\frac{1}{2}(\widehat{\overline{\rho}}_O-\overline{\rho}_O)+\overline{\rho}_O)}_{=\overline{\rho}_M}-\frac{1}{K_{c,13}}\overline{\rho}_O\overline{\rho}_O\underbrace{(\widehat{\overline{\rho}}_{O_2}+\frac{1}{2}(\widehat{\overline{\rho}}_O-\overline{\rho}_O)+\overline{\rho}_O)}_{=\overline{\rho}_M}\right).
$$

$$(1.130)$$

1.1.1.2.2 Example calculation Let us consider the same example as the previous section with $T = 5000\ K$. We need numbers for all of the parameters of Eq. (1.130). For O, we find at $T = 5000\ K$ that

$$
\overline{h}_O^o = 3.48382\times10^{12}\ \frac{erg}{mole}, \tag{1.131}
$$

$$
\overline{s}_O^o = 2.20458\times10^9\ \frac{erg}{mole\ K}. \tag{1.132}
$$

So

$$
\overline{g}_O^o = \left(3.48382\times10^{12}\ \frac{erg}{mole}\right)-(5000\ K)\left(2.20458\times10^9\ \frac{erg}{mole\ K}\right),
$$
$$
= -7.53908\times10^{12}\ \frac{erg}{mole}. \tag{1.133}
$$

For O_2, we find at $T = 5000\ K$ that

$$
\overline{h}_{O_2}^o = 1.80749\times10^{12}\ \frac{erg}{mole}, \tag{1.134}
$$

$$
\overline{s}_{O_2}^o = 3.05406\times10^9\ \frac{erg}{mole\ K}. \tag{1.135}
$$

So

$$
\overline{g}_{O_2}^o = \left(1.80749\times10^{12}\ \frac{erg}{mole}\right)-(5000\ K)\left(3.05406\times10^9\ \frac{erg}{mole\ K}\right),
$$
$$
= -1.34628\times10^{13}\ \frac{erg}{mole}. \tag{1.136}
$$

Thus, by Eq. (1.123), we have

$$
\Delta G_{13}^o = 2(-7.53908\times10^{12})-(-1.34628\times10^{13}) = -1.61536\times10^{12}\ \frac{erg}{mole}. \tag{1.137}
$$

Thus, by Eq. (1.122) we get for our system

$$
K_{c,13} = \frac{1.01326\times10^6\ \frac{dyne}{cm^2}}{\left(8.31441\times10^7\ \frac{erg}{mole\ K}\right)(5000\ K)}
$$
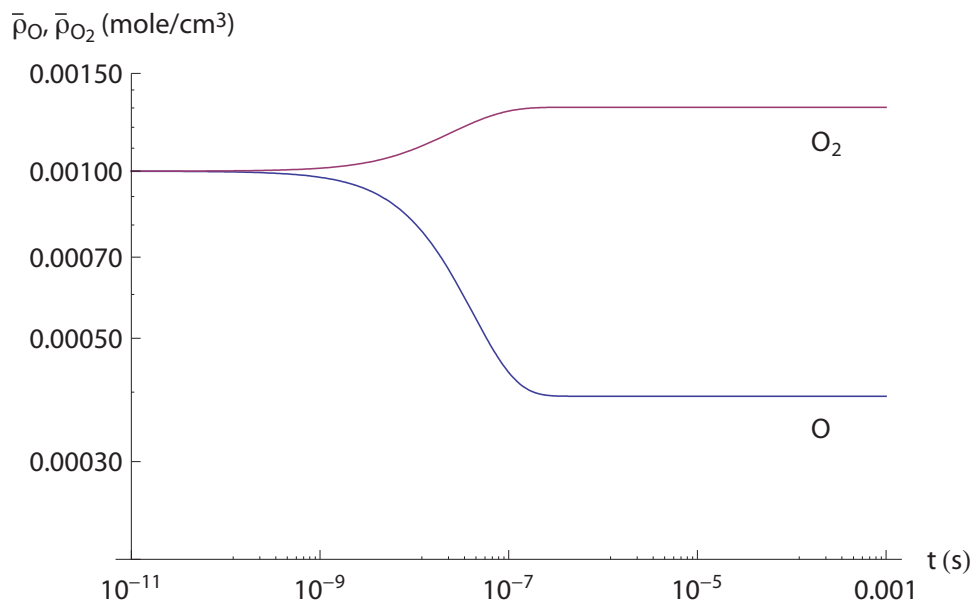
Figure 1.6: Plot of $\overline{\rho}_O(t)$ and $\overline{\rho}_{O_2}(t)$ for oxygen dissociation with reversible reaction.

$$\times \exp\left(-\left(\frac{-1.61536 \times 10^{12}\ \frac{erg}{mole}}{\left(8.31441 \times 10^7\ \frac{erg}{mole\ K}\right)(5000\ K)}\right)\right), \tag{1.138}$$

$$= 1.187 \times 10^{-4}\ \frac{mole}{cm^3}. \tag{1.139}$$

Substitution of all numerical parameters into Eq. (1.130) and expansion yields the following

$$\frac{d\overline{\rho}_O}{dt} = 3899.47 - (2.23342 \times 10^{10})\overline{\rho}_O^2 - (7.3003 \times 10^{12})\overline{\rho}_O^3 = f(\overline{\rho}_O), \tag{1.140}$$

$$\overline{\rho}_O(0) = 0.001. \tag{1.141}$$

A plot of the time-dependent behavior of $\overline{\rho}_O$ and $\overline{\rho}_{O_2}$ from solution of Eqs. (1.140, 1.141) is given in Figure 1.6. The behavior is similar to the predictions given by the pair of irreversible reactions in Fig. 1.1. Here, direct calculation of the equilibrium from time integration reveals

$$\overline{\rho}_O^{eq} = 0.000393328\ \frac{mole}{cm^3}. \tag{1.142}$$

Using Eq. (1.119) we find this corresponds to

$$\overline{\rho}_{O_2}^{eq} = 0.00130334\ \frac{mole}{cm^3}. \tag{1.143}$$
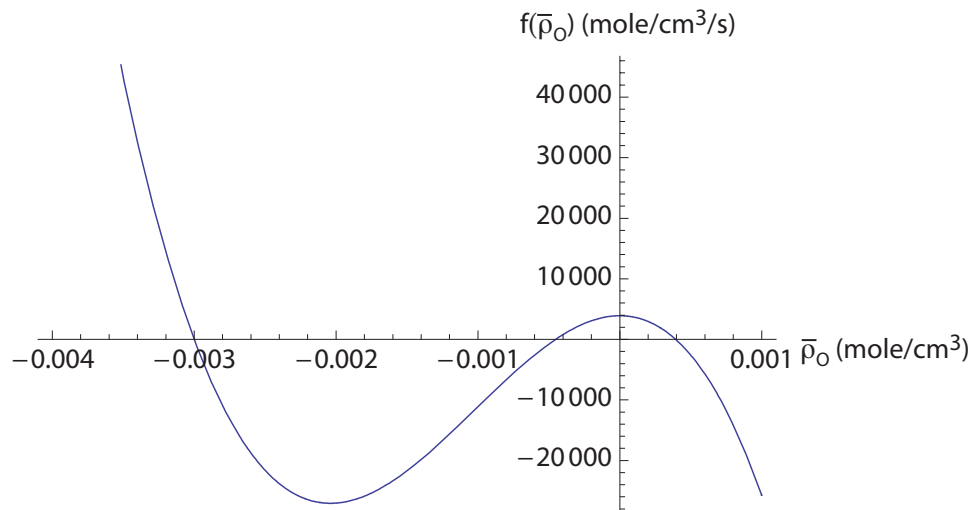
Figure 1.7: Plot of $f(\overline{\rho}_O)$ versus $\overline{\rho}_O$ for oxygen dissociation with reversible reaction.

We note the system begins to undergo significant reaction for $t \sim 10^{-9}$ s and is equilibrated when $t \sim 10^{-7}$ s.

The equilibrium is verified by solving the algebraic equation suggested by Eq. (1.140):

$$f(\overline{\rho}_O) = 3899.47 - (2.23342 \times 10^{10})\overline{\rho}_O^2 - (7.3003 \times 10^{12})\overline{\rho}_O^3 = 0. \tag{1.144}$$

This yields three roots:

$$\overline{\rho}_O^{eq} = -0.003 \, \frac{mole}{cm^3}, \qquad \text{non-physical}, \tag{1.145}$$

$$\overline{\rho}_O^{eq} = -0.000452678 \, \frac{mole}{cm^3}, \qquad \text{non-physical}, \tag{1.146}$$

$$\overline{\rho}_O^{eq} = 0.000393328 \, \frac{mole}{cm^3}, \qquad \text{physical}, \tag{1.147}$$

$$\tag{1.148}$$

consistent with the plot given in Figure 1.7.

Linearizing Eq. (1.141) in the neighborhood of the physical equilibrium yields the equation

$$\frac{d}{dt}\left(\overline{\rho}_O - 0.000393328\right) = -(2.09575 \times 10^7)\left(\overline{\rho}_O - 0.000393328\right) + \ldots \tag{1.149}$$

This has solution

$$\overline{\rho}_O = 0.000393328 + A \exp\left(-2.09575 \times 10^7 t\right). \tag{1.150}$$

Again, A is an arbitrary constant. Obviously the equilibrium is stable. Moreover, the time constant of relaxation to equilibrium is

$$\tau = \frac{1}{2.09575 \times 10^7} = 4.77156 \times 10^{-8} \, s. \tag{1.151}$$

This is consistent with the time scale to equilibrium which comes from integrating the full equation.

1.1.2 Zel'dovich mechanism of NO production

Let us consider next a more complicated reaction system: that of NO production known as the Zel'dovich[11] mechanism. This is an important model for the production of a major pollutant from combustion processes. It is most important for high temperature applications. Related calculations and analysis of this system are given by Al-Khateeb, *et al.*[12]

1.1.2.1 Mathematical model

The model has several versions. One is

$$1: \qquad N + NO \; \leftrightharpoons \; N_2 + O, \tag{1.152}$$

$$2: \qquad N + O_2 \; \leftrightharpoons \; NO + O. \tag{1.153}$$

Similar to our model for O_2 dissociation, N_2 and O_2 are preferred at low temperature. As the temperature rises, N and O begin to appear. It is possible when they are mixed for NO to appear as a product.

1.1.2.1.1 Standard model form Here, we have the reaction of $N = 5$ molecular species with

$$\overline{\boldsymbol{\rho}} = \begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_{N} \\ \overline{\rho}_{N_2} \\ \overline{\rho}_{O} \\ \overline{\rho}_{O_2} \end{pmatrix}. \tag{1.154}$$

Note that "N" here serves two purposes: one to denote the number of species, the other to denote elemental nitrogen. The context should allow the reader to distinguish the two. We have $L = 2$ elements, with N, $(l = 1)$ and O, $(l = 2)$. The stoichiometric matrix $\boldsymbol{\phi}$ of dimension $L \times N = 2 \times 5$ is

$$\boldsymbol{\phi} = \begin{pmatrix} 1 & 1 & 2 & 0 & 0 \\ 1 & 0 & 0 & 1 & 2 \end{pmatrix}. \tag{1.155}$$

The first row of $\boldsymbol{\phi}$ is for the N atom; the second row is for the O atom.

---

[11] Yakov Borisovich Zel'dovich, 1915-1987, prolific Soviet physicist and father of thermonuclear weapons.
[12] Al-Khateeb, A. N., Powers, J. M., Paolucci, S., Sommese, A. J., Diller, J. A., Hauenstein, J. D., and Mengers, J. D., 2009, "One-Dimensional Slow Invariant Manifolds for Spatially Homogeneous Reactive Systems," *Journal of Chemical Physics*, 131(2): 024118.

We have $J = 2$ reactions. The reaction vector of length $J = 2$ is

$$
\mathbf{r} = \begin{pmatrix} r_1 \\ r_2 \end{pmatrix} = \begin{pmatrix} \underbrace{a_1 T^{\beta_1} \exp\left(-\dfrac{T_{a,1}}{T}\right)}_{k_1} \left(\overline{\rho}_N \overline{\rho}_{NO} - \dfrac{1}{K_{c,1}} \overline{\rho}_{N_2} \overline{\rho}_O\right) \\ \underbrace{a_2 T^{\beta_2} \exp\left(-\dfrac{T_{a,2}}{T}\right)}_{k_2} \left(\overline{\rho}_N \overline{\rho}_{O_2} - \dfrac{1}{K_{c,2}} \overline{\rho}_{NO} \overline{\rho}_O\right) \end{pmatrix}, \tag{1.156}
$$

$$
= \begin{pmatrix} k_1 \left(\overline{\rho}_N \overline{\rho}_{NO} - \dfrac{1}{K_{c,1}} \overline{\rho}_{N_2} \overline{\rho}_O\right) \\ k_2 \left(\overline{\rho}_N \overline{\rho}_{O_2} - \dfrac{1}{K_{c,2}} \overline{\rho}_{NO} \overline{\rho}_O\right) \end{pmatrix}. \tag{1.157}
$$

Here, we have

$$
k_1 = a_1 T^{\beta_1} \exp\left(-\frac{T_{a,1}}{T}\right), \tag{1.158}
$$

$$
k_2 = a_2 T^{\beta_2} \exp\left(-\frac{T_{a,2}}{T}\right). \tag{1.159}
$$

In matrix form, the model can be written as

$$
\frac{d}{dt} \begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_N \\ \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \underbrace{\begin{pmatrix} -1 & 1 \\ -1 & -1 \\ 1 & 0 \\ 1 & 1 \\ 0 & -1 \end{pmatrix}}_{=\boldsymbol{\nu}} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{1.160}
$$

Here, the matrix $\boldsymbol{\nu}$ has dimension $N \times J = 5 \times 2$. The model is of our general form, Eq. (1.16):

$$
\frac{d\overline{\boldsymbol{\rho}}}{dt} = \boldsymbol{\nu} \cdot \mathbf{r}. \tag{1.161}
$$

Note that our stoichiometric constraint on element conservation for each reaction, Eq. (1.22), $\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \mathbf{0}$ holds here:

$$
\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \begin{pmatrix} 1 & 1 & 2 & 0 & 0 \\ 1 & 0 & 0 & 1 & 2 \end{pmatrix} \begin{pmatrix} -1 & 1 \\ -1 & -1 \\ 1 & 0 \\ 1 & 1 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}. \tag{1.162}
$$

We get 4 zeros because there are 2 reactions each with 2 element constraints.

1.1.2.1.2   Reduced form   Here, we describe non-traditional, but useful, reductions by using standard techniques from linear algebra to bring the model equations into a reduced form in which all of the linear constraints have been explicitly removed.

Let us perform a series of row operations to find all of the linear dependencies. Our aim is to convert the matrix $\boldsymbol{\nu}$ into an upper triangular form. The lower left corner of $\boldsymbol{\nu}$ already has a zero, so there is no need to worry about it. Let us add the first and fourth equations to eliminate the 1 in the $4, 1$ slot. This gives

$$
\frac{d}{dt}
\begin{pmatrix}
\overline{\rho}_{NO} \\
\overline{\rho}_N \\
\overline{\rho}_{N_2} \\
\overline{\rho}_{NO} + \overline{\rho}_O \\
\overline{\rho}_{O_2}
\end{pmatrix}
=
\begin{pmatrix}
-1 & 1 \\
-1 & -1 \\
1 & 0 \\
0 & 2 \\
0 & -1
\end{pmatrix}
\begin{pmatrix}
r_1 \\
r_2
\end{pmatrix}.
\tag{1.163}
$$

Next, add the first and third equations to get

$$
\frac{d}{dt}
\begin{pmatrix}
\overline{\rho}_{NO} \\
\overline{\rho}_N \\
\overline{\rho}_{NO} + \overline{\rho}_{N_2} \\
\overline{\rho}_{NO} + \overline{\rho}_O \\
\overline{\rho}_{O_2}
\end{pmatrix}
=
\begin{pmatrix}
-1 & 1 \\
-1 & -1 \\
0 & 1 \\
0 & 2 \\
0 & -1
\end{pmatrix}
\begin{pmatrix}
r_1 \\
r_2
\end{pmatrix}.
\tag{1.164}
$$

Now, multiply the first equation by -1 and add it to the second to get

$$
\frac{d}{dt}
\begin{pmatrix}
\overline{\rho}_{NO} \\
-\overline{\rho}_{NO} + \overline{\rho}_N \\
\overline{\rho}_{NO} + \overline{\rho}_{N_2} \\
\overline{\rho}_{NO} + \overline{\rho}_O \\
\overline{\rho}_{O_2}
\end{pmatrix}
=
\begin{pmatrix}
-1 & 1 \\
0 & -2 \\
0 & 1 \\
0 & 2 \\
0 & -1
\end{pmatrix}
\begin{pmatrix}
r_1 \\
r_2
\end{pmatrix}.
\tag{1.165}
$$

Next multiply the fifth equation by -2 and add it to the second to get

$$
\frac{d}{dt}
\begin{pmatrix}
\overline{\rho}_{NO} \\
-\overline{\rho}_{NO} + \overline{\rho}_N \\
\overline{\rho}_{NO} + \overline{\rho}_{N_2} \\
\overline{\rho}_{NO} + \overline{\rho}_O \\
-\overline{\rho}_{NO} + \overline{\rho}_N - 2\overline{\rho}_{O_2}
\end{pmatrix}
=
\begin{pmatrix}
-1 & 1 \\
0 & -2 \\
0 & 1 \\
0 & 2 \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
r_1 \\
r_2
\end{pmatrix}.
\tag{1.166}
$$

Next add the second and fourth equations to get

$$
\frac{d}{dt}
\begin{pmatrix}
\overline{\rho}_{NO} \\
-\overline{\rho}_{NO} + \overline{\rho}_N \\
\overline{\rho}_{NO} + \overline{\rho}_{N_2} \\
\overline{\rho}_N + \overline{\rho}_O \\
-\overline{\rho}_{NO} + \overline{\rho}_N - 2\overline{\rho}_{O_2}
\end{pmatrix}
=
\begin{pmatrix}
-1 & 1 \\
0 & -2 \\
0 & 1 \\
0 & 0 \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
r_1 \\
r_2
\end{pmatrix}.
\tag{1.167}
$$

Next multiply the third equation by 2 and add it to the second to get

$$\frac{d}{dt}\begin{pmatrix} \overline{\rho}_{NO} \\ -\overline{\rho}_{NO} + \overline{\rho}_N \\ \overline{\rho}_{NO} + \overline{\rho}_N + 2\overline{\rho}_{N_2} \\ \overline{\rho}_N + \overline{\rho}_O \\ -\overline{\rho}_{NO} + \overline{\rho}_N - 2\overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ 0 & -2 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{1.168}$$

Rewritten, this becomes

$$\underbrace{\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 2 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ -1 & 1 & 0 & 0 & -2 \end{pmatrix}}_{=\mathbf{L}^{-1}} \frac{d}{dt} \begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_N \\ \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \underbrace{\begin{pmatrix} -1 & 1 \\ 0 & -2 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{pmatrix}}_{=\mathbf{U}} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{1.169}$$

A way to think of this type of row echelon form is that it defines two free variables, those associated with the non-zero pivots of $\mathbf{U}$: $\overline{\rho}_{NO}$ and $\overline{\rho}_N$. The remaining three variables $\overline{\rho}_{N_2}, \overline{\rho}_O$ and $\overline{\rho}_{O_2}$, are bound variables which can be expressed in terms of the free variables. Note that our set of free and bound variables is not unique; had we formed other linear combinations, we could have arrived at a different set which would be as useful as ours.

The last three of the ordinary differential equations of Eq. (1.169) are homogeneous and can be integrated to form

$$\overline{\rho}_{NO} + \overline{\rho}_N + 2\overline{\rho}_{N_2} = C_1, \tag{1.170}$$
$$\overline{\rho}_N + \overline{\rho}_O = C_2, \tag{1.171}$$
$$-\overline{\rho}_{NO} + \overline{\rho}_N - 2\overline{\rho}_{O_2} = C_3. \tag{1.172}$$

The constants C_1, C_2 and C_3 are determined from the initial conditions on all five state variables. In matrix form, we can say

$$\begin{pmatrix} 1 & 1 & 2 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ -1 & 1 & 0 & 0 & -2 \end{pmatrix} \begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_N \\ \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix}. \tag{1.173}$$

Considering the free variables, $\overline{\rho}_{NO}$ and $\overline{\rho}_N$, to be known, we move them to the right side to get

$$\begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \begin{pmatrix} \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} C_1 - \overline{\rho}_{NO} - \overline{\rho}_N \\ C_2 - \overline{\rho}_N \\ C_3 + \overline{\rho}_{NO} - \overline{\rho}_N \end{pmatrix}. \tag{1.174}$$

Solving for the bound variables, we find

$$
\begin{pmatrix} \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2}C_1 - \frac{1}{2}\overline{\rho}_{NO} - \frac{1}{2}\overline{\rho}_N \\ C_2 - \overline{\rho}_N \\ -\frac{1}{2}C_3 - \frac{1}{2}\overline{\rho}_{NO} + \frac{1}{2}\overline{\rho}_N \end{pmatrix}.
\tag{1.175}
$$

We can rewrite this as

$$
\begin{pmatrix} \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2}C_1 \\ C_2 \\ -\frac{1}{2}C_3 \end{pmatrix} + \begin{pmatrix} -\frac{1}{2} & -\frac{1}{2} \\ 0 & -1 \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_N \end{pmatrix}.
\tag{1.176}
$$

We can get a more elegant form by defining $\xi_{NO} = \overline{\rho}_{NO}$ and $\xi_N = \overline{\rho}_N$. Thus, we can say our state variables have the form

$$
\begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_N \\ \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \frac{1}{2}C_1 \\ C_2 \\ -\frac{1}{2}C_3 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ -\frac{1}{2} & -\frac{1}{2} \\ 0 & -1 \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \xi_{NO} \\ \xi_N \end{pmatrix}.
\tag{1.177}
$$

By translating via $\xi_{NO} = \overline{\xi}_{NO} + \widehat{\rho}_{NO}$ and $\xi_N = \overline{\xi}_N + \widehat{\rho}_N$ and choosing the constants C_1, C_2, and C_3 appropriately, we can arrive at

$$
\underbrace{\begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_N \\ \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix}}_{\overline{\boldsymbol{\rho}}} = \underbrace{\begin{pmatrix} \widehat{\rho}_{NO} \\ \widehat{\rho}_N \\ \widehat{\rho}_{N_2} \\ \widehat{\rho}_O \\ \widehat{\rho}_{O_2} \end{pmatrix}}_{\widehat{\boldsymbol{\rho}}} + \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 1 \\ -\frac{1}{2} & -\frac{1}{2} \\ 0 & -1 \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix}}_{\mathbf{D}} \underbrace{\begin{pmatrix} \overline{\xi}_{NO} \\ \overline{\xi}_N \end{pmatrix}}_{=\overline{\boldsymbol{\xi}}}.
\tag{1.178}
$$

This takes the form of Eq. (1.37):

$$
\overline{\boldsymbol{\rho}} = \widehat{\boldsymbol{\rho}} + \mathbf{D} \cdot \overline{\boldsymbol{\xi}}.
\tag{1.179}
$$

Here, the matrix $\mathbf{D}$ is of dimension $N \times R = 5 \times 2$. It spans the same column space as does the $N \times J$ matrix $\boldsymbol{\nu}$ which is of rank R. Here, in fact $R = J = 2$, so $\mathbf{D}$ has the same dimension as $\boldsymbol{\nu}$. In general it will not. If $\mathbf{c}_1$ and $\mathbf{c}_2$ are the column vectors of $\mathbf{D}$, we see that $-\mathbf{c}_1 - \mathbf{c}_2$ forms the first column vector of $\boldsymbol{\nu}$ and $\mathbf{c}_1 - \mathbf{c}_2$ forms the second column vector of $\boldsymbol{\nu}$. Note that $\boldsymbol{\phi} \cdot \mathbf{D} = \mathbf{0}$:

$$
\boldsymbol{\phi} \cdot \mathbf{D} = \begin{pmatrix} 1 & 1 & 2 & 0 & 0 \\ 1 & 0 & 0 & 1 & 2 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ -\frac{1}{2} & -\frac{1}{2} \\ 0 & -1 \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}.
\tag{1.180}
$$

Equations (1.170-1.172) can also be linearly combined in a way which has strong physical relevance. We rewrite the system as three equations in which the first is identical to Eq. (1.170); the second is the difference of Eqs. (1.171) and (1.172); and the third is half of Eq. (1.170) minus half of Eq. (1.172) plus Eq. (1.171):

$$\overline{\rho}_{NO} + \overline{\rho}_N + 2\overline{\rho}_{N_2} = C_1, \tag{1.181}$$

$$\overline{\rho}_O + \overline{\rho}_{NO} + 2\overline{\rho}_{O_2} = C_2 - C_3, \tag{1.182}$$

$$\overline{\rho}_{NO} + \overline{\rho}_N + \overline{\rho}_{N_2} + \overline{\rho}_O + \overline{\rho}_{O_2} = \frac{1}{2}(C_1 - C_3) + C_2. \tag{1.183}$$

Equation (1.181) insists that the number of nitrogen elements be constant; Eq. (1.182) demands the number of oxygen elements be constant; and Eq. (1.183) requires the number of moles of molecular species be constant. For general reactions, including the earlier studied oxygen dissociation problem, the number of moles of molecular species will not be constant. Here, because each reaction considered has two molecules reacting to form two molecules, we are guaranteed the number of moles will be constant. Hence, we get an additional linear constraint beyond the two for element conservation. Note that since our reaction is isothermal, isochoric and mole-preserving, it will also be isobaric.

1.1.2.1.3 Example calculation Let us consider an isothermal reaction at

$$T = 6000 \ K. \tag{1.184}$$

The high temperature is useful in generating results which are easily visualized. It insures that there will be significant concentrations of all molecular species. Let us also take as an initial condition

$$\widehat{\overline{\rho}}_{NO} = \widehat{\overline{\rho}}_N = \widehat{\overline{\rho}}_{N_2} = \widehat{\overline{\rho}}_O = \widehat{\overline{\rho}}_{O_2} = 1 \times 10^{-6} \ \frac{mole}{cm^3}. \tag{1.185}$$

For this temperature and concentrations, the pressure, which will remain constant through the reaction, is $P = 2.4942 \times 10^6 \ dyne/cm^2$. This is a little greater than atmospheric.

Kinetic data for this reaction are adopted from Baulch, *et al.*[13] The data for reaction 1 is

$$a_1 = 2.107 \times 10^{13} \ \left(\frac{mole}{cm^3}\right)^{-1} \frac{1}{s}, \qquad \beta_1 = 0, \qquad T_{a1} = 0 \ K. \tag{1.186}$$

For reaction 2, we have

$$a_2 = 5.8394 \times 10^9 \ \left(\frac{mole}{cm^3}\right)^{-1} \frac{1}{K^{1.01} \ s}, \qquad \beta_2 = 1.01, \qquad T_{a2} = 3120 \ K. \tag{1.187}$$

---

[13]Baulch, *et al.*, 2005, "Evaluated Kinetic Data for Combustion Modeling: Supplement II," *Journal of Physical and Chemical Reference Data*, 34(3): 757-1397.

Here, the so-called activation temperature $T_{a,j}$ for reaction j is really the activation energy scaled by the universal gas constant:

$$T_{a,j} = \frac{\overline{\mathcal{E}}_j}{\overline{R}}. \tag{1.188}$$

Substituting numbers, we obtain for the reaction rates

$$
\begin{aligned}
k_1 &= (2.107 \times 10^{13})(6000)^0 \exp\left(\frac{-0}{6000}\right) = 2.107 \times 10^{13} \left(\frac{mole}{cm^3}\right)^{-1} \frac{1}{s}, &(1.189)\\
k_2 &= (5.8394 \times 10^9)(6000)^{1.01} \exp\left(\frac{-3120}{6000}\right) = 2.27231 \times 10^{13} \left(\frac{mole}{cm^3}\right)^{-1} \frac{1}{s}. &
\end{aligned}
$$
$$\tag{1.190}$$

We will also need thermodynamic data. The data here will be taken from the `Chemkin` database.[14] Thermodynamic data for common materials is also found in most thermodynamic texts. For our system at 6000 K, we find

$$
\begin{aligned}
\overline{g}^o_{NO} &= -1.58757 \times 10^{13} \, \frac{erg}{mole}, &(1.191)\\
\overline{g}^o_{N} &= -7.04286 \times 10^{12} \, \frac{erg}{mole}, &(1.192)\\
\overline{g}^o_{N_2} &= -1.55206 \times 10^{13} \, \frac{erg}{mole}, &(1.193)\\
\overline{g}^o_{O} &= -9.77148 \times 10^{12} \, \frac{erg}{mole}, &(1.194)\\
\overline{g}^o_{O_2} &= -1.65653 \times 10^{13} \, \frac{erg}{mole}. &(1.195)
\end{aligned}
$$

We use Eq. (1.124) to find ΔG^o_j for each reaction:

$$\mathbf{\Delta G}^{oT} = \overline{\mathbf{g}}^{oT} \cdot \boldsymbol{\nu}, \tag{1.196}$$

$$
\begin{pmatrix} \Delta G^o_1 & \Delta G^o_2 \end{pmatrix} = \begin{pmatrix} \overline{g}^o_{NO} & \overline{g}^o_{N} & \overline{g}^o_{N_2} & \overline{g}^o_{O} & \overline{g}^o_{O_2} \end{pmatrix}
\begin{pmatrix} -1 & 1 \\ -1 & -1 \\ 1 & 0 \\ 1 & 1 \\ 0 & -1 \end{pmatrix}. \tag{1.197}
$$

Thus, for each reaction, we find ΔG^o_j:

$$
\begin{aligned}
\Delta G^o_1 &= \overline{g}^o_{N_2} + \overline{g}^o_{O} - \overline{g}^o_{N} - \overline{g}^o_{NO}, &(1.198)\\
&= -1.55206 \times 10^{13} - 9.77148 \times 10^{12} + 7.04286 \times 10^{12} + 1.58757 \times 10^{13},
\end{aligned}
$$

[14]R. J. Kee, et al., 2000, "The `Chemkin` Thermodynamic Data Base," part of the `Chemkin` Collection Release 3.6, Reaction Design, San Diego, CA.

$$(1.199)$$

$$= -2.37351 \times 10^{12} \, \frac{erg}{mole}, \tag{1.200}$$

$$\Delta G_2^o = \overline{g}_{NO}^o + \overline{g}_O^o - \overline{g}_N^o - \overline{g}_{O_2}^o, \tag{1.201}$$

$$= -1.58757 \times 10^{13} - 9.77148 \times 10^{12} + 7.04286 \times 10^{12} + 1.65653 \times 10^{13}, \tag{1.202}$$

$$= -2.03897 \times 10^{12} \, \frac{erg}{mole}. \tag{1.203}$$

At $6000 \, K$, we find the equilibrium constants for the $J = 2$ reactions are

$$K_{c,1} = \exp\left(\frac{-\Delta G_1^o}{\overline{R}T}\right), \tag{1.204}$$

$$= \exp\left(\frac{2.37351 \times 10^{12}}{(8.314 \times 10^7)(6000)}\right) \tag{1.205}$$

$$= 116.52, \tag{1.206}$$

$$K_{c,2} = \exp\left(\frac{-\Delta G_2^o}{\overline{R}T}\right), \tag{1.207}$$

$$= \exp\left(\frac{2.03897 \times 10^{12}}{(8.314 \times 10^7)(6000)}\right), \tag{1.208}$$

$$= 59.5861. \tag{1.209}$$

Again, omitting details, we find the two differential equations governing the evolution of the free variables are

$$\frac{d\overline{\rho}_{NO}}{dt} = 0.72331 + 2.2181 \times 10^7 \overline{\rho}_N + 1.1452 \times 10^{13} \overline{\rho}_N^2$$
$$-9.4353 \times 10^5 \overline{\rho}_{NO} - 3.1960 \times 10^{13} \overline{\rho}_N \overline{\rho}_{NO}, \tag{1.210}$$

$$\frac{d\overline{\rho}_N}{dt} = 0.72331 - 2.3266 \times 10^7 \overline{\rho}_N - 1.1271 \times 10^{13} \overline{\rho}_N^2$$
$$+5.8187 \times 10^5 \overline{\rho}_{NO} - 9.9994 \times 10^{12} \overline{\rho}_N \overline{\rho}_{NO}, \tag{1.211}$$

$$\overline{\rho}_{NO}(0) = 1 \times 10^{-6} \, \frac{mole}{cm^3}, \tag{1.212}$$

$$\overline{\rho}_N(0) = 1 \times 10^{-6} \, \frac{mole}{cm^3}. \tag{1.213}$$

Solving numerically, we obtain the solution shown in Fig. 1.8. The numerics show a relaxation to final concentrations of

$$\lim_{t \to \infty} \overline{\rho}_{NO} = 7.336 \times 10^{-7} \, \frac{mole}{cm^3}, \tag{1.214}$$

$$\lim_{t \to \infty} \overline{\rho}_N = 3.708 \times 10^{-8} \, \frac{mole}{cm^3}. \tag{1.215}$$
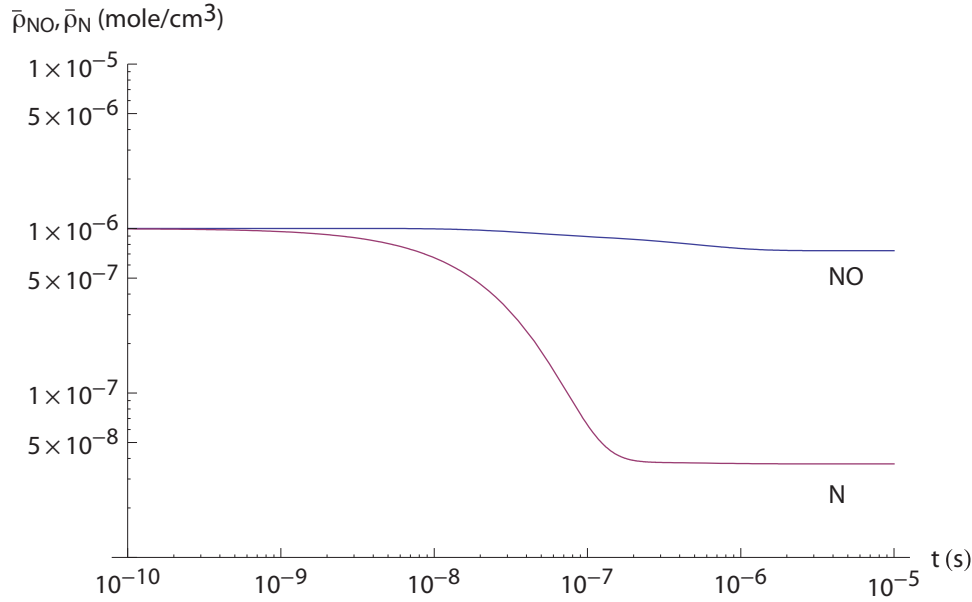
Figure 1.8: NO and N concentrations versus time for $T = 6000\ K$, $P = 2.4942 \times 10^6\ dyne/cm^2$ Zel'dovich mechanism.

Equations (1.210-1.211) are of the form

$$\frac{d\overline{\rho}_{NO}}{dt} = f_{NO}(\overline{\rho}_{NO}, \overline{\rho}_N), \tag{1.216}$$

$$\frac{d\overline{\rho}_N}{dt} = f_N(\overline{\rho}_{NO}, \overline{\rho}_N). \tag{1.217}$$

At equilibrium, we must have

$$f_{NO}(\overline{\rho}_{NO}, \overline{\rho}_N) = 0, \tag{1.218}$$

$$f_N(\overline{\rho}_{NO}, \overline{\rho}_N) = 0. \tag{1.219}$$

We find three finite roots to this problem:

$$1 \ : \ (\overline{\rho}_{NO}, \overline{\rho}_N) = (-1.605 \times 10^{-6}, -3.060 \times 10^{-8})\ \frac{mole}{cm^3}, \qquad \text{non-physical}, \tag{1.220}$$

$$2 \ : \ (\overline{\rho}_{NO}, \overline{\rho}_N) = (-5.173 \times 10^{-8}, -2.048 \times 10^{-6})\ \frac{mole}{cm^3}, \qquad \text{non-physical}, \tag{1.221}$$

$$3 \ : \ (\overline{\rho}_{NO}, \overline{\rho}_N) = (7.336 \times 10^{-7}, 3.708 \times 10^{-8})\ \frac{mole}{cm^3}, \qquad \text{physical}. \tag{1.222}$$

Obviously, because of negative concentrations, roots 1 and 2 are non-physical. Root 3 however is physical; moreover, it agrees with the equilibrium we found by direct numerical integration of the full non-linear equations.

We can use local linear analysis in the neighborhood of each equilibria to rigorously ascertain the stability of each root. Taylor series expansion of Eqs. (1.216-1.217) in the neighborhood of an equilibrium point yields

$$\frac{d}{dt}\left(\overline{\rho}_{NO} - \overline{\rho}_{NO}^{eq}\right) = \underbrace{f_{NO}|_e}_{=0} + \left.\frac{\partial f_{NO}}{\partial \overline{\rho}_{NO}}\right|_e \left(\overline{\rho}_{NO} - \overline{\rho}_{NO}^{eq}\right) + \left.\frac{\partial f_{NO}}{\partial \overline{\rho}_N}\right|_e \left(\overline{\rho}_N - \overline{\rho}_N^{eq}\right) + \dots,$$

(1.223)

$$\frac{d}{dt}\left(\overline{\rho}_N - \overline{\rho}_N^{eq}\right) = \underbrace{f_N|_e}_{=0} + \left.\frac{\partial f_N}{\partial \overline{\rho}_{NO}}\right|_e \left(\overline{\rho}_{NO} - \overline{\rho}_{NO}^{eq}\right) + \left.\frac{\partial f_N}{\partial \overline{\rho}_N}\right|_e \left(\overline{\rho}_N - \overline{\rho}_N^{eq}\right) + \dots. \quad (1.224)$$

Evaluation of Eqs. (1.223-1.224) near the physical root, root 3, yields the system

$$\frac{d}{dt}\begin{pmatrix} \overline{\rho}_{NO} - 7.336 \times 10^{-7} \\ \overline{\rho}_N - 3.708 \times 10^{-8} \end{pmatrix} = \underbrace{\begin{pmatrix} -2.129 \times 10^6 & -4.155 \times 10^5 \\ 2.111 \times 10^5 & -3.144 \times 10^7 \end{pmatrix}}_{=\mathbf{J} = \left.\frac{\partial \mathbf{f}}{\partial \boldsymbol{\rho}}\right|_e} \begin{pmatrix} \overline{\rho}_{NO} - 7.336 \times 10^{-7} \\ \overline{\rho}_N - 3.708 \times 10^{-8} \end{pmatrix}.$$

(1.225)

This is of the form

$$\frac{d}{dt}\left(\overline{\boldsymbol{\rho}} - \overline{\boldsymbol{\rho}}^{eq}\right) = \left.\frac{\partial \mathbf{f}}{\partial \boldsymbol{\rho}}\right|_e \cdot \left(\overline{\boldsymbol{\rho}} - \overline{\boldsymbol{\rho}}^{eq}\right) = \mathbf{J} \cdot \left(\overline{\boldsymbol{\rho}} - \overline{\boldsymbol{\rho}}^{eq}\right). \quad (1.226)$$

It is the eigenvalues of the Jacobian[15] matrix $\mathbf{J}$ that give the time scales of evolution of the concentrations as well as determine the stability of the local equilibrium point. Recall that we can usually decompose square matrices via the diagonalization

$$\mathbf{J} = \mathbf{S} \cdot \boldsymbol{\Lambda} \cdot \mathbf{S}^{-1}. \quad (1.227)$$

Here, $\mathbf{S}$ is the matrix whose columns are composed of the right eigenvectors of $\mathbf{J}$, and $\boldsymbol{\Lambda}$ is the diagonal matrix whose diagonal is populated by the eigenvalues of $\mathbf{J}$. For some matrices (typically not those encountered after our removal of linear dependencies), diagonalization is not possible, and one must resort to the so-called near-diagonal Jordan form. This will not be relevant to our discussion, but could be easily handled if necessary. We also recall the eigenvector matrix and eigenvalue matrix are defined by the standard eigenvalue problem

$$\mathbf{J} \cdot \mathbf{S} = \mathbf{S} \cdot \boldsymbol{\Lambda}. \quad (1.228)$$

We also recall that the components λ of $\boldsymbol{\Lambda}$ are found by solving the characteristic polynomial which arises from the equation

$$\det\left(\mathbf{J} - \lambda \mathbf{I}\right) = 0, \quad (1.229)$$

---

[15]after Carl Gustav Jacob Jacobi, 1804-1851, German mathematician.

where $\mathbf{I}$ is the identity matrix. Defining $\mathbf{z}$ such that

$$\mathbf{S} \cdot \mathbf{z} \equiv \overline{\boldsymbol{\rho}} - \overline{\boldsymbol{\rho}}^{eq}, \tag{1.230}$$

and using the decomposition Eq. (1.227), Eq. (1.226) can be rewritten to form

$$\frac{d}{dt}(\mathbf{S} \cdot \mathbf{z}) = \underbrace{\mathbf{S} \cdot \boldsymbol{\Lambda} \cdot \mathbf{S}^{-1}}_{\mathbf{J}} \cdot \underbrace{(\mathbf{S} \cdot \mathbf{z})}_{\overline{\boldsymbol{\rho}} - \overline{\boldsymbol{\rho}}^{eq}}, \tag{1.231}$$

$$\mathbf{S} \cdot \frac{d\mathbf{z}}{dt} = \mathbf{S} \cdot \boldsymbol{\Lambda} \cdot \mathbf{z}, \tag{1.232}$$

$$\mathbf{S}^{-1} \cdot \mathbf{S} \cdot \frac{d\mathbf{z}}{dt} = \mathbf{S}^{-1} \cdot \mathbf{S} \cdot \boldsymbol{\Lambda} \cdot \mathbf{z}, \tag{1.233}$$

$$\frac{d\mathbf{z}}{dt} = \boldsymbol{\Lambda} \cdot \mathbf{z}. \tag{1.234}$$

Eq. (1.234) is in diagonal form. This has solution for each component of $\mathbf{z}$ of

$$z_1 = C_1 \exp(\lambda_1 t), \tag{1.235}$$

$$z_2 = C_2 \exp(\lambda_2 t), \tag{1.236}$$

$$\vdots \tag{1.237}$$

Here, our matrix $\mathbf{J}$, see Eq. (1.225), has two real, negative eigenvalues in the neighborhood of the physical root 3:

$$\lambda_1 = -3.143 \times 10^7 \frac{1}{s}, \tag{1.238}$$

$$\lambda_2 = -2.132 \times 10^6 \frac{1}{s}. \tag{1.239}$$

Thus, we can conclude that the physical equilibrium is linearly stable. The local time constants near equilibrium are given by the reciprocal of the magnitude of the eigenvalues. These are

$$\tau_1 = 1/|\lambda_1| = 3.181 \times 10^{-8} \ s, \tag{1.240}$$

$$\tau_2 = 1/|\lambda_2| = 4.691 \times 10^{-7} \ s. \tag{1.241}$$

Evolution on these two time scales is predicted in Fig. 1.8. This in fact a multiscale problem. One of the major difficulties in the numerical simulation of combustion problems comes in the effort to capture the effects at all relevant scales. The problem is made more difficult as the breadth of the scales expands. In this problem, the breadth of scales is not particularly challenging. Near equilibrium the ratio of the slowest to the fastest time scale, the *stiffness* ratio κ, is

$$\kappa = \frac{\tau_2}{\tau_1} = \frac{4.691 \times 10^{-7} \ s}{3.181 \times 10^{-8} \ s} = 14.75. \tag{1.242}$$

Many combustion problems can have stiffness ratios over 10^6. This is more prevalent at lower temperatures.

We can do a similar linearization near the initial state, find the local eigenvalues, and the local time scales. At the initial state here, we find those local time scales are

$$\tau_1 = 2.403 \times 10^{-8} \ s, \tag{1.243}$$

$$\tau_2 = 2.123 \times 10^{-8} \ s. \tag{1.244}$$

So, initially the stiffness, $\kappa = (2.403 \times 10^{-8} \ s)/(2.123 \times 10^{-8} \ s) = 1.13$ is much less, but the time scale itself is small. It is seen from Fig. 1.8 that this initial time scale of 10^{-8} s well predicts where significant evolution of species concentrations commences. For $t < 10^{-8}$ s, the model predicts essentially no activity. This can be correlated with the mean time between molecular collisions–the theory on which estimates of the collision frequency factors a_j are obtained.

We briefly consider the non-physical roots, 1 and 2. A similar eigenvalue analysis of root 1 reveals that the eigenvalues of its local Jacobian matrix are

$$\lambda_1 = -1.193 \times 10^7 \ \frac{1}{s}, \tag{1.245}$$

$$\lambda_2 = 5.434 \times 10^6 \ \frac{1}{s}. \tag{1.246}$$

Thus, root 1 is a saddle and is unstable.

For root 2, we find

$$\lambda_1 = 4.397 \times 10^7 + i7.997 \times 10^6 \ \frac{1}{s}, \tag{1.247}$$

$$\lambda_2 = 4.397 \times 10^7 - i7.997 \times 10^6 \ \frac{1}{s}. \tag{1.248}$$

The eigenvalues are complex with a positive real part. This indicates the root is an unstable spiral source.

A detailed phase portrait is shown in Fig. 1.9. Here, we see all three finite roots. Their local character of sink, saddle, or spiral source is clearly displayed. We see that trajectories are attracted to a curve labeled SIM for "Slow Invariant Manifold." A part of the SIM is constructed by the trajectory which originates at root 1 and travels to root 3. The other part is constructed by connecting an equilibrium point at infinity into root 3. Details are omitted here and are given in a related problem by Al-Khateeb, *et al.*[16]

1.1.2.2 Stiffness, time scales, and numerics

One of the key challenges in computational chemistry is accurately predicting species concentration evolution with time. The problem is made difficult because of the common presence

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[16]Al-Khateeb, A. N., Powers, J. M., Paolucci, S., Sommese, A. J., Diller, J. A., Hauenstein, J. D., and Mengers, J. D., 2009, "One-Dimensional Slow Invariant Manifolds for Spatially Homogeneous Reactive Systems," *Journal of Chemical Physics*, 131(2): 024118.
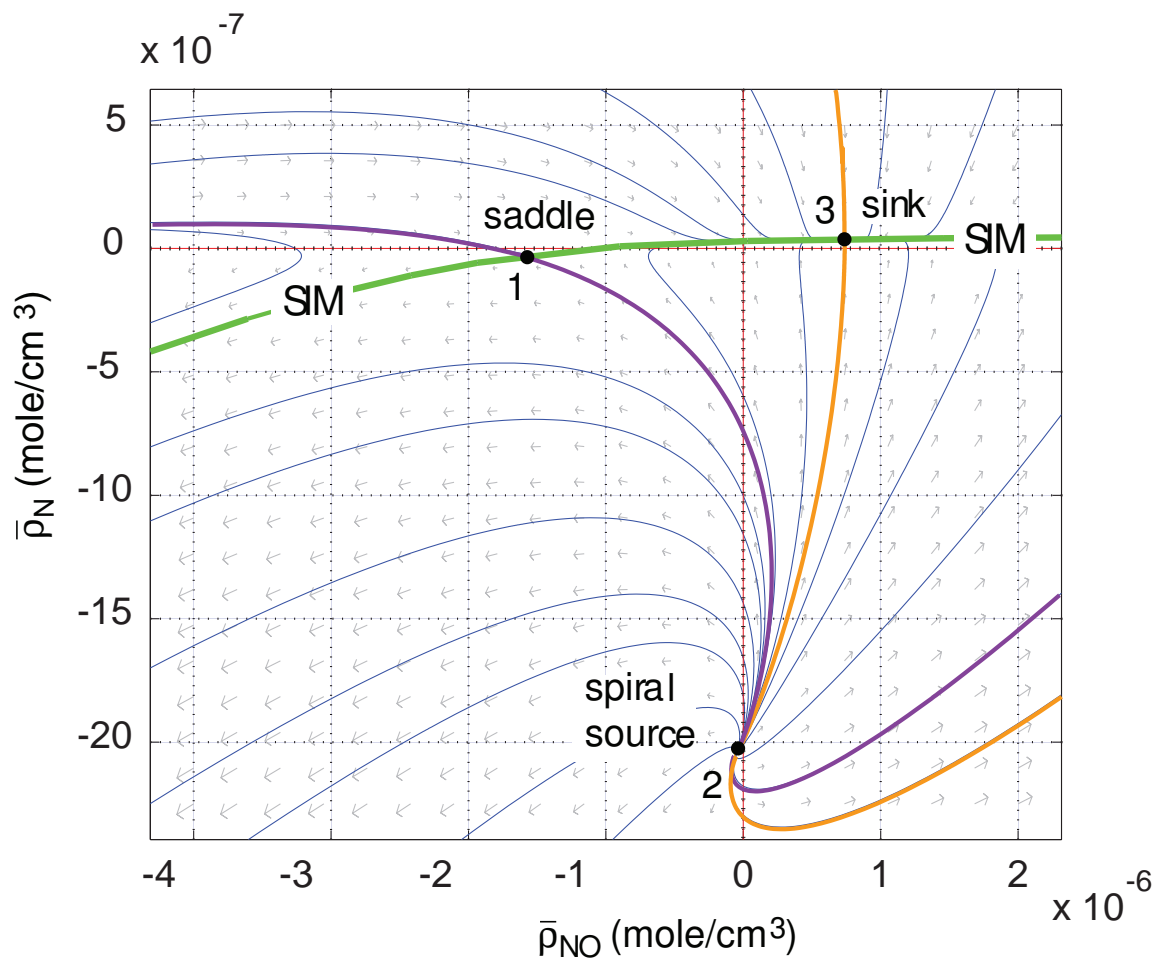
Figure 1.9: NO and N phase portraits for $T = 6000\ K$, $P = 2.4942 \times 10^6\ dyne/cm^2$ Zel'dovich mechanism.
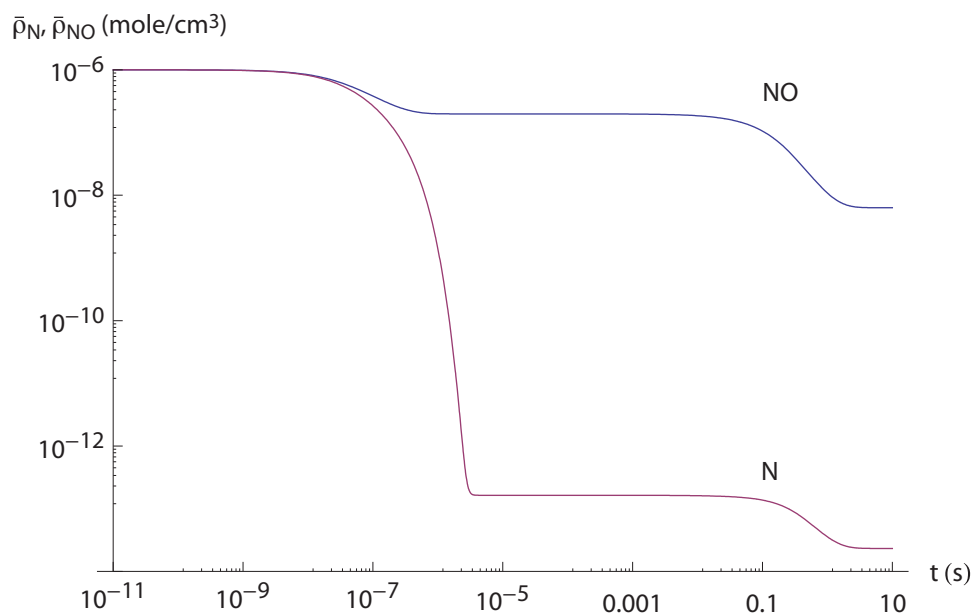
Figure 1.10: $\overline{\rho}_{NO}$ and $\overline{\rho}_{N}$ versus time for Zel'dovich mechanism at $T = 1500\ K$, $P = 6.23550 \times 10^5\ dyne/cm^2$.

of physical phenomena which evolve on a widely disparate set of time scales. Systems which evolve on a wide range of scales are known as stiff, recognizing a motivating example in mass-spring-damper systems with stiff springs. Here, we will examine the effect of temperature and pressure on time scales and stiffness. We shall also look simplistically how different numerical approximation methods respond to stiffness.

1.1.2.2.1 Effect of temperature Let us see how the same Zel'dovich mechanism behaves at lower temperature, $T = 1500\ K$; all other parameters, including the initial species concentrations are the same as the previous high temperature example. The pressure however, lowers, and here is $P = 6.23550 \times 10^5\ dyne/cm^2$, which is close to atmospheric pressure. For this case, a plot of species concentrations versus time is given in Figure 1.10.

At $T = 1500\ K$, we notice some dramatic differences relative to the earlier studied $T = 6000\ K$. First, we see the reaction commences in around the same time, $t \sim 10^{-8}\ s$. For $t \sim 10^{-6}\ s$, there is a temporary cessation of significant reaction. We notice a long plateau in which species concentrations do not change over several decades of time. This is actually a pseudo-equilibrium. Significant reaction recommences for $t \sim 0.1\ s$. Only around $t \sim 1\ s$ does the system approach final equilibrium. We can perform an eigenvalue analysis both at the initial state and at the equilibrium state to estimate the time scales of reaction. For this dynamical system which is two ordinary differential equations in two unknowns, we will always find two eigenvalues, and thus two time scales. Let us call them τ_1 and τ_2. Both these scales will evolve with t.

At the initial state, we find

$$\tau_1 = 2.37 \times 10^{-8} \ s, \tag{1.249}$$
$$\tau_2 = 4.25 \times 10^{-7} \ s. \tag{1.250}$$

The onset of significant reaction is consistent with the prediction given by τ_1 at the initial state. Moreover, initially, the reaction is not very stiff; the stiffness ratio is $\kappa = 17.9$.

At equilibrium, we find

$$\lim_{t \to \infty} \overline{\rho}_{NO} = 4.6 \times 10^{-9} \ \frac{mole}{cm^3}, \tag{1.251}$$
$$\lim_{t \to \infty} \overline{\rho}_N = 4.2 \times 10^{-14} \ \frac{mole}{cm^3}, \tag{1.252}$$

and

$$\tau_1 = 7.86 \times 10^{-7} \ s, \tag{1.253}$$
$$\tau_2 = 3.02 \times 10^{-1} \ s. \tag{1.254}$$

The slowest time scale near equilibrium is an excellent indicator of how long the system takes to relax to its final state. Note also that near equilibrium, the stiffness ratio is large, $\kappa = \tau_2/\tau_1 \sim 3.8 \times 10^5$. Because it is large, the scales in this problem are widely disparate, and accurate numerical solution becomes challenging.

In summary, we find the effect of lowering temperature while leaving initial concentrations constant:

- lowers the pressure somewhat, slightly slowing the collision time, and slightly slowing the fastest time scales, and

- slows the slowest time scales many orders of magnitude, stiffening the system significantly, since collisions may not induce reaction with their lower collision speed.

1.1.2.2.2   Effect of initial pressure   Let us maintain the initial temperature at $T = 1500 \ K$, but drop the initial concentration of each species to

$$\widehat{\overline{\rho}}_{NO} = \widehat{\overline{\rho}}_N = \widehat{\overline{\rho}}_{N_2} = \widehat{\overline{\rho}}_{O_2} = \widehat{\overline{\rho}}_O = 10^{-8} \ \frac{mole}{cm^3}. \tag{1.255}$$

With this decrease in number of moles, the pressure now is

$$P = 6.23550 \times 10^3 \ \frac{dyne}{cm^2}. \tag{1.256}$$

This pressure is two orders of magnitude lower than atmospheric. We solve for the species concentration profiles and show the results of numerical prediction in Figure 1.11. Relative to the high pressure $P = 6.2355 \times 10^5 \ dyne/cm^2$, $T = 1500 \ K$ case, we notice some similarities
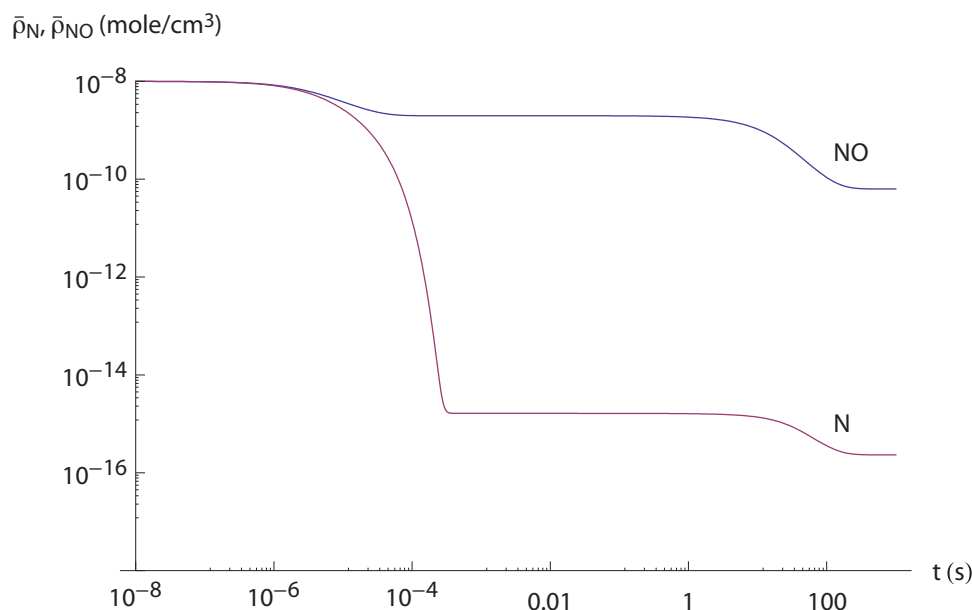
Figure 1.11: $\overline{\rho}_{NO}$ and $\overline{\rho}_N$ versus time for Zel'dovich mechanism at $T = 1500\ K$, $P = 6.2355 \times 10^3\ dyne/cm^2$.

and dramatic differences. The overall shape of the time-profiles of concentration variation is similar. But, we see the reaction commences at a much later time, $t \sim 10^{-6}\ s$. For $t \sim 10^{-4}\ s$, there is a temporary cessation of significant reaction. We notice a long plateau in which species concentrations do not change over several decades of time. This is again actually a pseudo-equilibrium. Significant reaction recommences for $t \sim 10\ s$. Only around $t \sim 100\ s$ does the system approach final equilibrium. We can perform an eigenvalue analysis both at the initial state and at the equilibrium state to estimate the time scales of reaction.

At the initial state, we find

$$\tau_1 = 2.37 \times 10^{-6}\ s, \tag{1.257}$$
$$\tau_2 = 4.25 \times 10^{-5}\ s. \tag{1.258}$$

The onset of significant reaction is consistent with the prediction given by τ_1 at the initial state. Moreover, initially, the reaction is not very stiff; the stiffness ratio is $\kappa = 17.9$. Interestingly, by decreasing the initial pressure by a factor of 10^2, we increased the initial time scales by a complementary factor of 10^2; moreover, we did not alter the stiffness.

At equilibrium, we find

$$\lim_{t \to \infty} \overline{\rho}_{NO} = 4.6 \times 10^{-11}\ \frac{mole}{cm^3}, \tag{1.259}$$
$$\lim_{t \to \infty} \overline{\rho}_N = 4.2 \times 10^{-16}\ \frac{mole}{cm^3}, \tag{1.260}$$
$$\tag{1.261}$$

and

$$\tau_1 \;=\; 7.86 \times 10^{-5} \; s, \tag{1.262}$$
$$\tau_2 \;=\; 3.02 \times 10^{1} \; s. \tag{1.263}$$

By decreasing the initial pressure by a factor of 10^2, we decreased the equilibrium concentrations by a factor of 10^2 and increased the time scales by a factor of 10^2, leaving the stiffness ratio unchanged.

In summary, we find the effect of lowering the initial concentrations significantly while leaving temperature constant

- lowers the pressure significantly, proportionally slowing the collision time, as well as the fastest and slowest time scales, and

- does not affect the stiffness of the system.

1.1.2.2.3 Stiffness and numerics The issue of how to simulate stiff systems of ordinary differential equations, such as presented by our Zel'dovich mechanism, is challenging. Here, a brief summary of some of the issues will be presented. The interested reader should consult the numerical literature for a full discussion. See for example the excellent text of Iserles.[17]

We have seen throughout this section that there are two time scales at work, and they are often disparate. The species evolution is generally characterized by an initial fast transient, followed by a long plateau, then a final relaxation to equilibrium. We noted from the phase plane of Fig. 1.9 that the final relaxation to equilibrium (shown along the green line labeled "SIM") is an attracting manifold for a wide variety of initial conditions. The relaxation onto the SIM is fast, and the motion on the SIM to equilibrium is relatively slow.

Use of common numerical techniques can often mask or obscure the actual dynamics. Numerical methods to solve systems of ordinary differential equations can be broadly categorized as *explicit* or *implicit*. We give a brief synopsis of each class of method. We cast each as a method to solve a system of the form

$$\frac{d\overline{\boldsymbol{\rho}}}{dt} = \mathbf{f}(\overline{\boldsymbol{\rho}}). \tag{1.264}$$

- *Explicit:* The simplest of these methods, the forward Euler method, discretizes Eq. (1.264) as follows:

$$\frac{\overline{\boldsymbol{\rho}}_{n+1} - \overline{\boldsymbol{\rho}}_n}{\Delta t} = \mathbf{f}(\overline{\boldsymbol{\rho}}_n), \tag{1.265}$$

so that

$$\overline{\boldsymbol{\rho}}_{n+1} = \overline{\boldsymbol{\rho}}_n + \Delta t \; \mathbf{f}(\overline{\boldsymbol{\rho}}_n). \tag{1.266}$$

Explicit methods are summarized as

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[17]A. Iserles, 2008, *A First Course in the Numerical Analysis of Differential Equations*, Cambridge University Press, Cambridge, UK.

- easy to program, since Eq. (1.266) can be solved explicitly to predict the new value $\overline{\boldsymbol{\rho}}_{n+1}$ in terms of the old values at step n.
- need to have $\Delta t < \tau_{fastest}$ in order to remain numerically stable,
- able to capture all physics and all time scales at great computational expense for stiff problems,
- requiring much computational effort for little payoff in the SIM region of the phase plane, and thus
- inefficient for some portions of stiff calculations.

- *Implicit:* The simplest of these methods, the backward Euler method, discretizes Eq. (1.264) as follows:

$$\frac{\overline{\boldsymbol{\rho}}_{n+1} - \overline{\boldsymbol{\rho}}_n}{\Delta t} = \mathbf{f}(\overline{\boldsymbol{\rho}}_{n+1}), \qquad (1.267)$$

so that

$$\overline{\boldsymbol{\rho}}_{n+1} = \overline{\boldsymbol{\rho}}_n + \Delta t \, \mathbf{f}(\overline{\boldsymbol{\rho}}_{n+1}). \qquad (1.268)$$

Implicit methods are summarized as

- more difficult to program since a non-linear set of algebraic equations, Eq. (1.268), must be solved at every time step with no guarantee of solution,
- requiring potentially significant computational time to advance each time step,
- capable of using very large time steps and remaining numerically stable,
- suspect to missing physics that occur on small time scales $\tau < \Delta t$, and
- for many purposes, especially when fine transients are unimportant, better performers than explicit methods,
- potentially dangerous when fine transients are necessary to capture high frequency physical instabilities.

A wide variety of software tools exist to solve systems of ordinary differential equations. Most of them use more sophisticated techniques than simple forward and backward Euler methods. One of the most powerful techniques is the use of *error control*. Here, the user specifies how far in time to advance and the error that is able to be tolerated. The algorithm, which is complicated, selects then internal time steps, for either explicit or implicit methods, to achieve a solution within the error tolerance at the specified output time. A well known public domain algorithm with error control is provided by `lsode.f`, which can be found in the `netlib` repository.[18]

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[18]Hindmarsh, A. C., 1983, "`ODEPACK`, a Systematized Collection of ODE Solvers," *Scientific Computing*, edited by R. S. Stepleman, et al., North-Holland, Amsterdam, pp. 55-64. `http://www.netlib.org/alliant/ode/prog/lsode.f`.

Δt (s)	Explicit $N_{internal}$	Explicit Δt_{eff} (s)	Implicit $N_{internal}$	Implicit Δt_{eff} (s)
10^2	10^6	10^{-4}	10^0	10^2
10^1	10^5	10^{-4}	10^0	10^1
10^0	10^4	10^{-4}	10^0	10^0
10^{-1}	10^3	10^{-4}	10^0	10^{-1}
10^{-2}	10^2	10^{-4}	10^0	10^{-2}
10^{-3}	10^1	10^{-4}	10^0	10^{-3}
10^{-4}	10^0	10^{-4}	10^0	10^{-4}
10^{-5}	10^0	10^{-5}	10^0	10^{-5}
10^{-6}	10^0	10^{-6}	10^0	10^{-6}

Table 1.3: Results from computing Zel'dovich NO production using implicit and explicit methods with error control in `dlsode.f`.

Let us exercise the Zel'dovich mechanism under the conditions simulated in Fig. 1.11, $T = 1500$ K, $P = 6.2355 \times 10^3$ $dyne/cm^2$. Recall in this case the fastest time scale near equilibrium is $\tau_1 = 7.86 \times 10^{-5}$ $s \sim 10^{-4}$ s at the initial state, and the slowest time scale is $\tau = 3.02 \times 10^1$ s at the final state. Let us solve for these conditions using `dlsode.f`, which uses internal time stepping for error control, in both an explicit and implicit mode. We specify a variety of values of Δt and report typical values of number of internal time steps selected by `dlsode.f`, and the corresponding effective time step Δt_{eff} used for the problem, for both explicit and implicit methods, as reported in Table 1.3.

Obviously if output is requested using $\Delta t > 10^{-4}$ s, the early time dynamics near $t \sim 10^{-4}$ s will be missed. For physically stable systems, codes such as `dlsode.f` will still provide a correct solution at the later times. For physically unstable systems, such as might occur in turbulent flames, it is not clear that one can use large time steps and expect to have fidelity to the underlying equations. The reason is the physical instabilities may evolve on the same time scale as the fine scales which are overlooked by large Δt.

1.2 Adiabatic, isochoric kinetics

It is more practical to allow for temperature variation within a combustor. The best model for this is adiabatic kinetics. Here, we will restrict our attention to isochoric problems.

1.2.1 Thermal explosion theory

There is a simple description known as *thermal explosion theory* which provides a good explanation for how initially slow exothermic reaction induces a sudden temperature rise accompanied by a final relaxation to equilibrium.

Let us consider a simple isomerization reaction in a closed volume

$$A \rightleftharpoons B. \tag{1.269}$$

An isomerization reaction is one in which the molecular structure may rearrange, but the elemental composition, and thus the molecular mass, of the molecule does not change. Let us take A and B to both be calorically perfect ideal gases with identical molecular masses $M_A = M_B = M$ and identical specific heats, $\overline{c}_{vA} = \overline{c}_{vB} = c_v$; $\overline{c}_{PA} = \overline{c}_{PB} = \overline{c}_P$. We can consider A and B to be isomers of an identical molecular species. So, we have $N = 2$ species reacting in $J = 1$ reactions. The number of elements L here is irrelevant.

1.2.1.1 One-step reversible kinetics

Let us insist our reaction process be isochoric and adiabatic, and commence with only A present. The reaction kinetics with $\beta = 0$ are

$$\frac{d\overline{\rho}_A}{dt} = \underbrace{\underbrace{- a \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right)}_{=k} \left(\overline{\rho}_A - \frac{1}{K_c}\overline{\rho}_B\right)}_{=r}, \tag{1.270}$$

$$\frac{d\overline{\rho}_B}{dt} = \underbrace{\underbrace{a \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right)}_{=k} \left(\overline{\rho}_A - \frac{1}{K_c}\overline{\rho}_B\right)}_{=r}, \tag{1.271}$$

$$\overline{\rho}_A(0) = \widehat{\overline{\rho}}_A, \tag{1.272}$$

$$\overline{\rho}_B(0) = 0. \tag{1.273}$$

For our alternate compact linear algebra based form, we note that

$$r = a \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right)\left(\overline{\rho}_A - \frac{1}{K_c}\overline{\rho}_B\right), \tag{1.274}$$

and that

$$\frac{d}{dt}\begin{pmatrix}\overline{\rho}_A \\ \overline{\rho}_B\end{pmatrix} = \begin{pmatrix}-1 \\ 1\end{pmatrix}(r). \tag{1.275}$$

Forming the appropriate linear combinations by replacing the second equation with the sum of the two equations yields

$$\frac{d}{dt}\begin{pmatrix}\overline{\rho}_A \\ \overline{\rho}_A + \overline{\rho}_B\end{pmatrix} = \begin{pmatrix}-1 \\ 0\end{pmatrix}(r). \tag{1.276}$$

Expanded, this is

$$\begin{pmatrix}1 & 0 \\ 1 & 1\end{pmatrix}\frac{d}{dt}\begin{pmatrix}\overline{\rho}_A \\ \overline{\rho}_B\end{pmatrix} = \begin{pmatrix}-1 \\ 0\end{pmatrix}(r). \tag{1.277}$$

Integrating the second of Eq. (1.276) yields

$$\frac{d}{dt}(\overline{\rho}_A + \overline{\rho}_B) = 0, \tag{1.278}$$

$$\overline{\rho}_A + \overline{\rho}_B = \widehat{\overline{\rho}}_A, \tag{1.279}$$

$$\overline{\rho}_B = \widehat{\overline{\rho}}_A - \overline{\rho}_A. \tag{1.280}$$

Thus, Eq. (1.270) reduces to

$$\frac{d\overline{\rho}_A}{dt} = -a \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right)\left(\overline{\rho}_A - \frac{1}{K_c}\left(\widehat{\overline{\rho}}_A - \overline{\rho}_A\right)\right). \tag{1.281}$$

Scaling, Eq. (1.281) can be rewritten as

$$\frac{d}{d(at)}\left(\frac{\overline{\rho}_A}{\widehat{\overline{\rho}}_A}\right) = -\exp\left(-\frac{\overline{\mathcal{E}}}{\overline{R}T_o}\frac{1}{T/T_o}\right)\left(\frac{\overline{\rho}_A}{\widehat{\overline{\rho}}_A} - \frac{1}{K_c}\left(1 - \frac{\overline{\rho}_A}{\widehat{\overline{\rho}}_A}\right)\right). \tag{1.282}$$

1.2.1.2   First law of thermodynamics

Recall the first law of thermodynamics, and neglecting potential and kinetic energy changes:

$$\frac{dE}{dt} = \dot{Q} - \dot{W}. \tag{1.283}$$

Here, E is the total internal energy. Because we insist the problem is adiabatic $\dot{Q} = 0$. Because we insist the problem is isochoric, there is no work done, so $\dot{W} = 0$. Thus, we have

$$\frac{dE}{dt} = 0. \tag{1.284}$$

Thus, we find

$$E = E_o. \tag{1.285}$$

Recall the total internal energy for a mixture of two calorically perfect ideal gases is

$$E = n_A \overline{e}_A + n_B \overline{e}_B, \tag{1.286}$$

$$= V\left(\frac{n_A}{V}\overline{e}_A + \frac{n_B}{V}\overline{e}_B\right), \tag{1.287}$$

$$= V\left(\overline{\rho}_A \overline{e}_A + \overline{\rho}_B \overline{e}_B\right), \tag{1.288}$$

$$= V\left(\overline{\rho}_A\left(\overline{h}_A - \frac{P_A}{\overline{\rho}_A}\right) + \overline{\rho}_B\left(\overline{h}_B - \frac{P_B}{\overline{\rho}_B}\right)\right), \tag{1.289}$$

$$= V\left(\overline{\rho}_A\left(\overline{h}_A - \overline{R}T\right) + \overline{\rho}_B\left(\overline{h}_B - \overline{R}T\right)\right), \tag{1.290}$$

$$= V\left(\overline{\rho}_A\left(\overline{c}_P(T - T_o) + \overline{h}_{T_o,A}^o - \overline{R}T\right) + \overline{\rho}_B\left(\overline{c}_P(T - T_o) + \overline{h}_{T_o,B}^o - \overline{R}T\right)\right), \tag{1.291}$$

$$= V\left((\overline{\rho}_A + \overline{\rho}_B)(\overline{c}_P(T - T_o) - \overline{R}T) + \overline{\rho}_A\overline{h}^o_{T_o,A} + \overline{\rho}_B\overline{h}^o_{T_o,B}\right), \tag{1.292}$$

$$= V\left((\overline{\rho}_A + \overline{\rho}_B)((\overline{c}_P - \overline{R})T - \overline{c}_P T_o) + \overline{\rho}_A\overline{h}^o_{T_o,A} + \overline{\rho}_B\overline{h}^o_{T_o,B}\right), \tag{1.293}$$

$$= V\left((\overline{\rho}_A + \overline{\rho}_B)((\overline{c}_P - \overline{R})T - (\overline{c}_P - \overline{R} + \overline{R})T_o) + \overline{\rho}_A\overline{h}^o_{T_o,A} + \overline{\rho}_B\overline{h}^o_{T_o,B}\right), \tag{1.294}$$

$$= V\left((\overline{\rho}_A + \overline{\rho}_B)(\overline{c}_v T - (\overline{c}_v + \overline{R})T_o) + \overline{\rho}_A\overline{h}^o_{T_o,A} + \overline{\rho}_B\overline{h}^o_{T_o,B}\right), \tag{1.295}$$

$$= V\left((\overline{\rho}_A + \overline{\rho}_B)\overline{c}_v(T - T_o) + \overline{\rho}_A(\overline{h}^o_{T_o,A} - \overline{R}T_o) + \overline{\rho}_B(\overline{h}^o_{T_o,B} - \overline{R}T_o)\right), \tag{1.296}$$

$$= V\left((\overline{\rho}_A + \overline{\rho}_B)\overline{c}_v(T - T_o) + \overline{\rho}_A\overline{e}^o_{T_o,A} + \overline{\rho}_B\overline{e}^o_{T_o,B}\right). \tag{1.297}$$

Now, at the initial state we have $T = T_o$, so

$$E_o = V\left(\widehat{\overline{\rho}}_A\overline{e}^o_{T_o,A} + \widehat{\overline{\rho}}_B\overline{e}^o_{T_o,B}\right). \tag{1.298}$$

So, we can say our caloric equation of state is

$$E - E_o = V\left((\overline{\rho}_A + \overline{\rho}_B)\overline{c}_v(T - T_o) + (\overline{\rho}_A - \widehat{\overline{\rho}}_A)\overline{e}^o_{T_o,A} + (\overline{\rho}_B - \widehat{\overline{\rho}}_B)\overline{e}^o_{T_o,B}\right), \tag{1.299}$$

$$= V\left((\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B)\overline{c}_v(T - T_o) + (\overline{\rho}_A - \widehat{\overline{\rho}}_A)\overline{e}^o_{T_o,A} + (\overline{\rho}_B - \widehat{\overline{\rho}}_B)\overline{e}^o_{T_o,B}\right). \tag{1.300}$$

As an aside, on a molar basis, we scale Eq. (1.300) to get

$$\overline{e} - \overline{e}_o = \overline{c}_v(T - T_o) + (y_A - y_{Ao})\overline{e}^o_{T_o,A} + (y_B - y_{Bo})\overline{e}^o_{T_o,B}. \tag{1.301}$$

And because we have assumed the molecular masses are the same, $M_A = M_B$, the mole fractions are the mass fractions, and we can write on a mass basis

$$e - e_o = c_v(T - T_o) + (Y_A - Y_{Ao})e^o_{T_o,A} + (Y_B - Y_{Bo})e^o_{T_o,B}. \tag{1.302}$$

Returning to Eq. (1.300), our energy conservation relation, Eq. (1.285), becomes

$$0 = V\left((\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B)\overline{c}_v(T - T_o) + (\overline{\rho}_A - \widehat{\overline{\rho}}_A)\overline{e}^o_{T_o,A} + (\overline{\rho}_B - \widehat{\overline{\rho}}_B)\overline{e}^o_{T_o,B}\right). \tag{1.303}$$

Now, we solve for T

$$0 = (\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B)\overline{c}_v(T - T_o) + (\overline{\rho}_A - \widehat{\overline{\rho}}_A)\overline{e}^o_{T_o,A} + (\overline{\rho}_B - \widehat{\overline{\rho}}_B)\overline{e}^o_{T_o,B}, \tag{1.304}$$

$$0 = \overline{c}_v(T - T_o) + \frac{\overline{\rho}_A - \widehat{\overline{\rho}}_A}{\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B}\overline{e}^o_{T_o,A} + \frac{\overline{\rho}_B - \widehat{\overline{\rho}}_B}{\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B}\overline{e}^o_{T_o,B}, \tag{1.305}$$

$$T = T_o + \frac{\widehat{\overline{\rho}}_A - \overline{\rho}_A}{\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B}\frac{\overline{e}^o_{T_o,A}}{\overline{c}_v} + \frac{\widehat{\overline{\rho}}_B - \overline{\rho}_B}{\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B}\frac{\overline{e}^o_{T_o,B}}{\overline{c}_v}. \tag{1.306}$$

Now, we impose our assumption that $\widehat{\overline{\rho}}_B = 0$, giving also $\overline{\rho}_B = \widehat{\overline{\rho}}_A - \overline{\rho}_A$,

$$T = T_o + \frac{\widehat{\overline{\rho}}_A - \overline{\rho}_A}{\widehat{\overline{\rho}}_A}\frac{\overline{e}^o_{T_o,A}}{\overline{c}_v} - \frac{\overline{\rho}_B}{\widehat{\overline{\rho}}_A}\frac{\overline{e}^o_{T_o,B}}{\overline{c}_v}, \tag{1.307}$$

$$= T_o + \frac{\widehat{\overline{\rho}}_A - \overline{\rho}_A}{\widehat{\overline{\rho}}_A}\frac{\overline{e}^o_{T_o,A} - \overline{e}^o_{T_o,B}}{\overline{c}_v}. \tag{1.308}$$

In summary, realizing that $\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B} = \overline{e}^o_{T_o,A} - \overline{e}^o_{T_o,B}$ we can write T as a function of $\overline{\rho}_A$:

$$T \;=\; T_o + \frac{(\widehat{\overline{\rho}}_A - \overline{\rho}_A)}{\widehat{\overline{\rho}}_A \overline{c}_v}(\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B}). \tag{1.309}$$

We see then that if $\overline{h}^o_{T_o,A} > \widehat{\overline{h}}^o_{T_o,B}$, that as $\overline{\rho}_A$ decreases from its initial value of $\widehat{\overline{\rho}}_A$ that T will increase. We can scale Eq. (1.309) to form

$$\left(\frac{T}{T_o}\right) = 1 + \left(1 - \frac{\overline{\rho}_A}{\widehat{\overline{\rho}}_A}\right)\left(\frac{\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B}}{\overline{c}_v T_o}\right). \tag{1.310}$$

We also note that our caloric state equation, Eq. (1.301) can, for $y_{Ao} = 1$, $y_{Bo} = 0$, be rewritten as

$$\overline{e} - \overline{e}_o \;=\; \overline{c}_v(T - T_o) + (y_A - 1)\overline{e}^o_{T_o,A} + y_B\overline{e}^o_{T_o,B}, \tag{1.311}$$

$$=\; \overline{c}_v(T - T_o) + ((1 - y_B) - 1)\overline{e}^o_{T_o,A} + y_B\overline{e}^o_{T_o,B}, \tag{1.312}$$

$$=\; \overline{c}_v(T - T_o) - y_B(\overline{e}^o_{T_o,A} - \overline{e}^o_{T_o,B}). \tag{1.313}$$

Similarly, on a mass basis, we can say,

$$e - e_o \;=\; c_v(T - T_o) - Y_B(e^o_{T_o,A} - e^o_{T_o,B}). \tag{1.314}$$

For this problem, we also have

$$K_c = \exp\left(\frac{-\Delta G^o}{\overline{R}T}\right), \tag{1.315}$$

with

$$\Delta G^o \;=\; \overline{g}^o_B - \overline{g}^o_A, \tag{1.316}$$

$$=\; \overline{h}^o_B - T\overline{s}^o_B - (\overline{h}^o_A - T\overline{s}^o_A), \tag{1.317}$$

$$=\; (\overline{h}^o_B - \overline{h}^o_A) - T(\overline{s}^o_B - \overline{s}^o_A), \tag{1.318}$$

$$=\; (\overline{h}^o_{T_o,B} - \overline{h}^o_{T_o,A}) - T(\overline{s}^o_{T_o,B} - \overline{s}^o_{T_o,A}). \tag{1.319}$$

So

$$K_c \;=\; \exp\left(\frac{\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B} - T(\overline{s}^o_{T_o,A} - \overline{s}^o_{T_o,B})}{\overline{R}T}\right), \tag{1.320}$$

$$=\; \exp\left(\frac{\overline{c}_v T_o}{\overline{R}T}\left(\frac{\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B} - T(\overline{s}^o_{T_o,A} - \overline{s}^o_{T_o,B})}{\overline{c}_v T_o}\right)\right), \tag{1.321}$$

$$=\; \exp\left(\frac{1}{\gamma - 1}\frac{1}{\frac{T}{T_o}}\left(\frac{\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B}}{\overline{c}_v T_o} - \frac{T}{T_o}\frac{(\overline{s}^o_{T_o,A} - \overline{s}^o_{T_o,B})}{\overline{c}_v}\right)\right). \tag{1.322}$$

Here, we have used the definition of the ratio of specific heats, $\gamma = \overline{c}_P/\overline{c}_v$ along with $\overline{R} = \overline{c}_P - \overline{c}_v$. So, we can solve Eq. (1.281) by first using Eq. (1.322) to eliminate K_c and then Eq. (1.309) to eliminate T.

1.2.1.3 Dimensionless form

Let us try writing dimensionless variables so that our system can be written in a compact dimensionless form. First, let us take dimensionless time τ to be

$$\tau = at. \tag{1.323}$$

Let us take dimensionless species concentration to be z with

$$z = \frac{\overline{\rho}_A}{\widehat{\overline{\rho}}_A}. \tag{1.324}$$

Let us take dimensionless temperature to be θ with

$$\theta = \frac{T}{T_o}. \tag{1.325}$$

Let us take dimensionless heat release to be q with

$$q = \frac{\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B}}{\overline{c}_v T_o}. \tag{1.326}$$

Let us take dimensionless activation energy to be Θ with

$$\Theta = \frac{\overline{\mathcal{E}}}{\overline{R} T_o}. \tag{1.327}$$

And let us take the dimensionless entropy change to be σ with

$$\sigma = \frac{(\overline{s}^o_{T_o,A} - \overline{s}^o_{T_o,B})}{\overline{c}_v}. \tag{1.328}$$

So, our equations become

$$\frac{dz}{d\tau} = -\exp\left(-\frac{\Theta}{\theta}\right)\left(z - \frac{1}{K_c}(1-z)\right), \tag{1.329}$$

$$\theta = 1 + (1-z)q, \tag{1.330}$$

$$K_c = \exp\left(\frac{1}{\gamma - 1}\frac{1}{\theta}(q - \theta\sigma)\right). \tag{1.331}$$

It is more common to consider the products. Let us define for general problems

$$\lambda = \frac{\overline{\rho}_B}{\overline{\rho}_A + \overline{\rho}_B} = \frac{\overline{\rho}_B}{\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B}. \tag{1.332}$$

Thus, λ is the mass fraction of product. For our problem, $\widehat{\overline{\rho}}_B = 0$ so

$$\lambda = \frac{\overline{\rho}_B}{\widehat{\overline{\rho}}_A} = \frac{\widehat{\overline{\rho}}_A - \overline{\rho}_A}{\widehat{\overline{\rho}}_A}. \tag{1.333}$$

Thus,

$$\lambda = 1 - z. \tag{1.334}$$

We can think of λ as a reaction progress variable as well. When $\lambda = 0$, we have $\tau = 0$, and the reaction has not begun. Thus, we get

$$\frac{d\lambda}{d\tau} = \exp\left(-\frac{\Theta}{\theta}\right)\left((1-\lambda) - \frac{1}{K_c}\lambda\right), \tag{1.335}$$

$$\theta = 1 + q\lambda, \tag{1.336}$$

$$K_c = \exp\left(\frac{1}{\gamma-1}\frac{1}{\theta}(q - \theta\sigma)\right). \tag{1.337}$$

1.2.1.4   Example calculation

Let us choose some values for the dimensionless parameters:

$$\Theta = 20, \quad \sigma = 0, \quad q = 10, \quad \gamma = \frac{7}{5}. \tag{1.338}$$

With these choices, our kinetics equations, Eqs. (1.335-1.337), reduce to

$$\frac{d\lambda}{d\tau} = \exp\left(\frac{-20}{1+10\lambda}\right)\left((1-\lambda) - \lambda\exp\left(\frac{-25}{1+10\lambda}\right)\right), \qquad \lambda(0) = 0. \tag{1.339}$$

The right side of Eq. (1.339) is at equilibrium for values of λ which drive it to zero. Numerical root finding methods show this to occur at $\lambda \sim 0.920539$. Near this root, Taylor series expansion shows the dynamics are approximated by

$$\frac{d}{d\tau}(\lambda - 0.920539) = -0.17993(\lambda - 0.920539) + \ldots \tag{1.340}$$

Thus, the local behavior near equilibrium is given by

$$\lambda = 0.920539 + C\exp\left(-0.17993\,\tau\right). \tag{1.341}$$

Here, C is some arbitrary constant. Clearly the equilibrium is stable, with a time constant of $1/0.17993 = 5.55773$.

   Numerical solution shows the full behavior of the dimensionless species concentration $\lambda(\tau)$; see Figure 1.12. Clearly the product concentration λ is small for some long period of time. At a critical time near $\tau = 2.7 \times 10^6$, there is a so-called thermal explosion with a rapid increase in λ. *Note that the estimate of the time constant near equilibrium is orders of magnitude less than the explosion time, $5.55773 \ll 2.7 \times 10^6$. Thus, linear analysis here is a poor tool to estimate an important physical quantity, the ignition time.* Once the ignition period is over, there is a rapid equilibration to the final state. The dimensionless temperature plot is shown in Figure 1.13. The temperature plot is similar in behavior to
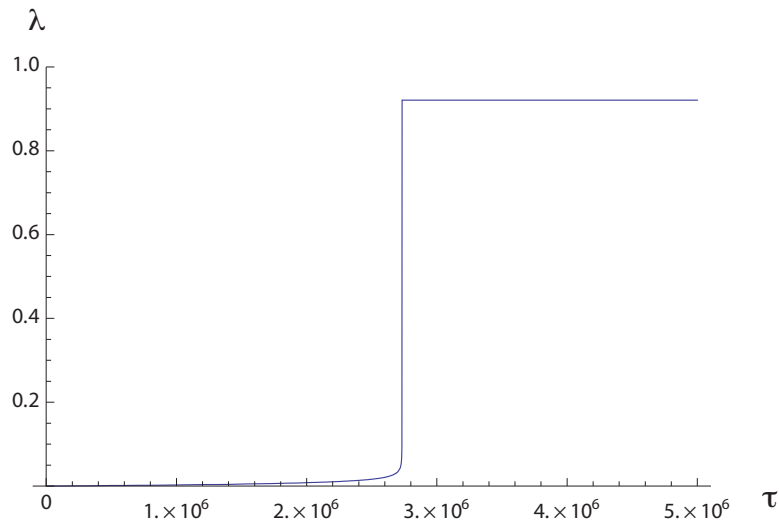
Figure 1.12: Dimensionless plot of reaction product concentration λ versus time τ for adiabatic isochoric combustion with simple reversible kinetics.
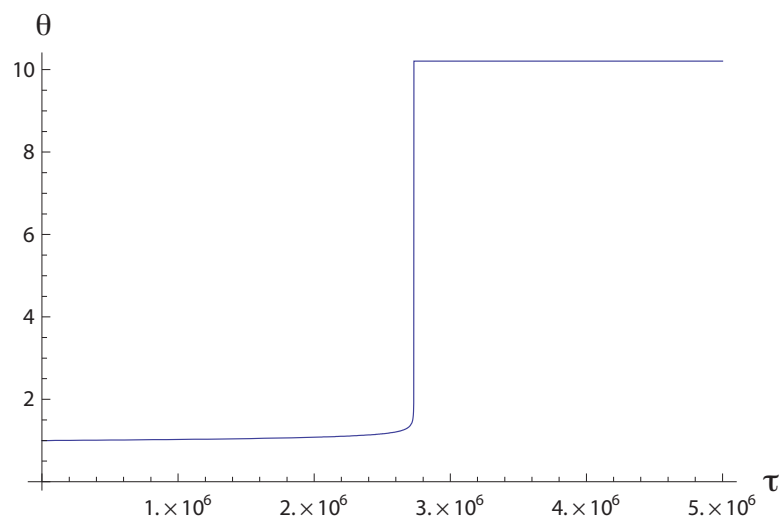
Figure 1.13: Dimensionless plot of temperature θ versus time τ for adiabatic, isochoric combustion with simple reversible kinetics.

the species concentration plot. At early time, the temperature is cool. At a critical time, the thermal explosion time, the temperature rapidly rises. This rapid rise, coupled with the exponential sensitivity of reaction rate to temperature, accelerates the formation of product. This process continues until the reverse reaction is activated to the extent it prevents further creation of product.

1.2.1.5   High activation energy asymptotics

Let us see if we can get an *analytic* prediction of the thermal explosion time, $\tau \sim 2.7 \times 10^6$. Such a prediction would be valuable to see how long a slowing reacting material might take to ignite. Our analysis is similar to that given by Buckmaster and Ludford in their Chapter 1.[19]

For convenience let us restrict ourselves to $\sigma = 0$. In this limit, Eqs. (1.335-1.337) reduce to

$$\frac{d\lambda}{d\tau} \;=\; \exp\left(-\frac{\Theta}{1+q\lambda}\right)\left((1-\lambda) - \lambda\exp\left(\frac{-q}{(\gamma-1)(1+q\lambda)}\right)\right), \qquad (1.342)$$

with $\lambda(0) = 0$. The key trouble in getting an analytic solution to Eq. (1.342) is the presence of λ in the denominator of an exponential term. We need to find a way to move it to the numerator. Asymptotic methods provide one such way.

Now, we recall for early time $\lambda \ll 1$. Let us assume λ takes the form

$$\lambda = \epsilon\lambda_1 + \epsilon^2\lambda_2 + \epsilon^3\lambda_3 + \dots \qquad (1.343)$$

Here, we will assume $0 < \epsilon \ll 1$ and that $\lambda_1(\tau) \sim \mathcal{O}(1)$, $\lambda_2(\tau) \sim \mathcal{O}(1)$, ..., and will define ϵ in terms of physical parameters shortly. Now, with this assumption we have

$$\frac{1}{1+q\lambda} = \frac{1}{1 + \epsilon q\lambda_1 + \epsilon^2 q\lambda_2 + \epsilon^3 q\lambda_3 + \dots}. \qquad (1.344)$$

Long division of the term on the right side yields the approximation

$$\frac{1}{1+q\lambda} = \;=\; 1 - \epsilon q\lambda_1 + \epsilon^2(q^2\lambda_1^2 - q\lambda_2) + \dots, \qquad (1.345)$$

$$=\; 1 - \epsilon q\lambda_1 + \mathcal{O}(\epsilon^2). \qquad (1.346)$$

So,

$$\exp\left(-\frac{\Theta}{1+q\lambda}\right) \sim \exp\left(-\Theta(1 - \epsilon q\lambda_1 + \mathcal{O}(\epsilon^2))\right), \qquad (1.347)$$

$$\sim \exp(-\Theta)\exp\left(\epsilon q\Theta\lambda_1 + \mathcal{O}(\epsilon^2)\right). \qquad (1.348)$$

We have moved λ from the denominator to the numerator of the most important exponential term.

---

[19] J. D. Buckmaster and G. S. S. Ludford, 1983, *Lectures on Mathematical Combustion*, SIAM, Philadelphia.

Now, let us take the *limit of high activation energy* by defining ϵ to be

$$\epsilon \equiv \frac{1}{\Theta}. \tag{1.349}$$

Let us let the assume the remaining parameters, q and γ are both $\mathcal{O}(1)$ constants. When Θ is large, ϵ will be small. With this definition, Eq. (1.348) becomes

$$\exp\left(-\frac{\Theta}{1+q\lambda}\right) \sim \exp\left(-\frac{1}{\epsilon}\right) \exp\left(q\lambda_1 + \mathcal{O}(\epsilon^2)\right). \tag{1.350}$$

With these assumptions and approximations, Eq. (1.342) can be written as

$$
\begin{aligned}
\frac{d}{d\tau}(\epsilon\lambda_1 + \ldots) &= \exp\left(-\frac{1}{\epsilon}\right)\exp\left(q\lambda_1 + \mathcal{O}(\epsilon^2)\right) \\
&\times \left((1 - \epsilon\lambda_1 - \ldots) - (\epsilon\lambda_1 + \ldots)\exp\left(\frac{-q}{(\gamma-1)(1+q\epsilon\lambda_1 + \ldots)}\right)\right).
\end{aligned} \tag{1.351}
$$

Now, let us rescale time via

$$\tau_* = \frac{1}{\epsilon}\exp\left(\frac{-1}{\epsilon}\right)\tau. \tag{1.352}$$

With this transformation, the chain rule shows how derivatives transform:

$$\frac{d}{d\tau} = \frac{d\tau_*}{d\tau}\frac{d}{d\tau_*} = \frac{1}{\epsilon\exp\left(\frac{1}{\epsilon}\right)}\frac{d}{d\tau_*}. \tag{1.353}$$

With this transformation, Eq. (1.351) becomes

$$
\begin{aligned}
\frac{1}{\epsilon\exp\left(\frac{1}{\epsilon}\right)}\frac{d}{d\tau_*}(\epsilon\lambda_1 + \ldots) &= \exp\left(-\frac{1}{\epsilon}\right)\exp\left(q\lambda_1 + \mathcal{O}(\epsilon^2)\right) \\
&\times \left((1 - \epsilon\lambda_1 - \ldots) - (\epsilon\lambda_1 + \ldots)\exp\left(\frac{-q}{(\gamma-1)(1+q\epsilon\lambda_1 + \ldots)}\right)\right).
\end{aligned} \tag{1.354}
$$

This simplifies to

$$
\begin{aligned}
\frac{d}{d\tau_*}(\lambda_1 + \ldots) &= \exp\left(q\lambda_1 + \mathcal{O}(\epsilon^2)\right) \\
&\times \left((1 - \epsilon\lambda_1 - \ldots) - (\epsilon\lambda_1 + \ldots)\exp\left(\frac{-q}{(\gamma-1)(1+q\epsilon\lambda_1 + \ldots)}\right)\right).
\end{aligned} \tag{1.355}
$$

Retaining only $\mathcal{O}(1)$ terms in Eq. (1.355), we get

$$\frac{d\lambda_1}{d\tau_*} = \exp(q\lambda_1). \tag{1.356}$$

This is supplemented by the initial condition $\lambda_1(0) = 0$. Separating variables and solving, we get

$$\exp(-q\lambda_1)d\lambda_1 = d\tau_*, \tag{1.357}$$

$$-\frac{1}{q}\exp(-q\lambda_1) = \tau_* + C. \tag{1.358}$$

Applying the initial condition gives

$$-\frac{1}{q}\exp(-q(0)) = C, \tag{1.359}$$

$$-\frac{1}{q} = C. \tag{1.360}$$

So

$$-\frac{1}{q}\exp(-q\lambda_1) = \tau_* - \frac{1}{q}, \tag{1.361}$$

$$\exp(-q\lambda_1) = -q\tau_* + 1, \tag{1.362}$$

$$\exp(-q\lambda_1) = -q\left(\tau_* - \frac{1}{q}\right), \tag{1.363}$$

$$-q\lambda_1 = \ln\left(-q\left(\tau_* - \frac{1}{q}\right)\right), \tag{1.364}$$

$$\lambda_1 = -\frac{1}{q}\ln\left(-q\left(\tau_* - \frac{1}{q}\right)\right). \tag{1.365}$$

For $q = 10$, a plot of $\lambda_1(\tau_*)$ is shown in Fig. 1.14. We note at a finite τ_* that λ_1 begins to exhibit unbounded growth. In fact, it is obvious from Eq. (1.356) that as

$$\tau_* \to \frac{1}{q},$$

that

$$\lambda_1 \to \infty.$$

That is, there exists a finite time for which λ_1 violates the assumptions of our asymptotic theory which assumes $\lambda_1 = \mathcal{O}(1)$. We associate this time with the ignition time, τ_{*i}:
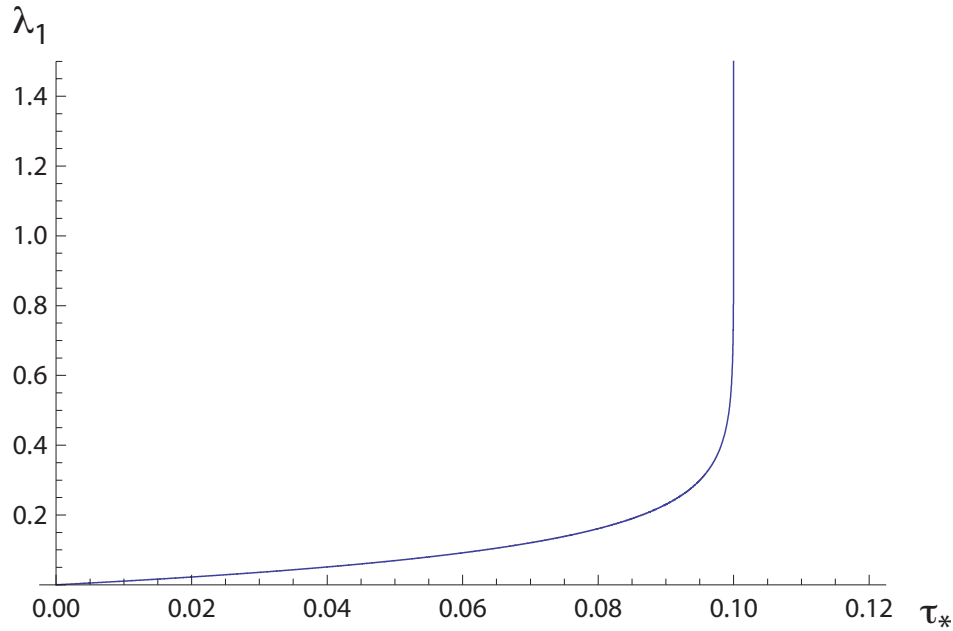
$$\tau_{*i} = \frac{1}{q}. \tag{1.366}$$

Figure 1.14: λ_1 versus τ_* for ignition problem.

Let us return this to more primitive variables:

$$\frac{1}{\epsilon} \exp\left(\frac{-1}{\epsilon}\right) \tau_i = \frac{1}{q}, \tag{1.367}$$

$$\tau_i = \frac{\epsilon \exp\left(\frac{1}{\epsilon}\right)}{q}, \tag{1.368}$$

$$\tau_i = \frac{\exp\Theta}{\Theta q}. \tag{1.369}$$

For our system with $\Theta = 20$ and $q = 10$, we estimate the dimensionless ignition time as

$$\tau_i = \frac{\exp 20}{(20)(10)} = 2.42583 \times 10^6. \tag{1.370}$$

This is a surprisingly good estimate, given the complexity of the problem. Recall the numerical solution showed ignition for $\tau \sim 2.7 \times 10^6$.

In terms of dimensional time, ignition time prediction becomes

$$t_i = \frac{\exp\Theta}{a\Theta q}, \tag{1.371}$$

$$= \frac{1}{a}\left(\frac{\overline{R}T_o}{\overline{\mathcal{E}}}\right)\left(\frac{\overline{c}_v T_o}{\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B}}\right) \exp\left(\frac{\overline{\mathcal{E}}}{\overline{R}T_o}\right). \tag{1.372}$$

Note the ignition is suppressed if the ignition time is lengthened, which happens when

- the activation energy $\overline{\mathcal{E}}$ is increased, since the exponential sensitivity is stronger than the algebraic sensitivity,

- the energy of combustion $(\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B})$ is decreased because it takes longer to react to drive the temperature to a critical value to induce ignition,

- the collision frequency factor a is decreased, which suppresses reaction.

1.2.2   Detailed $H_2 - O_2 - N_2$ kinetics

Here is an example which uses multiple reactions for an adiabatic isothermal system is given. Consider the full time-dependency of a problem similar to the thermal explosion problem just considered. We choose a non-intuitive set of parameters for the problem. Our choices will enable a direct comparison to a detonation of the same mixture via the same reaction mechanism in a later chapter; see Sec. 10.2.8.

A closed, fixed, adiabatic volume, $V = 0.3061251 \; cm^3$, contains at $t = 0 \; s$ a stoichiometric hydrogen-air mixture of $2 \times 10^{-5} \; mole$ of H_2, $1 \times 10^{-5} \; mole$ of O_2, and $3.76 \times 10^{-5} \; mole$ of N_2 at $P_o = 2.83230 \times 10^6 \; Pa$ and $T_o = 1542.7 \; K$.[20] Thus, the initial molar concentrations are

$$\overline{\rho}_{H_2} = 6.533 \times 10^{-5} \; mole/cm^3,$$

$$\overline{\rho}_{O_2} = 3.267 \times 10^{-5} \; mole/cm^3,$$

$$\overline{\rho}_{H_2} = 1.228 \times 10^{-4} \; mole/cm^3.$$

The initial mass fractions are calculated via $Y_i = M_i \overline{\rho}_i / \rho$. They are

$$Y_{H_2} = 0.0285,$$

$$Y_{O_2} = 0.226,$$

$$Y_{N_2} = 0.745.$$

To avoid issues associated with numerical roundoff errors at very early time for species with very small compositions, the minor species were initialized at a small non-zero value near machine precision; each was assigned a value of $10^{-15} \; mole$. The minor species all have $\overline{\rho}_i = 1.803 \times 10^{-16} \; mole/cm^3$. They have correspondingly small initial mass fractions.

We seek the reaction dynamics as the system proceeds from its initial state to its final state. We use the reversible detailed kinetics mechanism of Table 1.2. This problem requires a detailed numerical solution. Such a solution was performed by solving the appropriate equations for a mixture of nine interacting species: H_2, H, O, O_2, OH, H_2O, HO_2, H_2O_2, and N_2. The dynamics of the reaction process are reflected in Figs. 1.15-1.17.

---

[20]This temperature and pressure correspond to that of the same ambient mixture of H_2, O_2 and N_2 which was shocked from $1.01325 \times 10^5 \; Pa$, $298 \; K$, to a value associated with a freely propagating detonation. Relevant comparisons of reaction dynamics will be made later in Sec. 10.2.8.
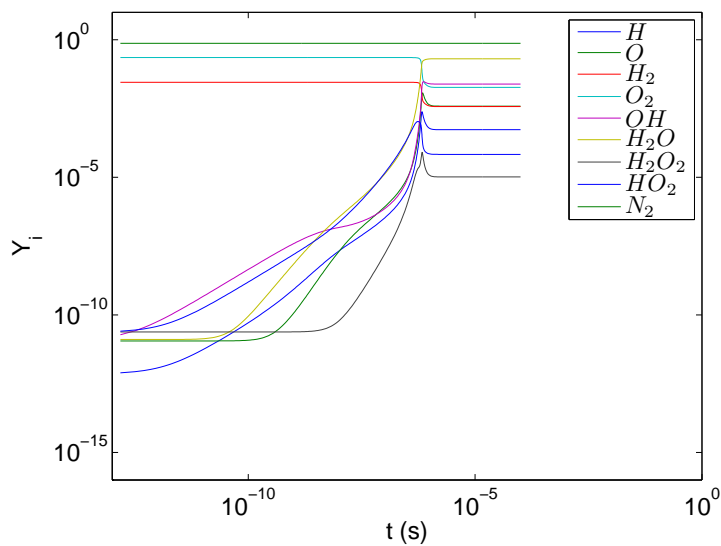
Figure 1.15: Plot of $Y_{H_2}(t)$, $Y_H(t)$, $Y_O(t)$, $Y_{O_2}(t)$, $Y_{OH}(t)$, $Y_{H_2O}(t)$, $Y_{HO_2}(t)$, $Y_{H_2O_2}(t)$, $Y_{N_2}(t)$, for adiabatic, isochoric combustion of a mixture of $2H_2 + O_2 + 3.76N_2$ initially at $T_o = 1542.7 \ K$, $P_o = 2.8323 \times 10^6 \ Pa$.
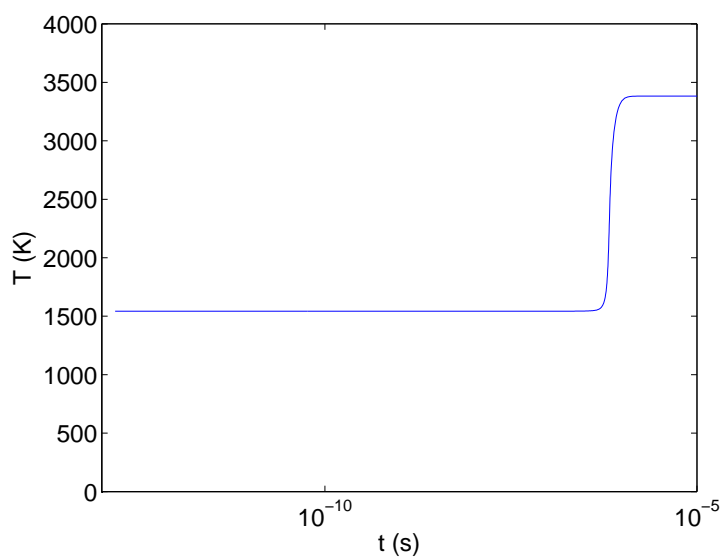
Figure 1.16: Plot of $T(t)$, for adiabatic, isochoric combustion of a mixture of $2H_2 + O_2 + 3.76N_2$ initially at $T_o = 1542.7 \ K$, $P_o = 2.8323 \times 10^6 \ Pa$.
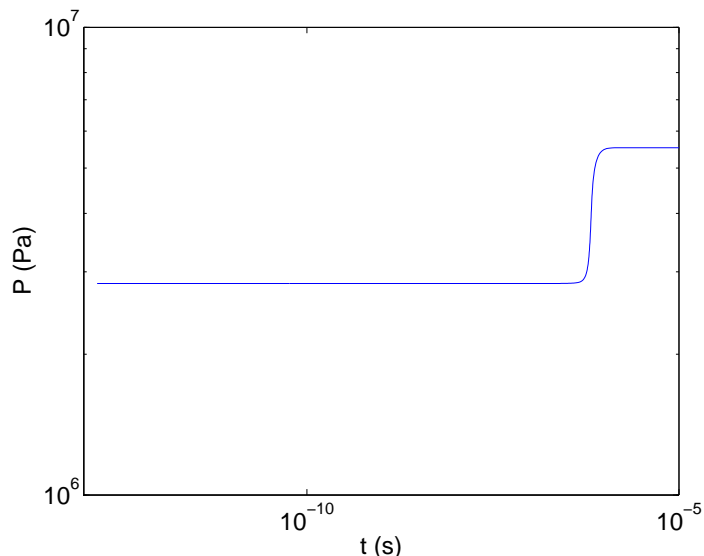
Figure 1.17: Plot of $P(t)$, for adiabatic, isochoric combustion of a mixture of $2H_2 + O_2 + 3.76N_2$ initially at $T_o = 1542.7 \ K$, $P_o = 2.8323 \times 10^6 \ Pa$.

At early time, $t < 10^{-7} \ s$, the pressure, temperature, and major reactant species concentrations (H_2, O_2, N_2) are nearly constant. However, the minor species, e.g. OH, HO_2, and the major product, H_2O, are undergoing very rapid growth, albeit with math fractions whose value remains small. In this period, the material is in what is known as the *induction period*.

After a certain critical mass of minor species has accumulated, exothermic recombination of these minor species to form the major product H_2O induces the temperature to rise, which accelerates further the reaction rates. This is manifested in a *thermal explosion*. A common definition of the end of the induction period is the *induction time*, $t = t_{ind}$, the time when dT/dt goes through a maximum. Here, one finds

$$t_{ind} = 6.6 \times 10^{-7} \ s. \tag{1.373}$$

A close-up view of the species concentration profiles is given in Fig. 1.18.

At the end of the induction zone, there is a final relaxation to equilibrium. The equilibrium mass fractions of each species are

$$Y_{O_2} = 1.85 \times 10^{-2}, \tag{1.374}$$
$$Y_H = 5.41 \times 10^{-4}, \tag{1.375}$$
$$Y_{OH} = 2.45 \times 10^{-2}, \tag{1.376}$$
$$Y_O = 3.88 \times 10^{-3}, \tag{1.377}$$
$$Y_{H_2} = 3.75 \times 10^{-3}, \tag{1.378}$$
$$Y_{H_2O} = 2.04 \times 10^{-1}, \tag{1.379}$$
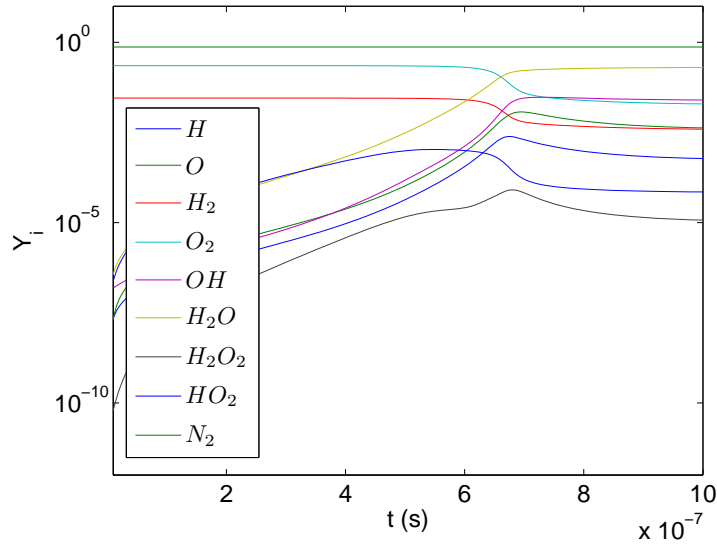
Figure 1.18: Plot near thermal explosion time of $Y_{H_2}(t)$, $Y_H(t)$, $Y_O(t)$, $Y_{O_2}(t)$, $Y_{OH}(t)$, $Y_{H_2O}(t)$, $Y_{HO_2}(t)$, $Y_{H_2O_2}(t)$, $Y_{N_2}(t)$, for adiabatic, isochoric combustion of a mixture of $2H_2 + O_2 + 3.76N_2$ initially at at $T_o = 1542.7\ K$, $P_o = 2.8323 \times 10^6\ Pa$.

$$Y_{HO_2} = 6.84 \times 10^{-5}, \tag{1.380}$$

$$Y_{H_2O_2} = 1.04 \times 10^{-5}, \tag{1.381}$$

$$Y_{N_2} = 7.45 \times 10^{-1}. \tag{1.382}$$

We note that because our model takes N_2 to be inert that its value remains unchanged. Other than N_2, the final products are dominated by H_2O. The equilibrium temperature is $3382.3\ K$ and $5.53 \times 10^6\ Pa$.

Chapter 2

Gas mixtures

One is often faced with mixtures of simple compressible substances, and it the thermodynamics of such mixtures upon which attention is now fixed. Here, a discussion of some of the fundamentals of mixture theory will be given. In general, thermodynamics of mixtures can be a challenging topic about which much remains to be learned. In particular, these notes will focus on ideal mixtures of ideal gases, for which results are often consistent with intuition. The chemical engineering literature contains a full discussion of the many nuances associated with non-ideal mixtures of non-ideal materials. Relevant background for this chapter is found in standard undergraduate texts.[1][2][3][4] Some of these notes on mixtures are adaptations of material found in these texts, especially Borgnakke and Sonntag.

2.1 Some general issues

Consider a mixture of N components, each a pure substance, so that the total mass and total number are

$$m = m_1 + m_2 + m_3 + \ldots + m_N = \sum_{i=1}^{N} m_i, \qquad \text{mass } (g), \qquad (2.1)$$

$$n = n_1 + n_2 + n_3 + \ldots + n_N = \sum_{i=1}^{N} n_i, \qquad \text{number } (mole). \qquad (2.2)$$

---

[1]Borgnakke, C., and Sonntag, R. E., 2009, *Fundamentals of Thermodynamics*, Seventh Edition, John Wiley, New York.

[2]Sandler, S. I., 1998, *Chemical and Engineering Thermodynamics*, Third Edition, John Wiley, New York.

[3]Smith, J. M., Van Ness, H. C., and Abbott, M., 2004, *Introduction to Chemical Engineering Thermodynamics*, Seventh Edition, McGraw-Hill, New York.

[4]Tester, J. W. and Modell, M., 1997, *Thermodynamics and Its Applications*, Third Edition, Prentice Hall, Upper Saddle River, New Jersey.

Recall 1 $mole = 6.02214129 \times 10^{23}$ $molecules$. The mass fraction of component i is defined as Y_i:

$$Y_i \equiv \frac{m_i}{m}, \qquad \text{mass fraction, dimensionless.} \tag{2.3}$$

The mole fraction of component i is defined as y_i:

$$y_i \equiv \frac{n_i}{n}, \qquad \text{mole fraction, dimensionless.} \tag{2.4}$$

Now, the molecular mass of species i is the mass of a mole of species i. It units are typically $g/mole$. Molecular mass is sometimes called "molecular weight," but this is formally incorrect, as it is a mass measure, not a force measure. Mathematically, the definition of M_i corresponds to

$$M_i \equiv \frac{m_i}{n_i}, \qquad \text{molecular mass} \left(\frac{g}{mole}\right). \tag{2.5}$$

One gets mass fraction in terms of mole fraction as

$$Y_i = \frac{m_i}{m}, \tag{2.6}$$

$$= \frac{n_i M_i}{m}, \tag{2.7}$$

$$= \frac{n_i M_i}{\sum_{j=1}^{N} m_j}, \tag{2.8}$$

$$= \frac{n_i M_i}{\sum_{j=1}^{N} n_j M_j}, \tag{2.9}$$

$$= \frac{\frac{n_i M_i}{n}}{\frac{1}{n} \sum_{j=1}^{N} n_j M_j}, \tag{2.10}$$

$$= \frac{\frac{n_i M_i}{n}}{\sum_{j=1}^{N} \frac{n_j M_j}{n}}, \tag{2.11}$$

$$= \frac{y_i M_i}{\sum_{j=1}^{N} y_j M_j}. \tag{2.12}$$

Similarly, one finds mole fraction in terms of mass fraction by the following:

$$y_i = \frac{n_i}{n}, \tag{2.13}$$

$$= \frac{\frac{m_i}{M_i}}{\sum_{j=1}^{N} \frac{m_j}{M_j}}, \tag{2.14}$$

$$= \frac{\frac{m_i}{M_i m}}{\sum_{j=1}^{N} \frac{m_j}{M_j m}}, \tag{2.15}$$

$$= \frac{\frac{Y_i}{M_i}}{\sum_{j=1}^{N} \frac{Y_j}{M_j}}. \tag{2.16}$$

The mixture itself has a mean molecular mass:

$$M \equiv \frac{m}{n}, \tag{2.17}$$

$$= \frac{\sum_{i=1}^{N} m_i}{n}, \tag{2.18}$$

$$= \sum_{i=1}^{N} \frac{n_i M_i}{n}, \tag{2.19}$$

$$= \sum_{i=1}^{N} y_i M_i. \tag{2.20}$$

Example 2.1

Air is often modelled as a mixture in the following molar ratios:

$$O_2 + 3.76 N_2. \tag{2.21}$$

Find the mole fractions, the mass fractions, and the mean molecular mass of the mixture.

Take O_2 to be species 1 and N_2 to be species 2. Consider the number of moles of O_2 to be

$$n_1 = 1 \ mole,$$

and N_2 to be

$$n_2 = 3.76 \ mole.$$

The molecular mass of O_2 is $M_1 = 32 \ g/mole$. The molecular mass of N_2 is $M_2 = 28 \ g/mole$. The total number of moles is

$$n = 1 \ mole + 3.76 \ mole = 4.76 \ mole.$$

So, the mole fractions are

$$y_1 = \frac{1 \ mole}{4.76 \ mole} = 0.2101.$$

$$y_2 = \frac{3.76 \ mole}{4.76 \ mole} = 0.7899.$$

Note that

$$\sum_{i=1}^{N} y_i = 1. \tag{2.22}$$

That is to say, $y_1 + y_2 = 0.2101 + 0.7899 = 1$. Now, for the masses, one has

$$m_1 = n_1 M_1 = (1 \ mole)\left(32 \ \frac{g}{mole}\right) = 32 \ g,$$

$$m_2 = n_2 M_2 = (3.76 \ mole)\left(28 \ \frac{g}{mole}\right) = 105.28 \ g,$$

So, one has

$$m = m_1 + m_2 = 32 \ g + 105.28 \ g = 137.28 \ g.$$

The mass fractions then are

$$Y_1 = \frac{m_1}{m} = \frac{32 \ g}{137.28 \ g} = 0.2331,$$

$$Y_2 = \frac{m_2}{m} = \frac{105.28 \ g}{137.28 \ g} = 0.7669.$$

Note that

$$\sum_{i=1}^{N} Y_i = 1. \tag{2.23}$$

That is, $Y_1 + Y_2 = 0.2331 + 0.7669 = 1$. Now, for the mixture molecular mass, one has

$$M = \frac{m}{n} = \frac{137.28 \ g}{4.76 \ mole} = 28.84 \ \frac{g}{mole}.$$

Check against another formula.

$$M = \sum_{i=1}^{N} y_i M_i = y_1 M_1 + y_2 M_2 = (0.2101) \left(32 \ \frac{g}{mole} \right) + (0.7899) \left(28 \ \frac{g}{mole} \right) = 28.84 \ \frac{g}{mole}.$$

Now, postulates for mixtures are not as well established as those for pure substances. The literature has much controversial discussion of the subject. A strong advocate of the axiomatic approach, C. A. Truesdell, proposed the following "metaphysical principles" for mixtures, which are worth considering.[5]

1. *All properties of the mixture must be mathematical consequences of properties of the constituents.*

2. *So as to describe the motion of a constituent, we may in imagination isolate it from the rest of the mixture, provided we allow properly for the actions of the other constituents upon it.*

3. *The motion of the mixture is governed by the same equations as is a single body.*

Most important for the present discussion is the first principle. When coupled with fluid mechanics, the second two take on additional importance. The approach of mixture theory is to divide and conquer. One typically treats each of the constituents as a single material and then devises appropriate average or mixture properties from those of the constituents. The best example of this is air, which is not a single material, but is often treated as such.

2.2   Ideal and non-ideal mixtures

A general extensive property, such as energy E, for an N-species mixture will be such that

$$E = E(T, P, n_1, n_2, \ldots, n_N). \tag{2.24}$$

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[5]C. A. Truesdell, 1984, *Rational Thermodynamics*, Springer-Verlag, New York.

A *partial molar property* is a generalization of an intensive property, and is defined such that it is the *partial derivative of an extensive property with respect to number of moles, with T and P held constant.* For internal energy, the partial molar internal energy is

$$\overline{e}_i \equiv \left. \frac{\partial E}{\partial n_i} \right|_{T,P,n_j,i \neq j}. \tag{2.25}$$

Pressure and temperature are held constant because those are convenient variables to control in an experiment. One also has the partial molar volume

$$\overline{v}_i = \left. \frac{\partial V}{\partial n_i} \right|_{T,P,n_j,i \neq j}. \tag{2.26}$$

It shall be soon seen that there are other natural ways to think of the volume per mole.

Now, in general one would expect to find

$$\overline{e}_i = \overline{e}_i(T, P, n_1, n_2, \ldots, n_N), \tag{2.27}$$
$$\overline{v}_i = \overline{v}_i(T, P, n_1, n_2, \ldots, n_N). \tag{2.28}$$

This is the case for what is known as a *non-ideal mixture*. An *ideal mixture* is defined as a mixture for which the partial molar properties $\overline{e}_i$ and $\overline{v}_i$ are not functions of the composition; that is to say

$$\overline{e}_i = \overline{e}_i(T, P), \qquad \text{if ideal mixture,} \tag{2.29}$$
$$\overline{v}_i = \overline{v}_i(T, P), \qquad \text{if ideal mixture.} \tag{2.30}$$

An ideal mixture also has the property that $\overline{h}_i = \overline{h}_i(T, P)$, while for a non-ideal mixture $\overline{h}_i = \overline{h}_i(T, P, n_1, \ldots, n_N)$. Though not obvious, it will turn out that some properties of an ideal mixture will depend on composition. For example, the entropy of a constituent of an ideal mixture will be such that

$$\overline{s}_i = \overline{s}_i(T, P, n_1, n_2, \ldots, n_N). \tag{2.31}$$

2.3 Ideal mixtures of ideal gases

The most straightforward mixture to consider is an ideal mixture of ideal gases. Even here, there are assumptions necessary that remain difficult to verify absolutely.

2.3.1 Dalton model

The most common model for a mixture of ideal gases is the *Dalton*[6] *model.* Key assumptions define this model:

---

[6]John Dalton, 1766-1844, English physicist.

- Each constituent shares a common temperature.

- Each constituent occupies the entire volume.

- Each constituent possesses a *partial pressure* which sums to form the total pressure of the mixture.

These features characterize a Dalton model for any gas, ideal or non-ideal. One also takes for convenience

- Each constituent behaves as an ideal gas.

- The mixture behaves as a single ideal gas.

It is more convenient to deal on a molar basis for such a theory. For the Dalton model, additional useful quantities, the species mass concentration ρ_i, the mixture mass concentration ρ, the species molar concentration $\overline{\rho}_i$, and the mixture molar concentration $\overline{\rho}$, can be defined. As will be seen, these definitions for concentrations are useful; however, they are not in common usage. Following Borgnakke and Sonntag, the bar notation, $\overline{\cdot}$, will be reserved for properties which are mole-based rather than mass-based. As mentioned earlier, the notion of a partial molal property is discussed extensively in the chemical engineering literature and has implications beyond those considered here. For the Dalton model, in which each component occupies the same volume, one has

$$V_i = V. \tag{2.32}$$

The mixture mass concentration, also called the density is simply

$$\rho = \frac{m}{V}, \qquad \left(\frac{g}{cm^3}\right). \tag{2.33}$$

The mixture molar concentration is

$$\overline{\rho} = \frac{n}{V}, \qquad \left(\frac{mole}{cm^3}\right). \tag{2.34}$$

For species i, the equivalents are

$$\rho_i = \frac{m_i}{V}, \qquad \left(\frac{g}{cm^3}\right), \tag{2.35}$$

$$\overline{\rho}_i = \frac{n_i}{V}, \qquad \left(\frac{mole}{cm^3}\right). \tag{2.36}$$

One can find a convenient relation between species molar concentration and species mole fraction by the following operations, beginning with Eq. (2.36):

$$\overline{\rho}_i = \frac{n_i}{V}\frac{n}{n}, \tag{2.37}$$

$$= \frac{n_i}{n}\frac{n}{V}, \tag{2.38}$$

$$= y_i\overline{\rho}. \tag{2.39}$$

A similar relation exists between species molar concentration and species mass fraction via

$$\overline{\rho}_i = \frac{n_i}{V}\frac{m}{m}\frac{M_i}{M_i}, \tag{2.40}$$

$$= \frac{m}{V}\frac{\overbrace{n_i M_i}^{=m_i}}{mM_i}, \tag{2.41}$$

$$= \rho\frac{\overbrace{m_i}^{=Y_i}}{m}\frac{1}{M_i}, \tag{2.42}$$

$$= \rho\frac{Y_i}{M_i}. \tag{2.43}$$

The specific volumes, mass and molar, are similar. One takes

$$v = \frac{V}{m}, \qquad \overline{v} = \frac{V}{n}, \tag{2.44}$$

$$v_i = \frac{V}{m_i}, \qquad \overline{v}_i = \frac{V}{n_i}. \tag{2.45}$$

Note that this definition of molar specific volume is *not* the partial molar volume defined in the chemical engineering literature, which takes the form $\overline{v}_i = \partial V/\partial n_i|_{T,P,n_j,i\neq j}$.

For the partial pressure of species i, one can say for the Dalton model

$$P = \sum_{i=1}^{N} P_i. \tag{2.46}$$

For species i, one has

$$P_i V = n_i \overline{R} T, \tag{2.47}$$

$$P_i = \frac{n_i \overline{R} T}{V}, \tag{2.48}$$

$$\underbrace{\sum_{i=1}^{N} P_i}_{=P} = \sum_{i=1}^{N} \frac{n_i \overline{R} T}{V}, \tag{2.49}$$

$$P = \frac{\overline{R} T}{V} \underbrace{\sum_{i=1}^{N} n_i}_{=n}. \tag{2.50}$$

So, for the mixture, one has

$$PV = n\overline{R}T. \tag{2.51}$$

One could also say

$$P = \frac{n}{V}\overline{R}T = \overline{\rho}\overline{R}T. \tag{2.52}$$

Here, n is the total number of moles in the system. Additionally $\overline{R}$ is the universal gas constant with value

$$\overline{R} = 8.3144621 \ \frac{J}{mole \ K}. \tag{2.53}$$

Sometimes this is expressed in terms of k_b the *Boltzmann[7] constant* and $\mathcal{N}_A$, Avogadro's[8] number:

$$\overline{R} = k_b \mathcal{N}_A, \tag{2.54}$$

$$\mathcal{N}_A = 6.02214129 \times 10^{23} \ \frac{molecule}{mole}, \tag{2.55}$$

$$k_b = 1.3806488 \times 10^{-23} \ \frac{J}{K \ molecule}. \tag{2.56}$$

With the Boltzmann constant and Avogadro's number, the ideal gas law, Eq. (2.51), can be rewritten as

$$PV = n\mathcal{N}_A k_b T, \tag{2.57}$$

where $n\mathcal{N}_A$ is the number of molecules.

Example 2.2

Compare the molar specific volume defined here with the partial molar volume from the chemical engineering literature.

The partial molar volume $\overline{v}_i$, is given by

$$\overline{v}_i = \left. \frac{\partial V}{\partial n_i} \right|_{T,P,n_j,i \neq j}. \tag{2.58}$$

For the ideal gas, one has

$$PV = \overline{R}T \sum_{k=1}^{N} n_k, \tag{2.59}$$

$$V = \frac{\overline{R}T \sum_{k=1}^{N} n_k}{P}, \tag{2.60}$$

$$\left. \frac{\partial V}{\partial n_i} \right|_{T,P,n_j,i \neq j} = \frac{\overline{R}T \sum_{k=1}^{N} \frac{\partial n_k}{\partial n_i}}{P}, \tag{2.61}$$

$$= \frac{\overline{R}T \sum_{k=1}^{N} \delta_{ki}}{P}, \tag{2.62}$$

$$= \frac{\overline{R}T \left(\overbrace{\delta_{1i}}^{=0} + \overbrace{\delta_{2i}}^{=0} + \ldots + \overbrace{\delta_{ii}}^{=1} + \ldots + \overbrace{\delta_{Ni}}^{=0} \right)}{P}, \tag{2.63}$$

---

[7]Ludwig Boltzmann, 1844-1906, Austrian physicist.

[8]Lorenzo Romano Amedeo Carlo Bernadette Avogadro di Quaregna e di Cerreto, 1776-1856, Italian scientist.

$$\overline{v}_i = \frac{\overline{R}T}{P}, \tag{2.64}$$

$$= \frac{V}{\sum_{k=1}^{N} n_k}, \tag{2.65}$$

$$= \frac{V}{n}. \tag{2.66}$$

Here, the so-called Kronecker[9] delta function has been employed, which is much the same as the identity matrix:

$$\delta_{ki} = 0, \qquad k \neq i, \tag{2.67}$$

$$\delta_{ki} = 1, \qquad k = i. \tag{2.68}$$

Contrast this with the earlier adopted definition of molar specific volume

$$\overline{v}_i = \frac{V}{n_i}. \tag{2.69}$$

So, why is there a difference? The molar specific volume is a simple definition. One takes the instantaneous volume V, which is shared by all species in the Dalton model, and scales it by the instantaneous number of moles of species i, and acquires a natural definition of molar specific volume consistent with the notion of a mass specific volume. On the other hand, the partial molar volume specifies how the volume changes if the number of moles of species i changes, *while holding T and P and all other species mole numbers constant*. One can imagine adding a mole of species i, which would necessitate a change in V in order to guarantee the P remain fixed.

2.3.1.1 Binary mixtures

Consider now a *binary mixture* of two components A and B. This is easily extended to a general mixture of N components. First, the total number of moles is the sum of the parts:

$$n = n_A + n_B. \tag{2.70}$$

Now, write the ideal gas law for each component:

$$P_A V_A = n_A \overline{R} T_A, \tag{2.71}$$

$$P_B V_B = n_B \overline{R} T_B. \tag{2.72}$$

But by the assumptions of the Dalton model, $V_A = V_B = V$, and $T_A = T_B = T$, so

$$P_A V = n_A \overline{R} T, \tag{2.73}$$

$$P_B V = n_B \overline{R} T. \tag{2.74}$$

One also has

$$PV = n \overline{R} T. \tag{2.75}$$

---

[9]Leopold Kronecker, 1823-1891, German mathematician.

Solving for n, n_A and n_B, one finds

$$n = \frac{PV}{\overline{R}T}, \tag{2.76}$$

$$n_A = \frac{P_A V}{\overline{R}T}, \tag{2.77}$$

$$n_B = \frac{P_B V}{\overline{R}T}. \tag{2.78}$$

Now, $n = n_A + n_B$, so one has

$$\frac{PV}{\overline{R}T} = \frac{P_A V}{\overline{R}T} + \frac{P_B V}{\overline{R}T}. \tag{2.79}$$

$$P = P_A + P_B. \tag{2.80}$$

That is the total pressure is the sum of the partial pressures. This is a mixture rule for pressure

One can also scale each constituent ideal gas law by the mixture ideal gas law to get

$$\frac{P_A V}{PV} = \frac{n_A \overline{R}T}{n \overline{R}T}, \tag{2.81}$$

$$\frac{P_A}{P} = \frac{n_A}{n}, \tag{2.82}$$

$$= y_A, \tag{2.83}$$

$$P_A = y_A P. \tag{2.84}$$

Likewise

$$P_B = y_B P. \tag{2.85}$$

Now, one also desires rational mixture rules for energy, enthalpy, and entropy. Invoke Truesdell's principles on a mass basis for internal energy. Then, the total internal energy E (with units J) for the binary mixture must be

$$E = me = m_A e_A + m_B e_B, \tag{2.86}$$

$$= m \left(\frac{m_A}{m} e_A + \frac{m_B}{m} e_B \right), \tag{2.87}$$

$$= m \left(Y_A e_A + Y_B e_B \right), \tag{2.88}$$

$$e = Y_A e_A + Y_B e_B. \tag{2.89}$$

For the enthalpy, one has

$$H = mh = m_A h_A + m_B h_B, \tag{2.90}$$

$$= m \left(\frac{m_A}{m} h_A + \frac{m_B}{m} h_B \right), \tag{2.91}$$

$$= m \left(Y_A h_A + Y_B h_B \right), \tag{2.92}$$

$$h = Y_A h_A + Y_B h_B. \tag{2.93}$$

It is easy to extend this to a mole fraction basis rather than a mass fraction basis. One can also obtain a gas constant for the mixture on a mass basis. For the mixture, one has

$$
PV = n\overline{R}T \equiv mRT, \tag{2.94}
$$

$$
\frac{PV}{T} \equiv mR = n\overline{R}, \tag{2.95}
$$

$$
= (n_A + n_B)\overline{R}, \tag{2.96}
$$

$$
= \left(\frac{m_A}{M_A} + \frac{m_B}{M_B}\right)\overline{R}, \tag{2.97}
$$

$$
= \left(m_A\frac{\overline{R}}{M_A} + m_B\frac{\overline{R}}{M_B}\right), \tag{2.98}
$$

$$
= (m_A R_A + m_B R_B), \tag{2.99}
$$

$$
R = \left(\frac{m_A}{m}R_A + \frac{m_B}{m}R_B\right), \tag{2.100}
$$

$$
R = (Y_A R_A + Y_B R_B). \tag{2.101}
$$

For the entropy, one has

$$
S = ms = = m_A s_A + m_B s_B, \tag{2.102}
$$

$$
= m\left(\frac{m_A}{m}s_A + \frac{m_B}{m}s_B\right), \tag{2.103}
$$

$$
= m\left(Y_A s_A + Y_B s_B\right), \tag{2.104}
$$

$$
s = Y_A s_A + Y_B s_B. \tag{2.105}
$$

Note that s_A is evaluated at T and P_A, while s_B is evaluated at T and P_B. For a calorically perfect ideal gas, one has

$$
s_A = \underbrace{s^o_{T_o,A} + c_{PA}\ln\left(\frac{T}{T_o}\right)}_{\equiv s^o_{T,A}} - R_A\ln\left(\frac{P_A}{P_o}\right), \tag{2.106}
$$

$$
= s^o_{T_o,A} + c_{PA}\ln\left(\frac{T}{T_o}\right) - R_A\ln\left(\frac{y_A P}{P_o}\right). \tag{2.107}
$$

Likewise

$$
s_B = \underbrace{s^o_{T_o,B} + c_{PB}\ln\left(\frac{T}{T_o}\right)}_{\equiv s^o_{T,B}} - R_B\ln\left(\frac{y_B P}{P_o}\right). \tag{2.108}
$$

Here, the "o" denotes some reference state. As a superscript, it typically means that the property is evaluated at a reference pressure. For example, $s^o_{T,A}$ denotes the portion of the entropy of component A that is evaluated at the reference pressure P_o and is allowed to vary with temperature T. Note also that $s_A = s_A(T, P, y_A)$ and $s_B = s_B(T, P, y_B)$, so the entropy

of a single constituent depends on the composition of the mixture and not just on T and P. This contrasts with energy and enthalpy for which $e_A = e_A(T)$, $e_B = e_B(T)$, $h_A = h_A(T)$, $h_B = h_B(T)$ if the mixture is composed of ideal gases. Occasionally, one finds h_A^o and h_B^o used as a notation. This denotes that the enthalpy is evaluated at the reference pressure. However, if the gas is ideal, the enthalpy is not a function of pressure and $h_A = h_A^o$, $h_B = h_B^o$.

If one is employing a calorically imperfect ideal gas model, then one finds for species i that

$$s_i = s_{T,i}^o - R_i \ln \left(\frac{y_i P}{P_o} \right), \qquad i = A, B. \tag{2.109}$$

2.3.1.2   Entropy of mixing

Example 2.3

Initially calorically perfect ideal gases A and B are segregated within the same large volume by a thin frictionless, thermally conducting diaphragm. Thus, both are at the same initial pressure and temperature, P_1 and T_1. The total volume is thermally insulated and fixed, so there are no global heat or work exchanges with the environment. The diaphragm is removed, and A and B are allowed to mix. Assume A has mass m_A and B has mass m_B. The gases are allowed to have distinct molecular masses, M_A and M_B. Find the final temperature T_2, pressure P_2, and the change in entropy.

The ideal gas law holds that at the initial state

$$V_{A1} = \frac{m_A R_A T_1}{P_1}, \qquad V_{B1} = \frac{m_B R_B T_1}{P_1}. \tag{2.110}$$

At the final state one has

$$V_2 = V_{A2} = V_{B2} = V_{A1} + V_{B1} = (m_A R_A + m_B R_B)\frac{T_1}{P_1}. \tag{2.111}$$

Mass conservation gives

$$m_2 = m_1 = m_A + m_B. \tag{2.112}$$

One also has the first law

$$
\begin{aligned}
E_2 - E_1 &= Q - W, \tag{2.113}\\
E_2 - E_1 &= 0, \tag{2.114}\\
E_2 &= E_1, \tag{2.115}\\
m_2 e_2 &= m_A e_{A1} + m_B e_{B1}, \tag{2.116}\\
(m_A + m_B)e_2 &= m_A e_{A1} + m_B e_{B1}, \tag{2.117}\\
0 &= m_A(e_{A1} - e_2) + m_B(e_{B1} - e_2), \tag{2.118}\\
0 &= m_A c_{vA}(T_1 - T_2) + m_B c_{vB}(T_1 - T_2), \tag{2.119}\\
T_2 &= \frac{m_A c_{vA} T_1 + m_B c_{vB} T_1}{m_A c_{vA} + m_B c_{vB}}, \tag{2.120}\\
&= T_1. \tag{2.121}
\end{aligned}
$$

The final pressure by Dalton's law then is

$$
\begin{align}
P_2 &= P_{A2} + P_{B2}, \tag{2.122}\\
&= \frac{m_A R_A T_2}{V_2} + \frac{m_B R_B T_2}{V_2}, \tag{2.123}\\
&= \frac{m_A R_A T_1}{V_2} + \frac{m_B R_B T_1}{V_2}, \tag{2.124}\\
&= \frac{(m_A R_A + m_B R_B)\, T_1}{V_2}, \tag{2.125}\\
&= \frac{(m_A R_A + m_B R_B)\, T_1}{(m_A R_A + m_B R_B)\frac{T_1}{P_1}}, \tag{2.126}\\
&= P_1. \tag{2.127}
\end{align}
$$

So, the initial and final temperatures and pressures are identical.

Now, the entropy change of gas A is

$$
\begin{align}
s_{A2} - s_{A1} &= c_{PA} \ln\left(\frac{T_{A2}}{T_{A1}}\right) - R_A \ln\left(\frac{P_{A2}}{P_{A1}}\right), \tag{2.128}\\
&= c_{PA} \ln\left(\frac{T_2}{T_1}\right) - R_A \ln\left(\frac{y_{A2} P_2}{y_{A1} P_1}\right), \tag{2.129}\\
&= c_{PA} \underbrace{\ln\left(\frac{T_1}{T_1}\right)}_{=0} - R_A \ln\left(\frac{y_{A2} P_1}{y_{A1} P_1}\right), \tag{2.130}\\
&= -R_A \ln\left(\frac{y_{A2} P_1}{(1) P_1}\right), \tag{2.131}\\
&= -R_A \ln y_{A2}. \tag{2.132}
\end{align}
$$

Likewise

$$
s_{B2} - s_{B1} = -R_B \ln y_{B2}. \tag{2.133}
$$

So, the change in entropy of the mixture is

$$
\begin{align}
\Delta S &= m_A(s_{A2} - s_{A1}) + m_B(s_{B2} - s_{B1}) \tag{2.134}\\
&= -m_A R_A \ln y_{A2} - m_B R_B \ln y_{B2}, \tag{2.135}\\
&= -\underbrace{(n_A M_A)}_{=m_A}\underbrace{\left(\frac{\overline{R}}{M_A}\right)}_{=R_A} \ln y_{A2} - \underbrace{(n_B M_B)}_{=m_B}\underbrace{\left(\frac{\overline{R}}{M_B}\right)}_{=R_B} \ln y_{B2}, \tag{2.136}\\
&= -\overline{R}(n_A \ln y_{A2} + n_B \ln y_{B2}), \tag{2.137}\\
&= -\overline{R}\left(n_A \underbrace{\ln\left(\frac{n_A}{n_A + n_B}\right)}_{\leq 0} + n_B \underbrace{\ln\left(\frac{n_B}{n_A + n_B}\right)}_{\leq 0} \right), \tag{2.138}\\
&\geq 0. \tag{2.139}
\end{align}
$$

For an N-component mixture, mixed in the same fashion such that P and T are constant, this extends to

$$\Delta S \;=\; -\overline{R}\sum_{k=1}^{N} n_k \ln y_k, \tag{2.140}$$

$$=\; -\overline{R}\sum_{k=1}^{N} \frac{n_k}{n} n \ln y_k, \tag{2.141}$$

$$=\; -\overline{R}n\sum_{k=1}^{N} \frac{n_k}{n} \ln y_k, \tag{2.142}$$

$$=\; -\overline{R}\frac{m}{M}\sum_{k=1}^{N} y_k \ln y_k, \tag{2.143}$$

$$=\; -Rm\sum_{k=1}^{N} \ln y_k^{y_k}, \tag{2.144}$$

$$=\; -Rm\left(\ln y_1^{y_1} + \ln y_2^{y_2} + \ldots + \ln y_N^{y_N}\right), \tag{2.145}$$

$$=\; -Rm\ln\left(y_1^{y_1} y_2^{y_2} \ldots y_N^{y_N}\right), \tag{2.146}$$

$$=\; -Rm\ln\left(\prod_{k=1}^{N} y_k^{y_k}\right), \tag{2.147}$$

$$\frac{\Delta s}{R} = \frac{\Delta \overline{s}}{\overline{R}} \;=\; -\ln\left(\prod_{k=1}^{N} y_k^{y_k}\right). \tag{2.148}$$

Note that there is a fundamental dependency of the mixing entropy on the mole fractions. Since $0 \leq y_k \leq 1$, the product is guaranteed to be between 0 and 1. The natural logarithm of such a number is negative, and thus the entropy change for the mixture is guaranteed positive semi-definite. Note also that for the entropy of mixing, Truesdell's third principle is not enforced.

Now, if one mole of pure N_2 is mixed with one mole of pure O_2, one certainly expects the resulting homogeneous mixture to have a higher entropy than the two pure components. But what if one mole of pure N_2 is mixed with another mole of pure N_2. Then, we would expect no increase in entropy. However, if we had the unusual ability to distinguish N_2 molecules whose origin was from each respective original chamber, then indeed there would be an entropy of mixing. Increases in entropy thus do correspond to increases in disorder.

2.3.1.3   Mixtures of constant mass fraction

If the mass fractions, and thus the mole fractions, remain constant during a process, the equations simplify. This is often the case for common non-reacting mixtures. Air at moderate values of temperature and pressure behaves this way. In this case, all of Truesdell's principles

can be enforced. For a calorically perfect ideal gas, one would have

$$
\begin{align}
e_2 - e_1 &= Y_A c_{vA}(T_2 - T_1) + Y_B c_{vB}(T_2 - T_1), \tag{2.149}\\
&= c_v(T_2 - T_1). \tag{2.150}
\end{align}
$$

where

$$
c_v \equiv Y_A c_{vA} + Y_B c_{vB}. \tag{2.151}
$$

Similarly for enthalpy

$$
\begin{align}
h_2 - h_1 &= Y_A c_{PA}(T_2 - T_1) + Y_B c_{PB}(T_2 - T_1), \tag{2.152}\\
&= c_P(T_2 - T_1). \tag{2.153}
\end{align}
$$

where

$$
c_P \equiv Y_A c_{PA} + Y_B c_{PB}. \tag{2.154}
$$

For the entropy

$$
\begin{align}
s_2 - s_1 &= Y_A(s_{A2} - s_{A1}) + Y_B(s_{B2} - s_{B1}), \tag{2.155}\\
&= Y_A \left(c_{PA} \ln\left(\frac{T_2}{T_1}\right) - R_A \ln\left(\frac{y_A P_2}{y_A P_1}\right) \right) + Y_B \left(c_{PB} \ln\left(\frac{T_2}{T_1}\right) - R_B \ln\left(\frac{y_B P_2}{y_B P_1}\right) \right), \\
&= Y_A \left(c_{PA} \ln\left(\frac{T_2}{T_1}\right) - R_A \ln\left(\frac{P_2}{P_1}\right) \right) + Y_B \left(c_{PB} \ln\left(\frac{T_2}{T_1}\right) - R_B \ln\left(\frac{P_2}{P_1}\right) \right), \tag{2.156}\\
&= c_P \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right). \tag{2.157}
\end{align}
$$

The mixture behaves as a pure substance when the appropriate mixture properties are defined. One can also take

$$
\gamma = \frac{c_P}{c_v}. \tag{2.158}
$$

Note that some intuitive definitions do not hold: with $\gamma_A = c_{PA}/c_{vA}$, $\gamma_B = c_{PB}/c_{vB}$, $\gamma \neq Y_A \gamma_A + Y_B \gamma_B$.

2.3.2 Summary of properties for the Dalton mixture model

2.3.2.1 Mass basis

Listed here is a summary of mixture properties for an N-component mixture of ideal gases on a mass basis:

$$
\begin{align}
M &= \sum_{i=1}^{N} y_i M_i, \tag{2.159}\\
\rho &= \sum_{i=1}^{N} \rho_i, \tag{2.160}
\end{align}
$$

$$v = \frac{1}{\sum_{i=1}^{N}\frac{1}{v_i}} = \frac{1}{\rho}, \tag{2.161}$$

$$e = \sum_{i=1}^{N} Y_i e_i, \tag{2.162}$$

$$h = \sum_{i=1}^{N} Y_i h_i, \tag{2.163}$$

$$R = \frac{\overline{R}}{M} = \sum_{i=1}^{N} Y_i R_i = \sum_{i=1}^{N} \frac{y_i \overbrace{M_i R_i}^{=\overline{R}}}{\underbrace{\sum_{j=1}^{N} y_j M_j}_{=M}} = \frac{\overline{R}}{M} \underbrace{\sum_{i=1}^{N} y_i}_{=1}, \tag{2.164}$$

$$c_v = \sum_{i=1}^{N} Y_i c_{vi}, \tag{2.165}$$

$$c_v = c_P - R, \qquad \text{if ideal gas} \tag{2.166}$$

$$c_P = \sum_{i=1}^{N} Y_i c_{Pi}, \tag{2.167}$$

$$\gamma = \frac{c_P}{c_v} = \frac{\sum_{i=1}^{N} Y_i c_{Pi}}{\sum_{i=1}^{N} Y_i c_{vi}}, \tag{2.168}$$

$$s = \sum_{i=1}^{N} Y_i s_i, \tag{2.169}$$

$$Y_i = \frac{y_i M_i}{M}, \tag{2.170}$$

$$P_i = y_i P, \tag{2.171}$$

$$\rho_i = Y_i \rho, \tag{2.172}$$

$$v_i = \frac{v}{Y_i} = \frac{1}{\rho_i}, \tag{2.173}$$

$$V = V_i, \tag{2.174}$$

$$T = T_i, \tag{2.175}$$

$$h_i = h_i^o, \qquad \text{if ideal gas}, \tag{2.176}$$

$$h_i = e_i + \frac{P_i}{\rho_i} = e_i + P_i v_i = \underbrace{e_i + R_i T}_{\text{if ideal gas}}, \tag{2.177}$$

$$h_i = \underbrace{h_{T_o,i}^o + \int_{T_o}^{T} c_{Pi}(\hat{T})\, d\hat{T}}_{\text{if ideal gas}}, \tag{2.178}$$

$$
s_i = \underbrace{\underbrace{s^o_{T_o,i} + \int_{T_o}^{T} \frac{c_{Pi}(\hat{T})}{\hat{T}}\, d\hat{T}}_{=s^o_{T,i}} - R_i \ln\left(\frac{P_i}{P_o}\right)}_{\text{if ideal gas}}, \tag{2.179}
$$

$$
s_i = \underbrace{s^o_{T,i} - R_i \ln\left(\frac{y_i P}{P_o}\right)}_{\text{if ideal gas}} = \underbrace{s^o_{T,i} - R_i \ln\left(\frac{P_i}{P_o}\right)}_{\text{if ideal gas}}, \tag{2.180}
$$

$$
P_i = \underbrace{\rho_i R_i T = \rho R_i T Y_i}_{\text{if ideal gas}} = \frac{R_i T}{v_i}, \tag{2.181}
$$

$$
P = \underbrace{\rho R T = \rho \overline{R} T \sum_{i=1}^{N} \frac{Y_i}{M_i}}_{\text{if ideal gas}} = \frac{RT}{v}, \tag{2.182}
$$

$$
h = \underbrace{\sum_{i=1}^{N} Y_i h^o_{T_o,i} + \int_{T_o}^{T} c_P(\hat{T})\, d\hat{T}}_{\text{if ideal gas}}, \tag{2.183}
$$

$$
h = e + \frac{P}{\rho} = e + Pv = \underbrace{e + RT}_{\text{if ideal gas}}, \tag{2.184}
$$

$$
s = \underbrace{\sum_{i=1}^{N} Y_i s^o_{T_o,i} + \int_{T_o}^{T} \frac{c_P(\hat{T})}{\hat{T}}\, d\hat{T} - R \ln\left(\frac{P}{P_o}\right) - R \ln\left(\prod_{i=1}^{N} y_i^{y_i}\right)}_{\text{if ideal gas}} \tag{2.185}
$$

These relations are not obvious. A few are derived in examples here.

Example 2.4

Derive the expression $h = e + P/\rho$.

Start from the equation for the constituent h_i, multiply by mass fractions, sum over all species, and use properties of mixtures:

$$
h_i = e_i + \frac{P_i}{\rho_i}, \tag{2.186}
$$

$$
Y_i h_i = Y_i e_i + Y_i \frac{P_i}{\rho_i}, \tag{2.187}
$$

$$
\sum_{i=1}^{N} Y_i h_i = \sum_{i=1}^{N} Y_i e_i + \sum_{i=1}^{N} Y_i \frac{P_i}{\rho_i}, \tag{2.188}
$$

$$\underbrace{\sum_{i=1}^{N} Y_i h_i}_{=h} = \underbrace{\sum_{i=1}^{N} Y_i e_i}_{=e} + \sum_{i=1}^{N} Y_i \frac{\rho_i R_i T}{\rho_i}, \tag{2.189}$$

$$h = e + T \underbrace{\sum_{i=1}^{N} Y_i R_i}_{=R}, \tag{2.190}$$

$$= e + RT, \tag{2.191}$$

$$= e + \frac{P}{\rho}. \tag{2.192}$$

Example 2.5
      Find the expression for mixture entropy of the ideal gas.

$$s_i = s_{T_o,i}^o + \int_{T_o}^{T} \frac{c_{Pi}(\hat{T})}{\hat{T}} \, d\hat{T} - R_i \ln\left(\frac{P_i}{P_o}\right), \tag{2.193}$$

$$Y_i s_i = Y_i s_{T_o,i}^o + Y_i \int_{T_o}^{T} \frac{c_{Pi}(\hat{T})}{\hat{T}} \, d\hat{T} - Y_i R_i \ln\left(\frac{P_i}{P_o}\right), \tag{2.194}$$

$$s = \sum_{i=1}^{N} Y_i s_i = \sum_{i=1}^{N} Y_i s_{T_o,i}^o + \sum_{i=1}^{N} Y_i \int_{T_o}^{T} \frac{c_{Pi}(\hat{T})}{\hat{T}} \, d\hat{T} - \sum_{i=1}^{N} Y_i R_i \ln\left(\frac{P_i}{P_o}\right), \tag{2.195}$$

$$= \sum_{i=1}^{N} Y_i s_{T_o,i}^o + \int_{T_o}^{T} \sum_{i=1}^{N} \frac{Y_i c_{Pi}(\hat{T})}{\hat{T}} \, d\hat{T} - \sum_{i=1}^{N} Y_i R_i \ln\left(\frac{P_i}{P_o}\right), \tag{2.196}$$

$$= s_{T_o}^o + \int_{T_o}^{T} \frac{c_P(\hat{T})}{\hat{T}} \, d\hat{T} - \sum_{i=1}^{N} Y_i R_i \ln\left(\frac{P_i}{P_o}\right). \tag{2.197}$$

All except the last term are natural extensions of the property for a single material. Consider now the last term involving pressure ratios.

$$-\sum_{i=1}^{N} Y_i R_i \ln\left(\frac{P_i}{P_o}\right) = -\left(\sum_{i=1}^{N} Y_i R_i \ln\left(\frac{P_i}{P_o}\right) + R \ln\frac{P}{P_o} - R \ln\frac{P}{P_o}\right), \tag{2.198}$$

$$= -R\left(\sum_{i=1}^{N} Y_i \frac{R_i}{R} \ln\left(\frac{P_i}{P_o}\right) + \ln\frac{P}{P_o} - \ln\frac{P}{P_o}\right), \tag{2.199}$$

$$= -R\left(\sum_{i=1}^{N} Y_i \frac{\overline{R}/M_i}{\sum_{j=1}^{N} Y_j \overline{R}/M_j} \ln\left(\frac{P_i}{P_o}\right) + \ln\frac{P}{P_o} - \ln\frac{P}{P_o}\right), \tag{2.200}$$

$$= -R\left(\sum_{i=1}^{N} \underbrace{\left(\frac{Y_i/M_i}{\sum_{j=1}^{N} Y_j/M_j}\right)}_{=y_i} \ln\left(\frac{P_i}{P_o}\right) + \ln\frac{P}{P_o} - \ln\frac{P}{P_o}\right), \tag{2.201}$$

$$= -R\left(\sum_{i=1}^{N} y_i \ln\left(\frac{P_i}{P_o}\right) + \ln\frac{P}{P_o} - \ln\frac{P}{P_o}\right), \tag{2.202}$$

$$= -R\left(\sum_{i=1}^{N} \ln\left(\frac{P_i}{P_o}\right)^{y_i} - \ln\frac{P}{P_o} + \ln\frac{P}{P_o}\right), \tag{2.203}$$

$$= -R\left(\ln\left(\prod_{i=1}^{N}\left(\frac{P_i}{P_o}\right)^{y_i}\right) + \ln\frac{P_o}{P} + \ln\frac{P}{P_o}\right), \tag{2.204}$$

$$= -R\left(\ln\left(\frac{P_o}{P}\prod_{i=1}^{N}\left(\frac{P_i}{P_o}\right)^{y_i}\right) + \ln\frac{P}{P_o}\right), \tag{2.205}$$

$$= -R\left(\ln\left(\frac{P_o}{P^{\sum_{i=1}^{N} y_i}}\frac{1}{P_o^{\sum_{i=1}^{N} y_i}}\prod_{i=1}^{N}(P_i)^{y_i}\right) + \ln\frac{P}{P_o}\right), \tag{2.206}$$

$$= -R\left(\ln\left(\prod_{i=1}^{N}\left(\frac{P_i}{P}\right)^{y_i}\right) + \ln\frac{P}{P_o}\right), \tag{2.207}$$

$$= -R\left(\ln\left(\prod_{i=1}^{N}\left(\frac{y_i P}{P}\right)^{y_i}\right) + \ln\frac{P}{P_o}\right), \tag{2.208}$$

$$= -R\left(\ln\left(\prod_{i=1}^{N} y_i^{y_i}\right) + \ln\frac{P}{P_o}\right). \tag{2.209}$$

So, the mixture entropy becomes

$$s = s_{T_o}^o + \int_{T_o}^{T}\frac{c_P(\hat{T})}{\hat{T}}\,d\hat{T} - R\left(\ln\left(\prod_{i=1}^{N} y_i^{y_i}\right) + \ln\frac{P}{P_o}\right), \tag{2.210}$$

$$= \underbrace{s_{T_o}^o + \int_{T_o}^{T}\frac{c_P(\hat{T})}{\hat{T}}\,d\hat{T} - R\ln\frac{P}{P_o}}_{\text{classical entropy of a single body}} - \underbrace{R\ln\left(\prod_{i=1}^{N} y_i^{y_i}\right)}_{\text{non–Truesdellian}}. \tag{2.211}$$

The extra entropy is not found in the theory for a single material, and in fact is not in the form suggested by Truesdell's postulates. While it is in fact possible to redefine the constituent entropy definition in such a fashion that the mixture entropy in fact takes on the classical form of a single material via the definition $s_i = s_{T_o,i}^o + \int_{T_o}^{T} c_{Pi}(\hat{T})/\hat{T}\,d\hat{T} - R_i\ln(P_i/P_o) + R_i\ln y_i$, this has the disadvantage of predicting *no entropy change* after mixing two pure substances. Such a theory would suggest that this obviously irreversible process is in fact reversible.

2.3.2.2 Molar basis

On a molar basis, one has equivalent relations to those found on a mass basis.

$$\overline{\rho} = \sum_{i=1}^{N}\overline{\rho}_i = \frac{n}{V} = \frac{\rho}{M}, \tag{2.212}$$

$$\overline{v} \;\; = \;\; \frac{1}{\sum_{i=1}^{N} \frac{1}{\overline{v}_i}} = \frac{V}{n} = \frac{1}{\overline{\rho}} = vM, \tag{2.213}$$

$$\overline{e} \;\; = \;\; \sum_{i=1}^{N} y_i \overline{e}_i = eM, \tag{2.214}$$

$$\overline{h} \;\; = \;\; \sum_{i=1}^{N} y_i \overline{h}_i = hM, \tag{2.215}$$

$$\overline{c}_v \;\; = \;\; \sum_{i=1}^{N} y_i \overline{c}_{vi} = c_v M, \tag{2.216}$$

$$\overline{c}_v \;\; = \;\; \overline{c}_P - \overline{R}, \tag{2.217}$$

$$\overline{c}_P \;\; = \;\; \sum_{i=1}^{N} y_i \overline{c}_{Pi} = c_P M \tag{2.218}$$

$$\gamma \;\; = \;\; \frac{\overline{c}_P}{\overline{c}_v} = \frac{\sum_{i=1}^{N} y_i \overline{c}_{Pi}}{\sum_{i=1}^{N} y_i \overline{c}_{vi}}, \tag{2.219}$$

$$\overline{s} \;\; = \;\; \sum_{i=1}^{N} y_i \overline{s}_i = sM, \tag{2.220}$$

$$\overline{\rho}_i \;\; = \;\; y_i \overline{\rho} = \frac{\rho_i}{M_i}, \tag{2.221}$$

$$\overline{v}_i \;\; = \;\; \frac{V}{n_i} = \frac{\overline{v}}{y_i} = \frac{1}{\overline{\rho}_i} = v_i M_i, \tag{2.222}$$

$$\overline{\mathrm{v}}_i \;\; = \;\; \left.\frac{\partial V}{\partial n_i}\right|_{P,T,n_j} = \underbrace{\frac{V}{n} = \overline{v} = vM}_{\text{if ideal gas}}, \tag{2.223}$$

$$P_i \;\; = \;\; y_i P, \tag{2.224}$$

$$P \;\; = \;\; \underbrace{\overline{\rho}\,\overline{R}T = \frac{\overline{R}T}{\overline{v}}}_{\text{if ideal gas}}, \tag{2.225}$$

$$P_i \;\; = \;\; \underbrace{\overline{\rho}_i \overline{R}T = \frac{\overline{R}T}{\overline{v}_i}}_{\text{if ideal gas}}, \tag{2.226}$$

$$\overline{h} \;\; = \;\; \overline{e} + \frac{P}{\overline{\rho}} = \overline{e} + P\overline{v} = \underbrace{\overline{e} + \overline{R}T}_{\text{if ideal gas}} = hM, \tag{2.227}$$

$$\overline{h}_i \;\; = \;\; \overline{h}_i^o, \qquad \text{if ideal gas}, \tag{2.228}$$

$$\overline{h}_i \;\; = \;\; \overline{e}_i + \frac{P_i}{\overline{\rho}_i} = \overline{e}_i + P_i \overline{v}_i = \overline{e}_i + P\overline{\mathrm{v}}_i = \underbrace{\overline{e}_i + \overline{R}T}_{\text{if ideal gas}} = h_i M_i, \tag{2.229}$$

$$\overline{h}_i = \underbrace{\overline{h}^o_{T_o,i} + \int_{T_o}^{T} \overline{c}_{Pi}(\hat{T})\ d\hat{T}}_{\text{if ideal gas}} = h_i M_i, \tag{2.230}$$

$$\overline{s}_i = \underbrace{\underbrace{\overline{s}^o_{T_o,i} + \int_{T_o}^{T} \frac{\overline{c}_{Pi}(\hat{T})}{\hat{T}}\ d\hat{T}}_{=\overline{s}^o_{T,i}} - \overline{R}\ln\left(\frac{y_i P}{P_o}\right)}_{\text{if ideal gas}}, \tag{2.231}$$

$$\overline{s}_i = \underbrace{\overline{s}^o_{T,i} - \overline{R}\ln\left(\frac{y_i P}{P_o}\right)}_{\text{if ideal gas}} = s_i M_i, \tag{2.232}$$

$$\overline{s} = \underbrace{\sum_{i=1}^{N} y_i \overline{s}^o_{T_o,i} + \int_{T_o}^{T} \frac{\overline{c}_P(\hat{T})}{\hat{T}}\ d\hat{T} - \overline{R}\ln\left(\frac{P}{P_o}\right) - \overline{R}\ln\left(\prod_{i=1}^{N} y_i^{y_i}\right)}_{\text{if ideal gas}} = sM. \tag{2.233}$$

2.3.3 Amagat model

The Amagat[10] model is an entirely different paradigm than the Dalton model. It is not used as often. In the Amagat model,

- all components share a common temperature T,

- all components share a common pressure P,

- each component has a different volume.

Consider, for example, a binary mixture of calorically perfect ideal gases, A and B. For the mixture, one has

$$PV = n\overline{R}T, \tag{2.234}$$

with

$$n = n_A + n_B. \tag{2.235}$$

For the components one has

$$PV_A = n_A \overline{R}T, \tag{2.236}$$
$$PV_B = n_B \overline{R}T. \tag{2.237}$$

Then, $n = n_A + n_B$ reduces to

$$\frac{PV}{\overline{R}T} = \frac{PV_A}{\overline{R}T} + \frac{PV_B}{\overline{R}T}. \tag{2.238}$$

---

[10]Emile Hilaire Amagat, 1841-1925, French physicist.

Thus

$$V \;\; = \;\; V_A + V_B,$$

$$1 \;\; = \;\; \frac{V_A}{V} + \frac{V_B}{V}.$$

(2.239)

(2.240)

Chapter 3

Mathematical foundations of thermodynamics

Every mathematician knows it is impossible to understand an elementary course in thermodynamics.

Vladimir Igorevich Arnol'd (1937-2010), "Contact Geometry: The Geometrical Method of Gibbs' Thermodynamics," in Proceedings of the Gibbs Symposium, D. Caldi and G. Mostow, eds., American Mathematical Society, 1990, p. 163.

This chapter focuses on mathematical formalism which can be applied to thermodynamics. Understanding of calculus of many variables at an undergraduate level is sufficient mathematical background for this chapter. Some details can be found in standard sources.[1][2][3]

3.1 Exact differentials and state functions

In thermodynamics, one is faced with many systems of the form of the well-known Gibbs equation:

$$de = Tds - Pdv. \tag{3.1}$$

This is known to be an exact differential with the consequence that internal energy e is a function of the state of the system and not the details of any process which led to the state. As a counter-example, the work,

$$\delta w = Pdv, \tag{3.2}$$

can be shown to be an inexact differential. Thus, the work depends upon the path of the process.

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[1]Abbott, M. M., and Van Ness, H. C., 1972, *Thermodynamics*, Schaum's Outline Series in Engineering, McGraw-Hill, New York. See Chapter 3.

[2]Borgnakke, C., and Sonntag, R. E, 2009, *Fundamentals of Thermodynamics*, Seventh Edition, John Wiley, New York. See Chapters 13 and 15.

[3]Vincenti, W. G., and Kruger, C. H., 1965, *Introduction to Physical Gas Dynamics*, John Wiley, New York. See Chapter 3.

Example 3.1

Show the work is not a state function.

If work were a state function, one might expect it to have the form

$$w = w(P, v), \qquad \textit{provisional assumption, to be tested.} \tag{3.3}$$

In such a case, one would have the corresponding differential form

$$dw = \left.\frac{\partial w}{\partial v}\right|_P dv + \left.\frac{\partial w}{\partial P}\right|_v dP. \tag{3.4}$$

Now, since $dw = P dv + 0 dP$, one deduces that

$$\left.\frac{\partial w}{\partial v}\right|_P = P, \tag{3.5}$$

$$\left.\frac{\partial w}{\partial P}\right|_v = 0. \tag{3.6}$$

Integrating Eq. (3.5), one finds

$$w = Pv + f(P), \tag{3.7}$$

where $f(P)$ is some function of P to be determined. Differentiating Eq. (3.7) with respect to P, one gets

$$\left.\frac{\partial w}{\partial P}\right|_v = v + \frac{df(P)}{dP}. \tag{3.8}$$

Now, use Eq. (3.6) to eliminate $\partial w/\partial P|_v$ in Eq. (3.8) so as to obtain

$$0 = v + \frac{df(P)}{dP}, \tag{3.9}$$

$$\frac{df(P)}{dP} = -v. \tag{3.10}$$

Equation (3.10) cannot be: a function of P only cannot be a function of v. So, w cannot be a state property:

$$w \neq w(P, v). \tag{3.11}$$

Consider now the more general form

$$\psi_1 dx_1 + \psi_2 dx_2 + \ldots + \psi_N dx_N = \sum_{i=1}^{N} \psi_i dx_i. \tag{3.12}$$

Here, ψ_i and x_i, $i = 1, \ldots, N$, may be thermodynamic variables. This form is known in mathematics as a *Pfaff*[4] *differential form*. As formulated, one takes at this stage

---

[4] Johann Friedrich Pfaff, 1765-1825, German mathematician.

- x_i: independent thermodynamic variables,

- ψ_i: thermodynamic variables which are functions of x_i

Now, if the differential in Eq. (3.12), when set to a differential dy, can be integrated to form the function

$$y = y(x_1, x_2, \ldots, x_N), \tag{3.13}$$

the differential is said to be *exact*. In such a case, one has

$$dy = \psi_1 dx_1 + \psi_2 dx_2 + \ldots + \psi_N dx_N = \sum_{i=1}^{N} \psi_i dx_i. \tag{3.14}$$

Now, if the algebraic definition of Eq. (3.13) holds, what amounts to the definition of the partial derivative gives the parallel result that

$$dy = \left.\frac{\partial y}{\partial x_1}\right|_{x_j, j \neq 1} dx_1 + \left.\frac{\partial y}{\partial x_2}\right|_{x_j, j \neq 2} dx_2 + \ldots + \left.\frac{\partial y}{\partial x_N}\right|_{x_j, j \neq N} dx_N. \tag{3.15}$$

Now, combining Eqs. (3.14) and (3.15) to eliminate dy, one gets

$$\psi_1 dx_1 + \psi_2 dx_2 + \ldots + \psi_N dx_N = \left.\frac{\partial y}{\partial x_1}\right|_{x_j, j \neq 1} dx_1 + \left.\frac{\partial y}{\partial x_2}\right|_{x_j, j \neq 2} dx_2 + \ldots + \left.\frac{\partial y}{\partial x_N}\right|_{x_j, j \neq N} dx_N. \tag{3.16}$$

Rearranging, one gets

$$0 = \left(\left.\frac{\partial y}{\partial x_1}\right|_{x_j, j \neq 1} - \psi_1\right) dx_1 + \left(\left.\frac{\partial y}{\partial x_2}\right|_{x_j, j \neq 2} - \psi_2\right) dx_2 + \ldots + \left(\left.\frac{\partial y}{\partial x_N}\right|_{x_j, j \neq N} - \psi_N\right) dx_N. \tag{3.17}$$

The variables x_i, $i = 1, \ldots, N$, are independent. Thus, their differentials, dx_i, $i = 1, \ldots, N$, are all independent in Eq. (3.17), and in general non-zero. For equality, one must require that *each* of the coefficients be zero, so

$$\psi_1 = \left.\frac{\partial y}{\partial x_1}\right|_{x_j, j \neq 1}, \quad \psi_2 = \left.\frac{\partial y}{\partial x_2}\right|_{x_j, j \neq 2}, \ldots, \quad \psi_N = \left.\frac{\partial y}{\partial x_N}\right|_{x_j, j \neq N}. \tag{3.18}$$

When dy is exact, one says that each of the ψ_i and x_i are *conjugate* to each other.

From here on out, for notational ease, the $j \neq 1, j \neq 2, \ldots, j \neq N$ will be ignored in the notation for the partial derivatives. It becomes especially confusing for higher order derivatives, and is fairly obvious for all derivatives.

If y and all its derivatives are continuous and differentiable, then one has for all $i = 1, \ldots, N$ and $k = 1, \ldots, N$ that

$$\frac{\partial^2 y}{\partial x_k \partial x_i} = \frac{\partial^2 y}{\partial x_i \partial x_k}. \tag{3.19}$$

Now, from Eq. (3.18), one has

$$\psi_k = \left.\frac{\partial y}{\partial x_k}\right|_{x_j}, \qquad \psi_l = \left.\frac{\partial y}{\partial x_l}\right|_{x_j}. \tag{3.20}$$

Taking the partial of the first of Eq. (3.20) with respect to x_l and the second with respect to x_k, one gets

$$\left.\frac{\partial \psi_k}{\partial x_l}\right|_{x_j} = \frac{\partial^2 y}{\partial x_l \partial x_k}, \qquad \left.\frac{\partial \psi_l}{\partial x_k}\right|_{x_j} = \frac{\partial^2 y}{\partial x_k \partial x_l}. \tag{3.21}$$

Since by Eq. (3.19) the order of the mixed second partials does not matter, one deduces from Eq. (3.21) that

$$\left.\frac{\partial \psi_k}{\partial x_l}\right|_{x_j} = \left.\frac{\partial \psi_l}{\partial x_k}\right|_{x_j} \tag{3.22}$$

This is a necessary and sufficient condition for the exact-ness of Eq. (3.12). It is a generalization of what can be found in most introductory calculus texts for functions of two variables.

For the Gibbs equation, (3.1), $de = -Pdv + Tds$, one has

$$y \to e, \quad x_1 \to v, \quad x_2 \to s, \quad \psi_1 \to -P \quad \psi_2 \to T. \tag{3.23}$$

and one expects the natural, or *canonical* form of

$$e = e(v, s). \tag{3.24}$$

Here, $-P$ is conjugate to v, and T is conjugate to s. Application of the general form of Eq. (3.22) to the Gibbs equation (3.1) gives then

$$\left.\frac{\partial T}{\partial v}\right|_s = -\left.\frac{\partial P}{\partial s}\right|_v. \tag{3.25}$$

Equation (3.25) is known as a *Maxwell*[5] *relation*. Moreover, specialization of Eq. (3.20) to the Gibbs equation (3.1) gives

$$-P = \left.\frac{\partial e}{\partial v}\right|_s, \qquad T = \left.\frac{\partial e}{\partial s}\right|_v. \tag{3.26}$$

If the general differential $dy = \sum_{i=1}^{N} \psi_i dx_i$ is exact, one also can show

- The path integral $y_B - y_A = \int_A^B \sum_{i=1}^{N} \psi_i dx_i$ is independent of the path of the integral.

- The integral around a closed contour is zero:

$$\oint dy = \oint \sum_{i=1}^{N} \psi_i dx_i = 0. \tag{3.27}$$

---

[5]James Clerk Maxwell, 1831-1879, Scottish physicist and mathematician.

- The function y can only be determined to within an additive constant. That is, there is no absolute value of y; physical significance is only ascribed to differences in y. In fact, other means, extraneous to this analysis, can be used to provide absolute specification of key thermodynamic variables. This will be important especially for flows with reaction.

Example 3.2

Show the heat transfer q is not a state function. Assume all processes are fully reversible. The first law gives

$$de = \delta q - \delta w, \tag{3.28}$$
$$\delta q = de + \delta w, \tag{3.29}$$
$$= de + P dv. \tag{3.30}$$

Take now the non-canonical, although acceptable, form $e = e(T, v)$. Then, one gets

$$de = \left.\frac{\partial e}{\partial v}\right|_T dv + \left.\frac{\partial e}{\partial T}\right|_v dT. \tag{3.31}$$

So

$$\delta q = \left.\frac{\partial e}{\partial v}\right|_T dv + \left.\frac{\partial e}{\partial T}\right|_v dT + P dv, \tag{3.32}$$

$$= \underbrace{\left(\left.\frac{\partial e}{\partial v}\right|_T + P\right)}_{\equiv M} dv + \underbrace{\left.\frac{\partial e}{\partial T}\right|_v}_{\equiv N} dT. \tag{3.33}$$

$$= M\ dv + N\ dT. \tag{3.34}$$

Now, by Eq. (3.22), for δq to be exact, one must have

$$\left.\frac{\partial M}{\partial T}\right|_v = \left.\frac{\partial N}{\partial v}\right|_T, \tag{3.35}$$

$$\tag{3.36}$$

This reduces to

$$\frac{\partial^2 e}{\partial T \partial v} + \left.\frac{\partial P}{\partial T}\right|_v = \frac{\partial^2 e}{\partial v \partial T}. \tag{3.37}$$

This can only be true if $\partial P/\partial T|_v = 0$. But this is not the case; consider an ideal gas for which $\partial P/\partial T|_v = 0 = R/v$. So, δq is not exact.

Example 3.3

Show conditions for ds to be exact in the Gibbs equation.

$$de = T ds - P dv, \tag{3.38}$$

$$ds \ = \ \frac{de}{T} + \frac{P}{T}dv, \tag{3.39}$$

$$= \ \frac{1}{T}\left(\left.\frac{\partial e}{\partial v}\right|_T dv + \left.\frac{\partial e}{\partial T}\right|_v dT\right) + \frac{P}{T}dv, \tag{3.40}$$

$$= \ \underbrace{\left(\frac{1}{T}\left.\frac{\partial e}{\partial v}\right|_T + \frac{P}{T}\right)}_{\equiv M} dv + \underbrace{\frac{1}{T}\left.\frac{\partial e}{\partial T}\right|_v}_{\equiv N} dT. \tag{3.41}$$

Again, invoking Eq. (3.22), one gets then

$$\left.\frac{\partial}{\partial T}\right|_v \underbrace{\left(\frac{1}{T}\left.\frac{\partial e}{\partial v}\right|_T + \frac{P}{T}\right)}_{M} \ = \ \left.\frac{\partial}{\partial v}\right|_T \underbrace{\left(\frac{1}{T}\left.\frac{\partial e}{\partial T}\right|_v\right)}_{N}, \tag{3.42}$$

$$\frac{1}{T}\frac{\partial^2 e}{\partial T\partial v} - \frac{1}{T^2}\left.\frac{\partial e}{\partial v}\right|_T + \frac{1}{T}\left.\frac{\partial P}{\partial T}\right|_v - \frac{P}{T^2} \ = \ \frac{1}{T}\frac{\partial^2 e}{\partial v\partial T}, \tag{3.43}$$

$$-\frac{1}{T^2}\left.\frac{\partial e}{\partial v}\right|_T + \frac{1}{T}\left.\frac{\partial P}{\partial T}\right|_v - \frac{P}{T^2} \ = \ 0. \tag{3.44}$$

This is the condition for an exact ds. Experiment can show if it is true. For example, for an ideal gas, one finds from experiment that $e = e(T)$ and $Pv = RT$, so one gets

$$0 + \frac{1}{T}\frac{R}{v} - \frac{1}{T^2}\frac{RT}{v} \ = \ 0, \tag{3.45}$$

$$0 \ = \ 0. \tag{3.46}$$

So, ds is exact for an ideal gas. In fact, the relation is verified for so many gases, ideal and non-ideal, that one simply asserts that ds is exact, rendering s to be path-independent and a state variable.

3.2   Two independent variables

Consider a general implicit function linking three variables, x, y, z:

$$f(x, y, z) = 0. \tag{3.47}$$

In (x, y, z) space, this will represent a surface. If the function can be inverted, it will be possible to write the explicit forms

$$x = x(y, z), \qquad y = y(x, z), \qquad z = z(x, y). \tag{3.48}$$

Differentiating the first two of the Eqs. (3.48) gives

$$dx \ = \ \left.\frac{\partial x}{\partial y}\right|_z dy + \left.\frac{\partial x}{\partial z}\right|_y dz, \tag{3.49}$$

$$dy \ = \ \left.\frac{\partial y}{\partial x}\right|_z dx + \left.\frac{\partial y}{\partial z}\right|_x dz \tag{3.50}$$

Now, use Eq. (3.50) to eliminate dy in Eq. (3.49):

$$dx = \left.\frac{\partial x}{\partial y}\right|_z \underbrace{\left(\left.\frac{\partial y}{\partial x}\right|_z dx + \left.\frac{\partial y}{\partial z}\right|_x dz\right)}_{=dy} + \left.\frac{\partial x}{\partial z}\right|_y dz, \tag{3.51}$$

$$\left(1 - \left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z\right) dx = \left(\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x + \left.\frac{\partial x}{\partial z}\right|_y\right) dz, \tag{3.52}$$

$$0dx + 0dz = \underbrace{\left(\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z - 1\right)}_{=0} dx + \underbrace{\left(\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x + \left.\frac{\partial x}{\partial z}\right|_y\right)}_{=0} dz. \tag{3.53}$$

Since x and y are independent, so are dx and dy, and the coefficients on each in Eq. (3.53) must be zero. Therefore, from the coefficient on dx in Eq. (3.53)

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z - 1 = 0, \tag{3.54}$$

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z = 1, \tag{3.55}$$

$$\left.\frac{\partial x}{\partial y}\right|_z = \frac{1}{\left.\frac{\partial y}{\partial x}\right|_z}, \tag{3.56}$$

and also from the coefficient on dz in Eq. (3.53)

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x + \left.\frac{\partial x}{\partial z}\right|_y = 0, \tag{3.57}$$

$$\left.\frac{\partial x}{\partial z}\right|_y = -\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x, \tag{3.58}$$

$$\left.\frac{\partial x}{\partial z}\right|_y \left.\frac{\partial y}{\partial x}\right|_z \left.\frac{\partial z}{\partial y}\right|_x = -1. \tag{3.59}$$

If one now divides Eq. (3.49) by a fourth differential, dw, one gets

$$\frac{dx}{dw} = \left.\frac{\partial x}{\partial y}\right|_z \frac{dy}{dw} + \left.\frac{\partial x}{\partial z}\right|_y \frac{dz}{dw}. \tag{3.60}$$

Demanding that z be held constant in Eq. (3.60) gives

$$\left.\frac{\partial x}{\partial w}\right|_z = \left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial w}\right|_z, \tag{3.61}$$

$$\frac{\left.\frac{\partial x}{\partial w}\right|_z}{\left.\frac{\partial y}{\partial w}\right|_z} = \left.\frac{\partial x}{\partial y}\right|_z, \tag{3.62}$$

$$\left.\frac{\partial x}{\partial w}\right|_z \left.\frac{\partial w}{\partial y}\right|_z = \left.\frac{\partial x}{\partial y}\right|_z. \tag{3.63}$$

If $x = x(y, w)$, one then gets

$$dx = \left.\frac{\partial x}{\partial y}\right|_w dy + \left.\frac{\partial x}{\partial w}\right|_y dw. \tag{3.64}$$

Divide now by dy while holding z constant so

$$\left.\frac{\partial x}{\partial y}\right|_z = \left.\frac{\partial x}{\partial y}\right|_w + \left.\frac{\partial x}{\partial w}\right|_y \left.\frac{\partial w}{\partial y}\right|_z. \tag{3.65}$$

These general operations can be applied to a wide variety of thermodynamic operations.

Example 3.4

Apply Eq. (3.65) to a standard (P, v, T) system and let

$$\left.\frac{\partial x}{\partial y}\right|_z = \left.\frac{\partial T}{\partial v}\right|_s. \tag{3.66}$$

So, $T = x$, $v = y$, and $s = z$. Let now $e = w$. So, Eq. (3.65) becomes

$$\left.\frac{\partial T}{\partial v}\right|_s = \left.\frac{\partial T}{\partial v}\right|_e + \left.\frac{\partial T}{\partial e}\right|_v \left.\frac{\partial e}{\partial v}\right|_s. \tag{3.67}$$

Now, by definition

$$c_v = \left.\frac{\partial e}{\partial T}\right|_v, \tag{3.68}$$

so

$$\left.\frac{\partial T}{\partial e}\right|_v = \frac{1}{c_v}. \tag{3.69}$$

Now, by Eq. (3.26), one has $\partial e/\partial v|_s = -P$, so one gets

$$\left.\frac{\partial T}{\partial v}\right|_s = \left.\frac{\partial T}{\partial v}\right|_e - \frac{P}{c_v}. \tag{3.70}$$

For an ideal gas, $e = e(T)$. Inverting, one gets $T = T(e)$, and so $\partial T/\partial v|_e = 0$, thus

$$\left.\frac{\partial T}{\partial v}\right|_s = -\frac{P}{c_v}. \tag{3.71}$$

For an isentropic process in a calorically perfect ideal gas, one gets

$$\frac{dT}{dv} = -\frac{P}{c_v} = -\frac{RT}{c_v v}, \tag{3.72}$$

$$\frac{dT}{T} = -\frac{R}{c_v}\frac{dv}{v}, \tag{3.73}$$

$$= -(\gamma - 1)\frac{dv}{v}, \tag{3.74}$$

$$\ln\frac{T}{T_o} = (\gamma - 1)\ln\frac{v_o}{v}, \tag{3.75}$$

$$\frac{T}{T_o} = \left(\frac{v_o}{v}\right)^{\gamma - 1}. \tag{3.76}$$

3.3 Legendre transformations

The Gibbs equation (3.1), $de = -Pdv + Tds$, is the fundamental equation of classical thermodynamics. It is a canonical form which suggests the most natural set of variables in which to express internal energy e are s and v:

$$e = e(v, s). \tag{3.77}$$

However, v and s may not be convenient for a particular problem. There may be other combinations of variables whose canonical form gives a more useful set of independent variables for a particular problem. An example is the enthalpy:

$$h \equiv e + Pv. \tag{3.78}$$

Differentiating the enthalpy gives

$$dh = de + Pdv + vdP. \tag{3.79}$$

Use now Eq. (3.79) to eliminate de in the Gibbs equation, Eq. (3.1), to give

$$\underbrace{dh - Pdv - vdP}_{=de} = -Pdv + Tds, \tag{3.80}$$

$$dh = Tds + vdP. \tag{3.81}$$

So, the canonical variables for h are s and P. One then expects

$$h = h(s, P). \tag{3.82}$$

This exercise can be systematized with the Legendre[6] transformation,[7] which defines a set of second order polynomial combinations of variables. Consider again the exact differential Eq. (3.14):

$$dy = \psi_1 dx_1 + \psi_2 dx_2 + \ldots + \psi_N dx_N. \tag{3.83}$$

For N independent variables x_i and N conjugate variables ψ_i, by definition there are $2^N - 1$ Legendre transformed variables:

$$\tau_1 = \tau_1(\psi_1, x_2, x_3, \ldots, x_N) = y - \psi_1 x_1, \tag{3.84}$$

$$\tau_2 = \tau_2(x_1, \psi_2, x_3, \ldots, x_N) = y - \psi_2 x_2, \tag{3.85}$$

$$\vdots$$

$$\tau_N = \tau_N(x_1, x_2, x_3, \ldots, \psi_N) = y - \psi_N x_N, \tag{3.86}$$

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[6]Adrien-Marie Legendre, 1752-1833, French mathematician.

[7]Two differentiable functions f and g are said to be Legendre transformations of each other if their first derivatives are inverse functions of each other: $Df = (Dg)^{-1}$. With some effort, not shown here, one can prove that the Legendre transformations of this section satisfy this general condition.

$$\tau_{1,2} \quad = \quad \tau_{1,2}(\psi_1, \psi_2, x_3, \ldots, x_N) = y - \psi_1 x_1 - \psi_2 x_2, \tag{3.87}$$

$$\tau_{1,3} \quad = \quad \tau_{1,3}(\psi_1, x_2, \psi_3, \ldots, x_N) = y - \psi_1 x_1 - \psi_3 x_3, \tag{3.88}$$

$$\vdots \tag{3.89}$$

$$\tau_{1,\ldots,N} \quad = \quad \tau_{1,\ldots,N}(\psi_1, \psi_2, \psi_3, \ldots, \psi_N) = y - \sum_{i=1}^{N} \psi_i x_i. \tag{3.90}$$

Each τ is a new dependent variable. *Each τ has the property that when it is known as a function of its N canonical variables, the remaining N variables from the original expression (the x_i and the conjugate ψ_i) can be recovered by differentiation of τ.* In general this is not true for arbitrary transformations.

Example 3.5

Let $y = y(x_1, x_2, x_3)$. This has the associated differential form

$$dy = \psi_1 dx_1 + \psi_2 dx_2 + \psi_3 dx_3. \tag{3.91}$$

Choose now a Legendre transformed variable $\tau_1 \equiv z(\psi_1, x_2, x_3)$:

$$z = y - \psi_1 x_1. \tag{3.92}$$

Then

$$dz = \left.\frac{\partial z}{\partial \psi_1}\right|_{x_1, x_2} d\psi_1 + \left.\frac{\partial z}{\partial x_2}\right|_{\psi_1, x_3} dx_2 + \left.\frac{\partial z}{\partial x_3}\right|_{\psi_1, x_2} dx_3. \tag{3.93}$$

Now, differentiating Eq. (3.92), one also gets

$$dz = dy - \psi_1 dx_1 - x_1 d\psi_1. \tag{3.94}$$

Elimination of dy in Eq. (3.94) by using Eq. (3.91) gives

$$dz \quad = \quad \underbrace{\psi_1\ dx_1 + \psi_2\ dx_2 + \psi_3\ dx_3}_{=dy} - \psi_1\ dx_1 - x_1\ d\psi_1, \tag{3.95}$$

$$= \quad -x_1\ d\psi_1 + \psi_2\ dx_2 + \psi_3\ dx_3. \tag{3.96}$$

Thus, from Eq. (3.93), one gets

$$x_1 = -\left.\frac{\partial z}{\partial \psi_1}\right|_{x_2, x_3}, \qquad \psi_2 = \left.\frac{\partial z}{\partial x_2}\right|_{\psi_1, x_3}, \qquad \psi_3 = \left.\frac{\partial z}{\partial x_3}\right|_{\psi_1, x_2}. \tag{3.97}$$

So, the original expression had three independent variables, x_1, x_2, x_3, and three conjugate variables ψ_1, ψ_2, ψ_3. Definition of the Legendre function z with canonical variables ψ_1, x_2, and x_3 allowed determination of the remaining variables x_1, ψ_2, and ψ_3 in terms of the canonical variables.

For the Gibbs equation, (3.1), $de = -Pdv + Tds$, one has $y = e$, two canonical variables, $x_1 = v$ and $x_2 = s$, and two conjugates, $\psi_1 = -P$ and $\psi_2 = T$. Thus, $N = 2$, and one can

expect $2^2 - 1 = 3$ Legendre transformations. They are

$$\tau_1 = y - \psi_1 x_1 = h = h(P, s) \quad = \quad e + Pv, \quad \text{enthalpy}, \tag{3.98}$$

$$\tau_2 = y - \psi_2 x_2 = a = a(v, T) \quad = \quad e - Ts, \quad \text{Helmholtz free energy}, \tag{3.99}$$

$$\tau_{1,2} = y - \psi_1 x_1 - \psi_2 x_2 = g = g(P, T) \quad = \quad e + Pv - Ts, \quad \text{Gibbs free energy}. \tag{3.100}$$

It has already been shown for the enthalpy that $dh = Tds + vdP$, so that the canonical variables are s and P. One then also has

$$dh = \left. \frac{\partial h}{\partial s} \right|_P ds + \left. \frac{\partial h}{\partial P} \right|_s dP, \tag{3.101}$$

from which one deduces that

$$T = \left. \frac{\partial h}{\partial s} \right|_P, \qquad v = \left. \frac{\partial h}{\partial P} \right|_s. \tag{3.102}$$

From Eq. (3.102), a second Maxwell relation can be deduced by differentiation of the first with respect to P and the second with respect to s:

$$\left. \frac{\partial T}{\partial P} \right|_s = \left. \frac{\partial v}{\partial s} \right|_P. \tag{3.103}$$

The relations for Helmholtz[8] and Gibbs free energies each supply additional useful relations including two new Maxwell relations. First, consider the Helmholtz free energy

$$a \quad = \quad e - Ts, \tag{3.104}$$

$$da \quad = \quad de - Tds - sdT, \tag{3.105}$$

$$\quad = \quad (-Pdv + Tds) - Tds - sdT, \tag{3.106}$$

$$\quad = \quad -Pdv - sdT. \tag{3.107}$$

So, the canonical variables for a are v and T. The conjugate variables are $-P$ and $-s$. Thus

$$da \quad = \quad \left. \frac{\partial a}{\partial v} \right|_T dv + \left. \frac{\partial a}{\partial T} \right|_v dT. \tag{3.108}$$

So, one gets

$$-P = \left. \frac{\partial a}{\partial v} \right|_T, \qquad -s = \left. \frac{\partial a}{\partial T} \right|_v. \tag{3.109}$$

and the consequent Maxwell relation

$$\left. \frac{\partial P}{\partial T} \right|_v = \left. \frac{\partial s}{\partial v} \right|_T. \tag{3.110}$$

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[8]Hermann von Helmholtz, 1821-1894, German physician and physicist.

For the Gibbs free energy

$$g = \underbrace{e + Pv}_{=h} - Ts, \tag{3.111}$$

$$= h - Ts, \tag{3.112}$$

$$dg = dh - Tds - sdT, \tag{3.113}$$

$$= \underbrace{(Tds + vdP)}_{=dh} - Tds - sdT, \tag{3.114}$$

$$= vdP - sdT. \tag{3.115}$$

So, for Gibbs free energy, the canonical variables are P and T while the conjugate variables are v and $-s$. One then has $g = g(P, T)$, which gives

$$dg = \left.\frac{\partial g}{\partial P}\right|_T dP + \left.\frac{\partial g}{\partial T}\right|_P dT. \tag{3.116}$$

So, one finds

$$v = \left.\frac{\partial g}{\partial P}\right|_T, \qquad -s = \left.\frac{\partial g}{\partial T}\right|_P. \tag{3.117}$$

The resulting Maxwell function is then

$$\left.\frac{\partial v}{\partial T}\right|_P = -\left.\frac{\partial s}{\partial P}\right|_T. \tag{3.118}$$

Example 3.6
Canonical Form

If

$$h(s, P) = c_P T_o \left(\frac{P}{P_o}\right)^{R/c_P} \exp\left(\frac{s}{c_P}\right) + (h_o - c_P T_o), \tag{3.119}$$

and c_P, T_o, R, P_o, and h_o are all constants, derive both thermal and caloric state equations $P(v, T)$ and $e(v, T)$.

Now, for this material

$$\left.\frac{\partial h}{\partial s}\right|_P = T_o \left(\frac{P}{P_o}\right)^{R/c_P} \exp\left(\frac{s}{c_P}\right), \tag{3.120}$$

$$\left.\frac{\partial h}{\partial P}\right|_s = \frac{RT_o}{P_o} \left(\frac{P}{P_o}\right)^{R/c_P - 1} \exp\left(\frac{s}{c_P}\right). \tag{3.121}$$

Now, since

$$\left.\frac{\partial h}{\partial s}\right|_P = T, \tag{3.122}$$

$$\left.\frac{\partial h}{\partial P}\right|_s = v, \tag{3.123}$$

one has

$$T = T_o \left(\frac{P}{P_o} \right)^{R/c_P} \exp \left(\frac{s}{c_P} \right), \tag{3.124}$$

$$v = \frac{RT_o}{P_o} \left(\frac{P}{P_o} \right)^{R/c_P - 1} \exp \left(\frac{s}{c_P} \right). \tag{3.125}$$

Dividing one by the other gives

$$\frac{T}{v} = \frac{P}{R}, \tag{3.126}$$

$$Pv = RT, \tag{3.127}$$

which is the thermal equation of state for an ideal gas. Substituting from Eq. (3.124) into the canonical equation for h, Eq. (3.119), one also finds for the caloric equation of state

$$h = c_P T + (h_o - c_P T_o), \tag{3.128}$$

$$h = c_P (T - T_o) + h_o. \tag{3.129}$$

which is useful in itself, and shows we actually have a calorically perfect gas. Substituting in for T and T_o,

$$h = c_P \left(\frac{Pv}{R} - \frac{P_o v_o}{R} \right) + h_o. \tag{3.130}$$

Using $h \equiv e + Pv$ we get

$$e + Pv = c_P \left(\frac{Pv}{R} - \frac{P_o v_o}{R} \right) + e_o + P_o v_o \tag{3.131}$$

so

$$e = \left(\frac{c_P}{R} - 1 \right) Pv - \left(\frac{c_P}{R} - 1 \right) P_o v_o + u_o, \tag{3.132}$$

$$e = \left(\frac{c_P}{R} - 1 \right) (Pv - P_o v_o) + e_o, \tag{3.133}$$

$$e = \left(\frac{c_P}{R} - 1 \right) (RT - RT_o) + e_o, \tag{3.134}$$

$$e = (c_P - R)(T - T_o) + e_o, \tag{3.135}$$

$$e = (c_P - (c_P - c_v))(T - T_o) + e_o, \tag{3.136}$$

$$e = c_v (T - T_o) + e_o. \tag{3.137}$$

So, *one* canonical equation gives us all the information one needs. Oftentimes, it is difficult to do a single experiment to get the canonical form.

3.4 Heat capacity

Recall that

$$c_v = \left. \frac{\partial e}{\partial T} \right|_v, \tag{3.138}$$

$$c_P = \left. \frac{\partial h}{\partial T} \right|_P. \tag{3.139}$$

Then, perform operations on the Gibbs equation, Eq. (3.1):

$$de = Tds - Pdv, \tag{3.140}$$

$$\left.\frac{\partial e}{\partial T}\right|_v = T \left.\frac{\partial s}{\partial T}\right|_v, \tag{3.141}$$

$$c_v = T \left.\frac{\partial s}{\partial T}\right|_v. \tag{3.142}$$

Likewise,

$$dh = Tds + vdP, \tag{3.143}$$

$$\left.\frac{\partial h}{\partial T}\right|_P = T \left.\frac{\partial s}{\partial T}\right|_P, \tag{3.144}$$

$$c_P = T \left.\frac{\partial s}{\partial T}\right|_P. \tag{3.145}$$

One finds further useful relations by operating on the Gibbs equation, Eq. (3.1):

$$de = Tds - Pdv, \tag{3.146}$$

$$\left.\frac{\partial e}{\partial v}\right|_T = T \left.\frac{\partial s}{\partial v}\right|_T - P, \tag{3.147}$$

$$= T \left.\frac{\partial P}{\partial T}\right|_v - P. \tag{3.148}$$

So, one can then say

$$e = e(T, v), \tag{3.149}$$

$$de = \left.\frac{\partial e}{\partial T}\right|_v dT + \left.\frac{\partial e}{\partial v}\right|_T dv, \tag{3.150}$$

$$= c_v dT + \left(T \left.\frac{\partial P}{\partial T}\right|_v - P \right) dv. \tag{3.151}$$

For an ideal gas, one has

$$\left.\frac{\partial e}{\partial v}\right|_T = T \left.\frac{\partial P}{\partial T}\right|_v - P = T \left(\frac{R}{v}\right) - \frac{RT}{v}, \tag{3.152}$$

$$= 0. \tag{3.153}$$

Consequently, e is not a function of v for an ideal gas, so $e = e(T)$ alone. Since $h = e + Pv$ for an ideal gas reduces to $h = e + RT$

$$h = e(T) + RT = h(T). \tag{3.154}$$

Now, return to general equations of state. With $s = s(T, v)$ or $s = s(T, P)$, one gets

$$ds = \left.\frac{\partial s}{\partial T}\right|_v dT + \left.\frac{\partial s}{\partial v}\right|_T dv, \tag{3.155}$$

$$ds = \left.\frac{\partial s}{\partial T}\right|_P dT + \left.\frac{\partial s}{\partial P}\right|_T dP. \tag{3.156}$$

Now, using Eqs. (3.103, 3.118, 3.142, 3.145) one gets

$$ds = \frac{c_v}{T}dT + \left.\frac{\partial P}{\partial T}\right|_v dv, \tag{3.157}$$

$$ds = \frac{c_P}{T}dT - \left.\frac{\partial v}{\partial T}\right|_P dP. \tag{3.158}$$

Subtracting one from the other, one finds

$$0 = \frac{c_v - c_P}{T}dT + \left.\frac{\partial P}{\partial T}\right|_v dv + \left.\frac{\partial v}{\partial T}\right|_P dP, \tag{3.159}$$

$$(c_P - c_v)dT = T\left.\frac{\partial P}{\partial T}\right|_v dv + T\left.\frac{\partial v}{\partial T}\right|_P dP. \tag{3.160}$$

Now, divide both sides by dT and hold *either* P or v constant. In either case, one gets

$$c_P - c_v = T\left.\frac{\partial P}{\partial T}\right|_v \left.\frac{\partial v}{\partial T}\right|_P. \tag{3.161}$$

Example 3.7

For an ideal gas find $c_P - c_v$. For the ideal gas, $Pv = RT$, one has

$$\left.\frac{\partial P}{\partial T}\right|_v = \frac{R}{v}, \qquad \left.\frac{\partial v}{\partial T}\right|_P = \frac{R}{P}. \tag{3.162}$$

So

$$c_P - c_v = T\frac{R}{v}\frac{R}{P}, \tag{3.163}$$

$$= T\frac{R^2}{RT}, \tag{3.164}$$

$$= R. \tag{3.165}$$

This holds even if the ideal gas is calorically imperfect. That is

$$c_P(T) - c_v(T) = R. \tag{3.166}$$

For the ratio of specific heats for a general material, one can use Eqs. (3.142) and (3.145) to get

$$\gamma = \frac{c_P}{c_v} = \frac{T \left.\frac{\partial s}{\partial T}\right|_P}{T \left.\frac{\partial s}{\partial T}\right|_v}. \tag{3.167}$$

Then apply Eq. (3.56) to get

$$\gamma = \left.\frac{\partial s}{\partial T}\right|_P \left.\frac{\partial T}{\partial s}\right|_v. \tag{3.168}$$

Then apply Eq. (3.58) to get

$$\gamma = \left(-\left.\frac{\partial s}{\partial P}\right|_T \left.\frac{\partial P}{\partial T}\right|_s\right)\left(-\left.\frac{\partial T}{\partial v}\right|_s \left.\frac{\partial v}{\partial s}\right|_T\right), \tag{3.169}$$

$$= \left(\left.\frac{\partial v}{\partial s}\right|_T \left.\frac{\partial s}{\partial P}\right|_T\right)\left(\left.\frac{\partial P}{\partial T}\right|_s \left.\frac{\partial T}{\partial v}\right|_s\right), \tag{3.170}$$

$$= \left.\frac{\partial v}{\partial P}\right|_T \left.\frac{\partial P}{\partial v}\right|_s \tag{3.171}$$

The first term can be obtained from $P - v - T$ data. The second term is related to the isentropic sound speed of the material, which is also a measurable quantity.

Example 3.8

For a calorically perfect ideal gas with gas constant R and specific heat at constant volume c_v, find expressions for the thermodynamic variable s and thermodynamic potentials e, h, a, and g, as functions of T and P.

First, get the entropy:

$$de = Tds - Pdv, \tag{3.172}$$
$$Tds = de + Pdv, \tag{3.173}$$
$$Tds = c_v dT + Pdv, \tag{3.174}$$
$$ds = c_v \frac{dT}{T} + \frac{P}{T}\,dv, \tag{3.175}$$
$$= c_v \frac{dT}{T} + R\frac{dv}{v}, \tag{3.176}$$
$$\int ds = \int c_v \frac{dT}{T} + \int R\frac{dv}{v}, \tag{3.177}$$
$$s - s_0 = c_v \ln\frac{T}{T_0} + R\ln\frac{v}{v_0}, \tag{3.178}$$
$$\frac{s - s_0}{c_v} = \ln\frac{T}{T_0} + \frac{R}{c_v}\ln\frac{RT/P}{RT_0/P_0}, \tag{3.179}$$
$$= \ln\left(\frac{T}{T_0}\right) + \ln\left(\frac{T}{T_0}\frac{P_0}{P}\right)^{R/c_v}, \tag{3.180}$$

$$= \ln\left(\frac{T}{T_0}\right)^{1+R/c_v} + \ln\left(\frac{P_0}{P}\right)^{R/c_v}, \tag{3.181}$$

$$= \ln\left(\frac{T}{T_0}\right)^{1+(c_p-c_v)/c_v} + \ln\left(\frac{P_0}{P}\right)^{(c_p-c_v)/c_v}, \tag{3.182}$$

$$= \ln\left(\frac{T}{T_0}\right)^{\gamma} + \ln\left(\frac{P_0}{P}\right)^{\gamma-1}, \tag{3.183}$$

$$s = s_0 + c_v \ln\left(\frac{T}{T_0}\right)^{\gamma} + c_v \ln\left(\frac{P_0}{P}\right)^{\gamma-1}. \tag{3.184}$$

Now, for the calorically perfect ideal gas, one has

$$e = e_o + c_v(T - T_o). \tag{3.185}$$

For the enthalpy, one gets

$$h = e + Pv, \tag{3.186}$$

$$= e + RT, \tag{3.187}$$

$$= e_o + c_v(T - T_o) + RT, \tag{3.188}$$

$$= e_o + c_v(T - T_o) + RT + RT_o - RT_o, \tag{3.189}$$

$$= \underbrace{e_o + RT_o}_{=h_o} + c_v(T - T_o) + R(T - T_o), \tag{3.190}$$

$$= h_o + \underbrace{(c_v + R)}_{=c_p}(T - T_o), \tag{3.191}$$

$$= h_o + c_p(T - T_o). \tag{3.192}$$

For the Helmholtz free energy, one gets

$$a = e - Ts, \tag{3.193}$$

$$= e_o + c_v(T - T_o) - T\left(s_0 + c_v \ln\left(\frac{T}{T_0}\right)^{\gamma} + c_v \ln\left(\frac{P_0}{P}\right)^{\gamma-1}\right). \tag{3.194}$$

For the Gibbs free energy, one gets

$$g = h - Ts, \tag{3.195}$$

$$= h_o + c_p(T - T_o) - T\left(s_0 + c_v \ln\left(\frac{T}{T_0}\right)^{\gamma} + c_v \ln\left(\frac{P_0}{P}\right)^{\gamma-1}\right). \tag{3.196}$$

3.5 Van der Waals gas

A van der Waals[9] gas is a common model for a non-ideal gas. It can capture some of the behavior of a gas as it approaches the vapor dome. Its form is

$$P(T, v) = \frac{RT}{v - b} - \frac{a}{v^2}, \tag{3.197}$$

---

[9]Johannes Diderik van der Waals, 1837-1923, Dutch thermodynamicist.

where b accounts for the finite volume of the molecules, and a accounts for intermolecular forces.

Example 3.9

Find a general expression for $e(T, v)$ if

$$P(T, v) = \frac{RT}{v - b} - \frac{a}{v^2}. \tag{3.198}$$

Proceed as before. First, we have

$$de = \left.\frac{\partial e}{\partial T}\right|_v dT + \left.\frac{\partial e}{\partial v}\right|_T dv, \tag{3.199}$$

recalling from Eqs. (3.138) and (3.148) that

$$\left.\frac{\partial e}{\partial T}\right|_v = c_v, \qquad \left.\frac{\partial e}{\partial v}\right|_T = T \left.\frac{\partial P}{\partial T}\right|_v - P. \tag{3.200}$$

Now, for the van der Waals gas, we have

$$\left.\frac{\partial P}{\partial T}\right|_v = \frac{R}{v - b}, \tag{3.201}$$

$$T \left.\frac{\partial P}{\partial T}\right|_v - P = \frac{RT}{v - b} - P, \tag{3.202}$$

$$= \frac{RT}{v - b} - \left(\frac{RT}{v - b} - \frac{a}{v^2}\right) = \frac{a}{v^2}. \tag{3.203}$$

So, we have

$$\left.\frac{\partial e}{\partial v}\right|_T = \frac{a}{v^2}, \tag{3.204}$$

$$e(T, v) = -\frac{a}{v} + f(T). \tag{3.205}$$

Here, $f(T)$ is some as-of-yet arbitrary function of T. To evaluate $f(T)$, take the derivative with respect to T holding v constant:

$$\left.\frac{\partial e}{\partial T}\right|_v = \frac{df}{dT} = c_v. \tag{3.206}$$

Since f is a function of T at most, here c_v can be a function of T at most, so we allow $c_v = c_v(T)$. Integrating, we find $f(T)$ as

$$f(T) = C + \int_{T_o}^{T} c_v(\hat{T}) d\hat{T}, \tag{3.207}$$

where C is an integration constant. Thus, e is

$$e(T, v) = C + \int_{T_o}^{T} c_v(\hat{T}) d\hat{T} - \frac{a}{v}. \tag{3.208}$$

Taking $C = e_o + a/v_o$, we get

$$e(T, v) = e_o + \int_{T_o}^{T} c_v(\hat{T})d\hat{T} + a\left(\frac{1}{v_o} - \frac{1}{v}\right). \tag{3.209}$$

We also find

$$h = e + Pv = e_o + \int_{T_o}^{T} c_v(\hat{T})d\hat{T} + a\left(\frac{1}{v_o} - \frac{1}{v}\right) + Pv, \tag{3.210}$$

$$h(T, v) = e_o + \int_{T_o}^{T} c_v(\hat{T})d\hat{T} + a\left(\frac{1}{v_o} - \frac{1}{v}\right) + \frac{RTv}{v - b} - \frac{a}{v}. \tag{3.211}$$

3.6 Redlich-Kwong gas

The Redlich[10]-Kwong equation of state[11] is

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)T^{1/2}}. \tag{3.212}$$

It is modestly more accurate than the van der Waals equation in predicting material behavior.

Example 3.10

For the case in which $b = 0$, find an expression for $e(T, v)$ consistent with the Redlich-Kwong state equation.

Here, the equation of state is now

$$P = \frac{RT}{v} - \frac{a}{v^2 T^{1/2}}. \tag{3.213}$$

Proceeding as before, we have

$$\left.\frac{\partial e}{\partial v}\right|_T = T\left.\frac{\partial P}{\partial T}\right|_v - P, \tag{3.214}$$

$$= T\left(\frac{R}{v} + \frac{a}{2v^2 T^{3/2}}\right) - \left(\frac{RT}{v} - \frac{a}{v^2 T^{1/2}}\right), \tag{3.215}$$

$$= \frac{3a}{2v^2 T^{1/2}}. \tag{3.216}$$

Integrating, we find

$$e(T, v) = -\frac{3a}{2v T^{1/2}} + f(T). \tag{3.217}$$

---

[10]Otto Redlich, 1896-1978, Austrian chemical engineer.

[11]Redlich, O., and Kwong, J. N. S., 1949, "On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions," *Chemical Reviews*, 44(1): 233-244.

Here, $f(T)$ is a yet-to-be-specified function of temperature only. Now, the specific heat is found by the temperature derivative of e:

$$c_v(T, v) = \left. \frac{\partial e}{\partial T} \right|_v = \frac{3a}{4vT^{3/2}} + \frac{df}{dT}. \tag{3.218}$$

Obviously, for this material, c_v is a function of both T and v.

Let us define $c_{vo}(T)$ via

$$\frac{df}{dT} \equiv c_{vo}(T). \tag{3.219}$$

Integrating, then one gets

$$f(T) = C + \int_{T_o}^T c_{vo}(\hat{T}) \, d\hat{T}. \tag{3.220}$$

Let us take $C = e_o + 3a/2/v_o/T_o^{1/2}$. Thus, we arrive at the following expressions for $c_v(T, v)$ and $e(T, v)$:

$$c_v(T, v) \;\; = \;\; c_{vo}(T) + \frac{3a}{4vT^{3/2}}, \tag{3.221}$$

$$e(T, v) \;\; = \;\; e_o + \int_{T_o}^T c_{vo}(\hat{T}) \, d\hat{T} + \frac{3a}{2} \left(\frac{1}{v_o T_o^{1/2}} - \frac{1}{vT^{1/2}} \right). \tag{3.222}$$

3.7   Mixtures with variable composition

Consider now mixtures of N species. The focus here will be on extensive properties and molar properties. Assume that each species has n_i moles, and the total number of moles is $n = \sum_{i=1}^N n_i$. Now, one might expect the extensive energy to be a function of the entropy, the volume, *and* the number of moles of each species:

$$E = E(V, S, n_i). \tag{3.223}$$

The extensive version of the Gibbs law in which *all of the n_i are held constant* is

$$dE = -PdV + TdS. \tag{3.224}$$

Thus

$$\left. \frac{\partial E}{\partial V} \right|_{S,n_i} = -P, \qquad \left. \frac{\partial E}{\partial S} \right|_{V,n_i} = T. \tag{3.225}$$

In general, since $E = E(S, V, n_i)$, one should expect, for systems in which *the n_i are allowed to change* that

$$dE = \left. \frac{\partial E}{\partial V} \right|_{S,n_i} dV + \left. \frac{\partial E}{\partial S} \right|_{V,n_i} dS + \sum_{i=1}^N \left. \frac{\partial E}{\partial n_i} \right|_{S,V,n_j} dn_i. \tag{3.226}$$

Defining the new thermodynamic property, the *chemical potential* $\overline{\mu}_i$, as

$$\overline{\mu}_i \equiv \left.\frac{\partial E}{\partial n_i}\right|_{S,V,n_j}, \tag{3.227}$$

one has the important *Gibbs equation for multicomponent systems*:

$$dE = -PdV + TdS + \sum_{i=1}^{N}\overline{\mu}_i dn_i. \tag{3.228}$$

Obviously, by its definition, $\overline{\mu}_i$ is on a per mole basis, so it is given the appropriate overline notation. In Eq. (3.228), the independent variables and their conjugates are

$$
\begin{align}
x_1 &= V, & \psi_1 &= -P, \tag{3.229}\\
x_2 &= S, & \psi_2 &= T, \tag{3.230}\\
x_3 &= n_1, & \psi_3 &= \overline{\mu}_1, \tag{3.231}\\
x_4 &= n_2, & \psi_4 &= \overline{\mu}_2, \tag{3.232}\\
&\vdots & &\vdots \\
x_{N+2} &= n_N, & \psi_{N+2} &= \overline{\mu}_N. \tag{3.233}
\end{align}
$$

Equation (3.228) has $2^{N+1}-1$ Legendre functions. Three are in wide usage: the extensive analog to those earlier found. They are

$$
\begin{align}
H &= E + PV, \tag{3.234}\\
A &= E - TS, \tag{3.235}\\
G &= E + PV - TS. \tag{3.236}
\end{align}
$$

A set of non-traditional, but perfectly acceptable additional Legendre functions would be formed from $E - \overline{\mu}_1 n_1$. Another set would be formed from $E + PV - \overline{\mu}_2 n_2$. There are many more, but one in particular is sometimes noted in the literature: the so-called *grand potential*, Ω. The grand potential is defined as

$$\Omega \equiv E - TS - \sum_{i=1}^{N}\overline{\mu}_i n_i. \tag{3.237}$$

Differentiating each defined Legendre function, Eqs. (3.234-3.237), and combining with Eq. (3.228), one finds

$$
\begin{align}
dH &= TdS + VdP + \sum_{i=1}^{N}\overline{\mu}_i dn_i, \tag{3.238}\\
dA &= -SdT - PdV + \sum_{i=1}^{N}\overline{\mu}_i dn_i, \tag{3.239}
\end{align}
$$

$$dG = -SdT + VdP + \sum_{i=1}^{N}\overline{\mu}_i dn_i, \tag{3.240}$$

$$d\Omega = -PdV - SdT - \sum_{i=1}^{N} n_i d\overline{\mu}_i. \tag{3.241}$$

Thus, canonical variables for H are $H = H(S, P, n_i)$. One finds a similar set of relations as before from each of the differential forms:

$$T = \left.\frac{\partial E}{\partial S}\right|_{V,n_i} = \left.\frac{\partial H}{\partial S}\right|_{P,n_i}, \tag{3.242}$$

$$P = -\left.\frac{\partial E}{\partial V}\right|_{S,n_i} = -\left.\frac{\partial A}{\partial V}\right|_{T,n_i} = -\left.\frac{\partial \Omega}{\partial V}\right|_{T,\overline{\mu}_i}, \tag{3.243}$$

$$V = \left.\frac{\partial H}{\partial P}\right|_{S,n_i} = \left.\frac{\partial G}{\partial P}\right|_{T,n_i}, \tag{3.244}$$

$$S = -\left.\frac{\partial A}{\partial T}\right|_{V,n_i} = -\left.\frac{\partial G}{\partial T}\right|_{P,n_i} = -\left.\frac{\partial \Omega}{\partial T}\right|_{V,\overline{\mu}_i}, \tag{3.245}$$

$$n_i = -\left.\frac{\partial \Omega}{\partial \overline{\mu}_i}\right|_{V,T,\overline{\mu}_j}, \tag{3.246}$$

$$\overline{\mu}_i = \left.\frac{\partial E}{\partial n_i}\right|_{S,V,n_j} = \left.\frac{\partial H}{\partial n_i}\right|_{S,P,n_j} = \left.\frac{\partial A}{\partial n_i}\right|_{T,V,n_j} = \left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_j}. \tag{3.247}$$

Each of these induces a corresponding Maxwell relation, obtained by cross differentiation. These are

$$\left.\frac{\partial T}{\partial V}\right|_{S,n_i} = -\left.\frac{\partial P}{\partial S}\right|_{V,n_i}, \tag{3.248}$$

$$\left.\frac{\partial T}{\partial P}\right|_{S,n_i} = \left.\frac{\partial V}{\partial S}\right|_{P,n_i}, \tag{3.249}$$

$$\left.\frac{\partial P}{\partial T}\right|_{V,n_i} = \left.\frac{\partial S}{\partial V}\right|_{T,n_i}, \tag{3.250}$$

$$\left.\frac{\partial V}{\partial T}\right|_{P,n_i} = -\left.\frac{\partial S}{\partial P}\right|_{T,n_i}, \tag{3.251}$$

$$\left.\frac{\partial \overline{\mu}_i}{\partial T}\right|_{P,n_j} = -\left.\frac{\partial S}{\partial n_i}\right|_{V,n_j}, \tag{3.252}$$

$$\left.\frac{\partial \overline{\mu}_i}{\partial P}\right|_{T,n_j} = \left.\frac{\partial V}{\partial n_i}\right|_{V,n_j}, \tag{3.253}$$

$$\left.\frac{\partial \overline{\mu}_l}{\partial n_k}\right|_{T,P,n_j} = \left.\frac{\partial \overline{\mu}_k}{\partial n_l}\right|_{T,P,n_j}, \tag{3.254}$$

$$\left.\frac{\partial S}{\partial V}\right|_{T,\overline{\mu}_i} = \left.\frac{\partial P}{\partial T}\right|_{V,\overline{\mu}_i}, \tag{3.255}$$

$$\left.\frac{\partial n_i}{\partial \overline{\mu}_k}\right|_{V,T,\overline{\mu}_j,j\neq k} = \left.\frac{\partial n_k}{\partial \overline{\mu}_i}\right|_{V,T,\overline{\mu}_j,j\neq i}. \tag{3.256}$$

3.8 Partial molar properties

3.8.1 Homogeneous functions

In mathematics, a *homogeneous function* $f(x_1,\ldots,x_N)$ *of order* m is one such that

$$f(\lambda x_1,\ldots,\lambda x_N) = \lambda^m f(x_1,\ldots,x_N). \tag{3.257}$$

If $m = 1$, one has

$$f(\lambda x_1,\ldots,\lambda x_N) = \lambda f(x_1,\ldots,x_N). \tag{3.258}$$

Thermodynamic variables are examples of homogeneous functions.

3.8.2 Gibbs free energy

Consider an extensive property, such as the Gibbs free energy G. One has the canonical form

$$G = G(T,P,n_1,n_2,\ldots,n_N). \tag{3.259}$$

One would like to show that if each of the mole numbers n_i is increased by a common factor, say λ, with T and P constant, that G increases by the same factor λ:

$$\lambda G(T,P,n_1,n_2,\ldots,n_N) = G(T,P,\lambda n_1,\lambda n_2,\ldots,\lambda n_N). \tag{3.260}$$

Differentiate both sides of Eq. (3.260) with respect to λ, while holding P, T, and n_j constant, to get

$$G(T,P,n_1,n_2,\ldots,n_N) =$$
$$\left.\frac{\partial G}{\partial(\lambda n_1)}\right|_{n_j,P,T}\frac{d(\lambda n_1)}{d\lambda} + \left.\frac{\partial G}{\partial(\lambda n_2)}\right|_{n_j,P,T}\frac{d(\lambda n_2)}{d\lambda} + \ldots + \left.\frac{\partial G}{\partial(\lambda n_N)}\right|_{n_j,P,T}\frac{d(\lambda n_N)}{d\lambda}, \tag{3.261}$$

$$= \left.\frac{\partial G}{\partial(\lambda n_1)}\right|_{n_j,P,T}n_1 + \left.\frac{\partial G}{\partial(\lambda n_2)}\right|_{n_j,P,T}n_2 + \ldots + \left.\frac{\partial G}{\partial(\lambda n_N)}\right|_{n_j,P,T}n_N, \tag{3.262}$$

This must hold for all λ, including $\lambda = 1$, so one requires

$$G(T,P,n_1,n_2,\ldots,n_N) = \left.\frac{\partial G}{\partial n_1}\right|_{n_j,P,T}n_1 + \left.\frac{\partial G}{\partial n_2}\right|_{n_j,P,T}n_2 + \ldots + \left.\frac{\partial G}{\partial n_N}\right|_{n_j,P,T}n_N,$$
$$\tag{3.263}$$

$$= \sum_{i=1}^{N}\left.\frac{\partial G}{\partial n_i}\right|_{n_j,P,T}n_i. \tag{3.264}$$

Recall now from p. 77 the definition *partial molar property*, the derivative of an extensive variable with respect to species n_i holding n_j, $i \neq j$, T, and P constant. Because the result has units which are per unit mole, an overline superscript is utilized. The partial molar Gibbs free energy of species i, $\overline{g}_i$ is then

$$\overline{g}_i \equiv \left. \frac{\partial G}{\partial n_i} \right|_{n_j, P, T}, \tag{3.265}$$

so that Eq. (3.264) becomes

$$G = \sum_{i=1}^{N} \overline{g}_i n_i. \tag{3.266}$$

Using the definition of chemical potential, Eq. (3.247), one also notes then that

$$G(T, P, n_2, n_2, \ldots, n_N) = \sum_{i=1}^{N} \overline{\mu}_i n_i. \tag{3.267}$$

The temperature and pressure dependence of G must lie entirely within $\overline{\mu}_i(T, P, n_j)$, which one notes is also allowed to be a function of n_j as well. Consequently, one also sees that the Gibbs free energy per unit mole of species i is the chemical potential of that species:

$$\overline{g}_i = \overline{\mu}_i. \tag{3.268}$$

Using Eq. (3.266) to eliminate G in Eq. (3.236), one recovers an equation for the energy:

$$E = -PV + TS + \sum_{i=1}^{N} \overline{\mu}_i n_i. \tag{3.269}$$

3.8.3   Other properties

A similar result also holds for any other extensive property such as V, E, H, A, or S. One can also show that

$$V = \sum_{i=1}^{N} n_i \left. \frac{\partial V}{\partial n_i} \right|_{n_j, A, T}, \tag{3.270}$$

$$E = \sum_{i=1}^{N} n_i \left. \frac{\partial E}{\partial n_i} \right|_{n_j, V, S} \tag{3.271}$$

$$H = \sum_{i=1}^{N} n_i \left. \frac{\partial H}{\partial n_i} \right|_{n_j, P, S}, \tag{3.272}$$

$$A = \sum_{i=1}^{N} n_i \left. \frac{\partial A}{\partial n_i} \right|_{n_j, T, V}, \tag{3.273}$$

$$S = \sum_{i=1}^{N} n_i \left. \frac{\partial S}{\partial n_i} \right|_{n_j, E, T}. \tag{3.274}$$

Note that these expressions do not formally involve partial molar properties since P and T are not constant.

Take now the appropriate partial molar derivatives of G for an ideal mixture of ideal gases to get some useful relations:

$$G = H - TS, \tag{3.275}$$

$$\left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_j} = \left.\frac{\partial H}{\partial n_i}\right|_{T,P,n_j} - T\left.\frac{\partial S}{\partial n_i}\right|_{T,P,n_j}. \tag{3.276}$$

Now, from the definition of an ideal mixture $\overline{h}_i = \overline{h}_i(T,P)$, so one has

$$H = \sum_{k=1}^{N} n_k \overline{h}_k(T,P), \tag{3.277}$$

$$\left.\frac{\partial H}{\partial n_i}\right|_{T,P,n_j} = \frac{\partial}{\partial n_i}\left(\sum_{k=1}^{N} n_k \overline{h}_k(T,P)\right), \tag{3.278}$$

$$= \sum_{k=1}^{N} \underbrace{\frac{\partial n_k}{\partial n_i}}_{=\delta_{ik}} \overline{h}_k(T,P), \tag{3.279}$$

$$= \sum_{k=1}^{N} \delta_{ik} \overline{h}_k(T,P), \tag{3.280}$$

$$= \overline{h}_i(T,P). \tag{3.281}$$

Here, the Kronecker delta function δ_{ki} has been again used. Now, for an ideal gas one further has $\overline{h}_i = \overline{h}_i(T)$. The analysis is more complicated for the entropy, in which

$$S = \sum_{k=1}^{N} n_k\left(\overline{s}_{T,k}^o - \overline{R}\ln\left(\frac{P_k}{P_o}\right)\right), \tag{3.282}$$

$$= \sum_{k=1}^{N} n_k\left(\overline{s}_{T,k}^o - \overline{R}\ln\left(\frac{y_k P}{P_o}\right)\right), \tag{3.283}$$

$$= \sum_{k=1}^{N} n_k\left(\overline{s}_{T,k}^o - \overline{R}\ln\left(\frac{P}{P_o}\right) - \overline{R}\ln\left(\frac{n_k}{\sum_{q=1}^{N} n_q}\right)\right), \tag{3.284}$$

$$= \sum_{k=1}^{N} n_k\left(\overline{s}_{T,k}^o - \overline{R}\ln\left(\frac{P}{P_o}\right)\right) - \overline{R}\sum_{k=1}^{N} n_k\ln\left(\frac{n_k}{\sum_{q=1}^{N} n_q}\right), \tag{3.285}$$

$$\left.\frac{\partial S}{\partial n_i}\right|_{T,P,n_j} = \frac{\partial}{\partial n_i}\sum_{k=1}^{N} n_k\left(\overline{s}_{T,k}^o - \overline{R}\ln\left(\frac{P}{P_o}\right)\right)$$

$$- \overline{R}\left.\frac{\partial}{\partial n_i}\right|_{T,P,n_j}\left(\sum_{k=1}^{N} n_k\ln\left(\frac{n_k}{\sum_{q=1}^{N} n_q}\right)\right), \tag{3.286}$$

$$= \sum_{k=1}^{N} \underbrace{\frac{\partial n_k}{\partial n_i}}_{=\delta_{ik}} \left(\overline{s}^o_{T,k} - \overline{R} \ln \left(\frac{P}{P_o} \right) \right)$$

$$- \overline{R} \left. \frac{\partial}{\partial n_i} \right|_{T,P,n_j} \left(\sum_{k=1}^{N} n_k \ln \left(\frac{n_k}{\sum_{q=1}^{N} n_q} \right) \right), \tag{3.287}$$

$$= \left(\overline{s}^o_{T,i} - \overline{R} \ln \left(\frac{P}{P_o} \right) \right) - \overline{R} \left. \frac{\partial}{\partial n_i} \right|_{T,P,n_j} \left(\sum_{k=1}^{N} n_k \ln \left(\frac{n_k}{\sum_{q=1}^{N} n_q} \right) \right). \tag{3.288}$$

Evaluation of the final term on the right side requires closer examination, and in fact, after tedious but straightforward analysis, yields a simple result which can easily be verified by direct calculation:

$$\left. \frac{\partial}{\partial n_i} \right|_{T,P,n_j} \left(\sum_{k=1}^{N} n_k \ln \left(\frac{n_k}{\sum_{q=1}^{N} n_q} \right) \right) = \ln \left(\frac{n_i}{\sum_{q=1}^{N} n_q} \right). \tag{3.289}$$

So, the partial molar entropy is in fact

$$\left. \frac{\partial S}{\partial n_i} \right|_{T,P,n_j} = \overline{s}^o_{T,i} - \overline{R} \ln \left(\frac{P}{P_o} \right) - \overline{R} \ln \left(\frac{n_i}{\sum_{q=1}^{N} n_q} \right), \tag{3.290}$$

$$= \overline{s}^o_{T,i} - \overline{R} \ln \left(\frac{P}{P_o} \right) - \overline{R} \ln y_i, \tag{3.291}$$

$$= \overline{s}^o_{T,i} - \overline{R} \ln \left(\frac{P_i}{P_o} \right), \tag{3.292}$$

$$= \overline{s}_i. \tag{3.293}$$

Thus, one can in fact claim for the ideal mixture of ideal gases that

$$\overline{g}_i = \overline{h}_i - T \overline{s}_i. \tag{3.294}$$

3.8.4　Relation between mixture and partial molar properties

A simple analysis shows how the partial molar property for an individual species is related to the partial molar property for the mixture. Consider, for example, the Gibbs free energy. The mixture-averaged Gibbs free energy per unit mole is

$$\overline{g} = \frac{G}{n}. \tag{3.295}$$

Now, take a partial molar derivative and analyze to get

$$\left. \frac{\partial \overline{g}}{\partial n_i} \right|_{T,P,n_j} = \frac{1}{n} \left. \frac{\partial G}{\partial n_i} \right|_{T,P,n_j} - \frac{G}{n^2} \left. \frac{\partial n}{\partial n_i} \right|_{T,P,n_j}, \tag{3.296}$$

$$= \frac{1}{n} \left. \frac{\partial G}{\partial n_i} \right|_{T,P,n_j} - \frac{G}{n^2} \left. \frac{\partial}{\partial n_i} \right|_{T,P,n_j} \left(\sum_{k=1}^{N} n_k \right), \tag{3.297}$$

$$= \frac{1}{n} \left. \frac{\partial G}{\partial n_i} \right|_{T,P,n_j} - \frac{G}{n^2} \sum_{k=1}^{N} \left. \frac{\partial n_k}{\partial n_i} \right|_{T,P,n_j}, \tag{3.298}$$

$$= \frac{1}{n} \left. \frac{\partial G}{\partial n_i} \right|_{T,P,n_j} - \frac{G}{n^2} \sum_{k=1}^{N} \delta_{ik}, \tag{3.299}$$

$$= \frac{1}{n} \left. \frac{\partial G}{\partial n_i} \right|_{T,P,n_j} - \frac{G}{n^2}, \tag{3.300}$$

$$= \frac{1}{n} \overline{g}_i - \frac{\overline{g}}{n}. \tag{3.301}$$

Multiplying by n and rearranging, one gets

$$\overline{g}_i = \overline{g} + n \left. \frac{\partial \overline{g}}{\partial n_i} \right|_{T,P,n_j}. \tag{3.302}$$

A similar result holds for other properties.

3.9 Frozen sound speed

Let us develop a relation for what is known as the "frozen sound speed," denoted as c. This quantity is a thermodynamic property defined by the relationship

$$c^2 \equiv \left. \frac{\partial P}{\partial \rho} \right|_{s,n_i}. \tag{3.303}$$

Later in Sec. 10.1.7 we shall see that this quantity describes the speed of acoustic waves, but at this point let us simply treat it as a problem in thermodynamics. The quantity is called "frozen" because the derivative is performed with all of the species mole numbers frozen at a constant value. Note that since $v = 1/\rho$,

$$c^2 = \left. \frac{\partial P}{\partial \rho} \right|_{s,n_i} = \frac{dv}{d\rho} \left. \frac{\partial P}{\partial v} \right|_{s,n_i} = -\frac{1}{\rho^2} \left. \frac{\partial P}{\partial v} \right|_{s,n_i} = -v^2 \left. \frac{\partial P}{\partial v} \right|_{s,n_i}. \tag{3.304}$$

So, we can say

$$(\rho c)^2 = - \left. \frac{\partial P}{\partial v} \right|_{s,n_i}. \tag{3.305}$$

Now, we know that the caloric equation of state for a mixture of ideal gases takes the form, from Eq. (2.162):

$$e = \sum_{i=1}^{N} Y_i e_i(T). \tag{3.306}$$

Employing the ideal gas law, we could say instead

$$e = \sum_{i=1}^{N} Y_i e_i \left(\frac{P}{\rho R} \right). \tag{3.307}$$

In terms of number of moles, n_i, we could say

$$e = \sum_{i=1}^{N} \underbrace{\frac{M_i n_i}{\rho V}}_{=Y_i} e_i \left(\frac{P}{\rho R} \right). \tag{3.308}$$

We can in fact generalize, and simply consider caloric equations of state of the form

$$e = e(P, \rho, n_i), \tag{3.309}$$

or in terms of the specific volume $v = 1/\rho$,

$$e = e(P, v, n_i). \tag{3.310}$$

These last two forms can be useful when temperature is unavailable, as can be the case for some materials.

Now, reconsider the Gibbs equation for a multicomponent system, Eq. (3.228):

$$dE = -P dV + T dS + \sum_{i=1}^{N} \overline{\mu}_i dn_i. \tag{3.311}$$

Let us scale Eq. (3.311) by a fixed mass m, recalling that $e = E/m$, $v = V/m$, and $s = S/m$, so as to obtain

$$de = -P dv + T ds + \sum_{i=1}^{N} \frac{\overline{\mu}_i}{m} dn_i. \tag{3.312}$$

Considering Eq. (3.312) with $dv = 0$ and $dn_i = 0$, and scaling by dP, we can say

$$\left. \frac{\partial e}{\partial P} \right|_{v, n_i} = T \left. \frac{\partial s}{\partial P} \right|_{v, n_i}. \tag{3.313}$$

Considering Eq. (3.312) with $dn_i = 0$, and $dP = 0$ and scaling by dv, we can say

$$\left. \frac{\partial e}{\partial v} \right|_{P, n_i} = -P + T \left. \frac{\partial s}{\partial v} \right|_{P, n_i}. \tag{3.314}$$

Applying now Eq. (3.59), we find

$$\left. \frac{\partial P}{\partial v} \right|_{s, n_i} \left. \frac{\partial s}{\partial P} \right|_{v, n_i} \left. \frac{\partial v}{\partial s} \right|_{P, n_i} = -1. \tag{3.315}$$

So, we get

$$\frac{\partial P}{\partial v}\bigg|_{s,n_i} = -\frac{\frac{\partial s}{\partial v}\big|_{P,n_i}}{\frac{\partial s}{\partial P}\big|_{v,n_i}}. \tag{3.316}$$

Substituting Eq. (3.316) into Eq. (3.305) we find

$$(\rho c)^2 = \frac{\frac{\partial s}{\partial v}\big|_{P,n_i}}{\frac{\partial s}{\partial P}\big|_{v,n_i}}. \tag{3.317}$$

Substituting Eqs. (3.313,3.314) into Eq. (3.317) we get

$$(\rho c)^2 = \frac{\frac{1}{T}\left(P + \frac{\partial e}{\partial v}\big|_{P,n_i}\right)}{\frac{1}{T}\frac{\partial e}{\partial P}\big|_{v,n_i}}, \tag{3.318}$$

$$= \frac{P + \frac{\partial e}{\partial v}\big|_{P,n_i}}{\frac{\partial e}{\partial P}\big|_{v,n_i}}. \tag{3.319}$$

So, the sound speed c is

$$c = v\sqrt{\frac{P + \frac{\partial e}{\partial v}\big|_{P,n_i}}{\frac{\partial e}{\partial P}\big|_{v,n_i}}}. \tag{3.320}$$

Eq. (3.320) is useful because we can identify the frozen sound speed from data for e, P, and v alone. If

$$\frac{\partial e}{\partial v}\bigg|_{P,n_i} > -P, \qquad \text{and} \qquad \frac{\partial e}{\partial P}\bigg|_{v,n_i} > 0, \tag{3.321}$$

we will have a real sound speed. Other combinations are possible as well, but not observed in nature.

Example 3.11

For an ideal mixture of calorically perfect ideal gases, find the frozen sound speed.

For a calorically perfect ideal gas, we have

$$e_i = e_i(T) = e_o + c_{vi}(T - T_o), \tag{3.322}$$

$$= e_o + c_{vi}\left(\frac{Pv}{R} - T_o\right). \tag{3.323}$$

and

$$e = \sum_{i=1}^{N} Y_i e_i, \tag{3.324}$$

$$= \sum_{i=1}^{N} \frac{m_i}{m} e_i, \tag{3.325}$$

$$= \sum_{i=1}^{N} \frac{n_i M_i}{m} e_i, \tag{3.326}$$

$$= \sum_{i=1}^{N} \frac{n_i M_i}{m} \left(e_o + c_{vi} \left(\frac{Pv}{R} - T_o \right) \right). \tag{3.327}$$

Thus, we get the two relevant partial derivatives

$$\left. \frac{\partial e}{\partial v} \right|_{P,n_i} = \sum_{i=1}^{N} \frac{n_i M_i}{m} c_{vi} \frac{P}{R} = \frac{P}{R} \sum_{i=1}^{N} Y_i c_{vi} = \frac{P c_v}{R}, \tag{3.328}$$

$$\left. \frac{\partial e}{\partial P} \right|_{v,n_i} = \sum_{i=1}^{N} \frac{n_i M_i}{m} c_{vi} \frac{v}{R} = \frac{v}{R} \sum_{i=1}^{N} Y_i c_{vi} = \frac{v c_v}{R}. \tag{3.329}$$

Now, substitute Eqs. (3.328, 3.329) into Eq. (3.320) to get

$$c = v \sqrt{\frac{P + \frac{P c_v}{R}}{\frac{v c_v}{R}}}, \tag{3.330}$$

$$= \sqrt{\frac{Pv + \frac{Pv c_v}{R}}{\frac{c_v}{R}}}, \tag{3.331}$$

$$= \sqrt{\frac{RT + \frac{RT c_v}{R}}{\frac{c_v}{R}}}, \tag{3.332}$$

$$= \sqrt{RT \frac{1 + \frac{c_v}{R}}{\frac{c_v}{R}}}, \tag{3.333}$$

$$= \sqrt{RT \frac{R + c_v}{c_v}}, \tag{3.334}$$

$$= \sqrt{RT \frac{(c_P - c_v) + c_v}{c_v}}, \tag{3.335}$$

$$= \sqrt{RT \frac{c_P}{c_v}}, \tag{3.336}$$

$$= \sqrt{\gamma RT}. \tag{3.337}$$

3.10   Irreversibility in a closed multicomponent system

Consider a thermodynamic system *closed to mass exchanges with its surroundings* coming into equilibrium. Allow the system to be exchanging work and heat with its surroundings. Assume the temperature difference between the system and its surroundings is so small that

both can be considered to be at temperature T. If δQ is introduced into the system, then the surroundings suffer a loss of entropy:

$$dS_{surr} = -\frac{\delta Q}{T}. \tag{3.338}$$

The system's entropy S can change via this heat transfer, as well as via other internal irreversible processes, such as internal chemical reaction. The second law of thermodynamics requires that the entropy change of the universe be positive semi-definite:

$$dS + dS_{surr} \geq 0. \tag{3.339}$$

Eliminating dS_{surr}, one requires for the system that

$$dS \geq \frac{\delta Q}{T}. \tag{3.340}$$

Consider temporarily the assumption that the work and heat transfer are both reversible. Thus, the irreversibilities must be associated with internal chemical reaction. Now, the first law for the entire system gives

$$
\begin{aligned}
dE &= \delta Q - \delta W, & (3.341)\\
&= \delta Q - PdV, & (3.342)\\
\delta Q &= dE + PdV. & (3.343)
\end{aligned}
$$

Note because the system is closed, there can be no species entering or exiting, and so there is no change dE attributable to dn_i. While within the system the dn_i may not be 0, the *net* contribution to the change in total internal energy is zero. A non-zero dn_i within the system simply re-partitions a fixed amount of total energy from one species to another. Substituting Eq. (3.343) into Eq. (3.340) to eliminate δQ, one gets

$$dS \geq \frac{1}{T}\underbrace{(dE + PdV)}_{=\delta Q}, \tag{3.344}$$

$$
\begin{aligned}
TdS - dE - PdV &\geq 0, & (3.345)\\
dE - TdS + PdV &\leq 0. & (3.346)
\end{aligned}
$$

Eq. (3.346) involves properties only and need not require assumptions of reversibility for processes in its derivation. In special cases, it reduces to simpler forms.

For processes which are isentropic and isochoric, the second law expression, Eq. (3.346), reduces to

$$dE|_{S,V} \leq 0. \tag{3.347}$$

For processes which are isoenergetic and isochoric, the second law expression, Eq. (3.346), reduces to

$$dS|_{E,V} \geq 0. \tag{3.348}$$

Now, using Eq. (3.228) to eliminate dS in Eq. (3.348), one can express the second law as

$$\underbrace{\left(\frac{1}{T}dE + \frac{P}{T}dV - \frac{1}{T}\sum_{i=1}^{N}\overline{\mu}_i dn_i\right)}_{=dS}\Bigg|_{E,V} \geq 0, \tag{3.349}$$

$$\underbrace{-\frac{1}{T}\sum_{i=1}^{N}\overline{\mu}_i dn_i}_{\text{irreversibility}} \geq 0. \tag{3.350}$$

The irreversibility associated with the internal chemical reaction must be the left side of Eq. (3.350).

Now, while most standard texts focusing on equilibrium thermodynamics go to great lengths to avoid the introduction of time, it really belongs in a discussion describing the approach to equilibrium. One can divide Eq. (3.350) by a *positive* time increment dt to get

$$-\frac{1}{T}\sum_{i=1}^{N}\overline{\mu}_i \frac{dn_i}{dt} \geq 0. \tag{3.351}$$

Since $T \geq 0$, one can multiply Eq. (3.351) by $-T$ to get

$$\sum_{i=1}^{N}\overline{\mu}_i \frac{dn_i}{dt} \leq 0. \tag{3.352}$$

This will hold *if* a model for dn_i/dt is employed which guarantees that the left side of Eq. (3.352) is negative semi-definite. One will expect then for dn_i/dt to be related to the chemical potentials $\overline{\mu}_i$.

Elimination of dE in Eq. (3.346) in favor of dH from $dH = dE + PdV + VdP$ gives

$$\underbrace{dH - PdV - VdP}_{=dE} - TdS + PdV \leq 0, \tag{3.353}$$

$$dH - VdP - TdS \leq 0. \tag{3.354}$$

Thus, one finds for isobaric, isentropic equilibration that

$$dH|_{P,S} \leq 0. \tag{3.355}$$

For the Helmholtz and Gibbs free energies, one analogously finds

$$dA|_{T,V} \leq 0, \tag{3.356}$$

$$dG|_{T,P} \leq 0. \tag{3.357}$$

The expression of the second law in terms of dG is especially useful as it may be easy in an experiment to control so that P and T are constant. This is especially true in an isobaric phase change, in which the temperature is guaranteed to be constant as well.

Now, one has Eq. (3.266):

$$G = \sum_{i=1}^{N} n_i \overline{g}_i, \tag{3.358}$$

$$= \sum_{i=1}^{N} n_i \overline{\mu}_i. \tag{3.359}$$

One also has from Eq. (3.240): $dG = -SdT + VdP + \sum_{i=1}^{N} \overline{\mu}_i dn_i$, holding T and P constant that

$$dG|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i dn_i. \tag{3.360}$$

Here, the dn_i are associated entirely with internal chemical reactions. Substituting Eq. (3.360) into Eq. (3.357), one gets the important version of the second law which holds that

$$dG|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i dn_i \leq 0. \tag{3.361}$$

In terms of time rates of change, one can divide Eq. (3.361) by a positive time increment $dt > 0$ to get

$$\left. \frac{\partial G}{\partial t} \right|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i \frac{dn_i}{dt} \leq 0. \tag{3.362}$$

3.11   Equilibrium in a two-component system

A major task of *non-equilibrium thermodynamics* is to find a functional form for dn_i/dt which guarantees satisfaction of the second law, Eq. (3.362) and gives predictions which agree with experiment. This will be discussed in more detail in the following chapter on thermochemistry. At this point, some simple examples will be given in which a naïve but useful functional form for dn_i/dt is posed which leads at least to predictions of the correct equilibrium values. A much better model which gives the correct dynamics in the time domain of the system as it approaches equilibrium will be presented in the following Chapter 4 on thermochemistry.

3.11.1   Phase equilibrium

Here, consider two examples describing systems in phase equilibrium.

Example 3.12

Consider an equilibrium two-phase mixture of liquid and vapor H_2O at $T = 100 \ C$, $x = 0.5$. Use the steam tables to check if equilibrium properties are satisfied.

In a two-phase gas liquid mixture one can expect the following reaction:

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}. \tag{3.363}$$

That is, one mole of liquid, in the forward phase change, evaporates to form one mole of gas. In the reverse phase change, one mole of gas condenses to form one mole of liquid.

Because T is fixed at $100°C$ and the material is a two phase mixture, the pressure is also fixed at a constant. Here, there are two phases at saturation; g for gas and l for liquid. Equation (3.361) reduces to

$$\overline{\mu}_l dn_l + \overline{\mu}_g dn_g \leq 0. \tag{3.364}$$

Now, for the pure H_2O if a loss of moles from one phase must be compensated by the addition to another. So, one must have

$$dn_l + dn_g = 0. \tag{3.365}$$

Hence

$$dn_g = -dn_l. \tag{3.366}$$

So, Eq. (3.364), using Eq. (3.366) becomes

$$\overline{\mu}_l dn_l - \overline{\mu}_g dn_l \leq 0, \tag{3.367}$$

$$dn_l(\overline{\mu}_l - \overline{\mu}_g) \leq 0. \tag{3.368}$$

At this stage of the analysis, most texts, grounded in equilibrium thermodynamics, assert that $\overline{\mu}_l = \overline{\mu}_g$, ignoring the fact that they could be different but dn_l could be zero. That approach will not be taken here. Instead divide Eq. (3.368) by a positive time increment, $dt \geq 0$ to write the second law as

$$\frac{dn_l}{dt}(\overline{\mu}_l - \overline{\mu}_g) \leq 0. \tag{3.369}$$

One convenient, albeit naïve, way to guarantee second law satisfaction is to let

$$\frac{dn_l}{dt} = -\kappa(\overline{\mu}_l - \overline{\mu}_g), \qquad \kappa \geq 0, \qquad \textit{convenient, but naïve model} \tag{3.370}$$

Here, κ is some positive semi-definite scalar rate constant which dictates the time scale of approach to equilibrium. Note that Eq. (3.370) is just a hypothesized model. It has *no experimental verification*; one can imagine that other more complex models exist which both agree with experiment and satisfy the second law. For the purposes of the present argument, however, Eq. (3.370) will suffice. With this assumption, the second law reduces to

$$-\kappa(\overline{\mu}_l - \overline{\mu}_g)^2 \leq 0, \qquad \kappa \geq 0, \tag{3.371}$$

which is always true.

Eq. (3.370) has two important consequences:

- Differences in chemical potential drive changes in the number of moles.

- The number of moles of liquid, n_l, *increases* when the chemical potential of the liquid is less than that of the gas, $\overline{\mu}_l < \overline{\mu}_g$. That is to say, when the liquid has a lower chemical potential than the gas, the gas is driven towards the phase with the lower potential. Because such a phase change is isobaric and isothermal, the Gibbs free energy is the appropriate variable to consider, and one takes $\overline{\mu} = \overline{g}$. When this is so, the Gibbs free energy of the mixture, $G = n_l \overline{\mu}_l + n_g \overline{\mu}_g$ is being driven to a lower value. So, when $dG = 0$, the system has a minimum G.

- The system is in equilibrium when the chemical potentials of liquid and gas are equal: $\overline{\mu}_l = \overline{\mu}_g$.

The chemical potentials, and hence the molar specific Gibbs free energies must be the same for each constituent of the binary mixture at the phase equilibrium. That is

$$\overline{g}_l = \overline{g}_g. \tag{3.372}$$

Now, since both the liquid and gas have the same molecular mass, one also has the mass specific Gibbs free energies equal at phase equilibrium:

$$g_l = g_g. \tag{3.373}$$

This can be verified from the steam tables, using the definition $g = h - Ts$. From standard thermodynamic tables

$$g_l = h_l - Ts_l = 419.02 \ \frac{kJ}{kg} - ((100 + 273.15) \ K) \left(1.3068 \ \frac{kJ}{kg \ K} \right) = -68.6 \ \frac{kJ}{kg}, \tag{3.374}$$

$$g_g = h_g - Ts_g = 2676.05 \ \frac{kJ}{kg} - ((100 + 273.15) \ K) \left(7.3548 \ \frac{kJ}{kg \ K} \right) = -68.4 \ \frac{kJ}{kg}. \tag{3.375}$$

The two values are essentially the same; the difference is likely due to table inaccuracies.

3.11.2 Chemical equilibrium: introduction

Here, consider two examples which identify the equilibrium state of a chemically reactive system.

3.11.2.1 Isothermal, isochoric system

The simplest system to consider is isothermal and isochoric. The isochoric assumption implies there is no work in coming to equilibrium.

Example 3.13

At high temperatures, collisions between diatomic nitrogen molecules induce the production of monatomic nitrogen molecules. The chemical reaction can be described by the model

$$N_2 + N_2 \rightleftharpoons 2N + N_2. \tag{3.376}$$

Here, one of the N_2 molecules behaves as an inert third body. An N_2 molecule has to collide with *something*, to induce the reaction. Some authors leave out the third body and write instead $N_2 \rightleftharpoons 2N$, but this does not reflect the true physics as well. The inert third body is especially important when the time scales of reaction are considered. It plays no role in equilibrium chemistry.

Consider 1 *kmole* of N_2 and 0 *kmole* of N at a pressure of 100 *kPa* and a temperature of 6000 *K*. Find the equilibrium concentrations of N and N_2 if the equilibration process is *isothermal* and *isochoric*. Also perform a first and second law analysis with the aid of the ideal gas tables.

The ideal gas law can give the volume.

$$P_1 = \frac{n_{N_2}\overline{R}T}{V}, \tag{3.377}$$

$$V = \frac{n_{N_2}\overline{R}T}{P_1}, \tag{3.378}$$

$$= \frac{(1\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)}{100\ kPa}, \tag{3.379}$$

$$= 498.84\ m^3. \tag{3.380}$$

Initially, the mixture is all N_2, so its partial pressure is the total pressure, and the initial partial pressure of N is 0.

Now, every time an N_2 molecule reacts and thus undergoes a negative change, 2 N molecules are created and thus undergo a positive change, so

$$-dn_{N_2} = \frac{1}{2}dn_N. \tag{3.381}$$

This can be parameterized by a reaction progress variable ζ, also called the *degree of reaction*, defined such that

$$d\zeta = -dn_{N_2}, \tag{3.382}$$

$$d\zeta = \frac{1}{2}dn_N. \tag{3.383}$$

As an aside, one can integrate this, taking $\zeta = 0$ at the initial state to get

$$\zeta = n_{N_2}|_{t=0} - n_{N_2}, \tag{3.384}$$

$$\zeta = \frac{1}{2}n_N. \tag{3.385}$$

Thus,

$$n_{N_2} = n_{N_2}|_{t=0} - \zeta, \tag{3.386}$$

$$n_N = 2\zeta. \tag{3.387}$$

One can also eliminate ζ to get n_N in terms of n_{N_2}:

$$n_N = 2\left(n_{N_2}|_{t=0} - n_{N_2}\right). \tag{3.388}$$

Now, for the reaction, one must have, for second law satisfaction, that

$$\overline{\mu}_{N_2}dn_{N_2} + \overline{\mu}_N dn_N \leq 0, \tag{3.389}$$

$$\overline{\mu}_{N_2}(-d\zeta) + \overline{\mu}_N(2d\zeta) \leq 0, \tag{3.390}$$

$$\left(-\overline{\mu}_{N_2} + 2\overline{\mu}_N\right)d\zeta \leq 0 \tag{3.391}$$

$$\left(-\overline{\mu}_{N_2} + 2\overline{\mu}_N\right)\frac{d\zeta}{dt} \leq 0. \tag{3.392}$$

In order to satisfy the second law, one can usefully, but naïvely, hypothesize that the *non-equilibrium* reaction kinetics are given by

$$\frac{d\zeta}{dt} = -k(-\overline{\mu}_{N_2} + 2\overline{\mu}_N), \qquad k \geq 0, \qquad \textit{convenient, but naïve model} \tag{3.393}$$

Note there are other ways to guarantee second law satisfaction. In fact, a more complicated model is well known to fit data well, and will be studied later in Chapter 4. For the present purposes, this naïve model will suffice. With this assumption, the second law reduces to

$$-k(-\overline{\mu}_{N_2} + 2\overline{\mu}_N)^2 \leq 0, \qquad k \geq 0, \tag{3.394}$$

which is always true. Obviously, the reaction ceases when $d\zeta/dt = 0$, which holds only when

$$2\overline{\mu}_N = \overline{\mu}_{N_2}. \tag{3.395}$$

Away from equilibrium, for the reaction to go forward, one must expect $d\zeta/dt > 0$, and then one must have

$$-\overline{\mu}_{N_2} + 2\overline{\mu}_N \leq 0, \tag{3.396}$$
$$2\overline{\mu}_N \leq \overline{\mu}_{N_2}. \tag{3.397}$$

The chemical potentials are the molar specific Gibbs free energies; thus, for the reaction to go forward, one must have

$$2\overline{g}_N \leq \overline{g}_{N_2}. \tag{3.398}$$

Substituting using the definitions of Gibbs free energy, one gets

$$2\left(\overline{h}_N - T\,\overline{s}_N\right) \leq \overline{h}_{N_2} - T\,\overline{s}_{N_2}, \tag{3.399}$$

$$2\left(\overline{h}_N - T\left(\overline{s}_{T,N}^o - \overline{R}\ln\left(\frac{y_N P}{P_o}\right)\right)\right) \leq \overline{h}_{N_2} - T\left(\overline{s}_{T,N_2}^o - \overline{R}\ln\left(\frac{y_{N_2} P}{P_o}\right)\right), \tag{3.400}$$

$$2\left(\overline{h}_N - T\,\overline{s}_{T,N}^o\right) - \left(\overline{h}_{N_2} - T\,\overline{s}_{T,N_2}^o\right) \leq -2\overline{R}T\ln\left(\frac{y_N P}{P_o}\right) + \overline{R}T\ln\left(\frac{y_{N_2} P}{P_o}\right), \tag{3.401}$$

$$-2\left(\overline{h}_N - T\,\overline{s}_{T,N}^o\right) + \left(\overline{h}_{N_2} - T\,\overline{s}_{T,N_2}^o\right) \geq 2\overline{R}T\ln\left(\frac{y_N P}{P_o}\right) - \overline{R}T\ln\left(\frac{y_{N_2} P}{P_o}\right), \tag{3.402}$$

$$-2\left(\overline{h}_N - T\,\overline{s}_{T,N}^o\right) + \left(\overline{h}_{N_2} - T\,\overline{s}_{T,N_2}^o\right) \geq \overline{R}T\ln\left(\frac{y_N^2 P^2}{P_o^2}\frac{P_o}{P y_{N_2}}\right), \tag{3.403}$$

$$-2\left(\overline{h}_N - T\,\overline{s}_{T,N}^o\right) + \left(\overline{h}_{N_2} - T\,\overline{s}_{T,N_2}^o\right) \geq \overline{R}T\ln\left(\frac{y_N^2}{y_{N_2}}\frac{P}{P_o}\right). \tag{3.404}$$

At the initial state, one has $y_N = 0$, so the right hand side approaches $-\infty$, and the inequality holds. At equilibrium, one has equality.

$$-2\left(\overline{h}_N - T\,\overline{s}_{T,N}^o\right) + \left(\overline{h}_{N_2} - T\,\overline{s}_{T,N_2}^o\right) = \overline{R}T\ln\left(\frac{y_N^2}{y_{N_2}}\frac{P}{P_o}\right). \tag{3.405}$$

Taking numerical values from Borgnakke and Sonntag's Table A.9:

$$-2\left(5.9727 \times 10^5\,\frac{kJ}{kmole} - (6000\ K)\left(216.926\,\frac{kJ}{kg\ K}\right)\right) +$$
$$\left(2.05848 \times 10^5\,\frac{kJ}{kmole} - (6000\ K)\left(292.984\,\frac{kJ}{kg\ K}\right)\right)$$
$$= \left(8.314\,\frac{kJ}{kmole\ K}\right)(6000\ K)\ln\left(\frac{y_N^2}{y_{N_2}}\frac{P}{P_o}\right),$$
$$\underbrace{-2.87635}_{\equiv \ln K_P} = \ln\left(\frac{y_N^2}{y_{N_2}}\frac{P}{P_o}\right), \tag{3.406}$$

$$\underbrace{0.0563399}_{\equiv K_P} = \frac{y_N^2}{y_{N_2}}\frac{P}{P_o}, \tag{3.407}$$

$$= \frac{\left(\frac{n_N}{n_N+n_{N_2}}\right)^2}{\left(\frac{n_{N_2}}{n_N+n_{N_2}}\right)}(n_N+n_{N_2})\frac{\overline{R}T}{P_oV}, \tag{3.408}$$

$$= \frac{n_N^2}{n_{N_2}}\frac{\overline{R}T}{P_oV}, \tag{3.409}$$

$$= \frac{\left(2\left(\left.n_{N_2}\right|_{t=0}-n_{N_2}\right)\right)^2}{n_{N_2}}\frac{\overline{R}T}{P_oV}, \tag{3.410}$$

$$= \frac{\left(2\left(1\ kmole-n_{N_2}\right)\right)^2}{n_{N_2}}\frac{(8.314)(6000)}{(100)(498.84)}. \tag{3.411}$$

This is a quadratic equation for n_{N_2}. It has two roots

$$n_{N_2} = 0.888154\ kmole \qquad \text{physical;} \qquad n_{N_2} = 1.12593\ kmole, \qquad \text{non-physical} \tag{3.412}$$

The second root generates more N_2 than at the start, and also yields non-physically negative $n_N = -0.25186\ kmole$. So, at equilibrium the physical root is

$$n_N = 2(1-n_{N_2}) = 2(1-0.888154) = 0.223693\ kmole. \tag{3.413}$$

The diatomic species is preferred.

Note in the preceding analysis, the term K_P was introduced. This is the so-called equilibrium "constant" which is really a function of temperature. It will be described in more detail later in Sec. 4.4, but one notes that it is commonly tabulated for some reactions. Its tabular value can be derived from the more fundamental quantities shown in this example. Borgnakke and Sonntag's Table A.11 gives for this reaction at 6000 K the value of $\ln K_P = -2.876$. Note that K_P is fundamentally defined in terms of thermodynamic properties for a system which may or may not be at chemical equilibrium. Only at chemical equilibrium, can it can further be related to mole fraction and pressure ratios.

The pressure at equilibrium is

$$P_2 = \frac{(n_{N_2}+n_N)\overline{R}T}{V}, \tag{3.414}$$

$$= \frac{(0.888154\ kmole + 0.223693\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)}{498.84}, \tag{3.415}$$

$$= 111.185\ kPa. \tag{3.416}$$

The pressure has increased because there are more molecules with the volume and temperature being equal.

The molar concentrations $\overline{\rho}_i$ at equilibrium, are

$$\overline{\rho}_N = \frac{0.223693\ kmole}{498.84\ m^3} = 4.484\times10^{-4}\ \frac{kmole}{m^3} = 4.484\times10^{-7}\ \frac{mole}{cm^3}, \tag{3.417}$$

$$\overline{\rho}_{N_2} = \frac{0.888154\ kmole}{498.84\ m^3} = 1.78044\times10^{-3}\ \frac{kmole}{m^3} = 1.78044\times10^{-6}\ \frac{mole}{cm^3}. \tag{3.418}$$

Now, consider the heat transfer. One knows for the isochoric process that $Q = E_2 - E_1$. The initial energy is given by

$$E_1 = n_{N_2}\overline{e}_{N_2}, \tag{3.419}$$

$$= n_{N_2}(\overline{h}_{N_2} - \overline{R}T), \tag{3.420}$$

$$= (1 \ kmole)\left(2.05848 \times 10^5 \ \frac{kJ}{kmole} - \left(8.314 \ \frac{kJ}{kmole \ K}\right)(6000 \ K)\right), \tag{3.421}$$

$$= 1.555964 \times 10^5 \ kJ. \tag{3.422}$$

The energy at the final state is

$$E_2 = n_{N_2}\overline{e}_{N_2} + n_N\overline{e}_N, \tag{3.423}$$

$$= n_{N_2}(\overline{h}_{N_2} - \overline{R}T) + n_N(\overline{h}_N - \overline{R}T), \tag{3.424}$$

$$= (0.888154 \ kmole)\left(2.05848 \times 10^5 \ \frac{kJ}{kmole} - \left(8.314 \ \frac{kJ}{kmole \ K}\right)(6000 \ K)\right) \tag{3.425}$$

$$+ (0.223693 \ kmole)\left(5.9727 \times 10^5 \ \frac{kJ}{kmole} - \left(8.314 \ \frac{kJ}{kmole \ K}\right)(6000 \ K)\right), \tag{3.426}$$

$$= 2.60966 \times 10^5 \ kJ. \tag{3.427}$$

So

$$Q = E_2 - E_1, \tag{3.428}$$

$$= 2.60966 \times 10^5 \ kJ - 1.555964 \times 10^5 \ kJ, \tag{3.429}$$

$$= 1.05002 \times 10^5 \ kJ. \tag{3.430}$$

Heat needed to be added to keep the system at the constant temperature. This is because the nitrogen dissociation process is *endothermic*.

One can check for second law satisfaction in two ways. Fundamentally, one can demand that Eq. (3.340), $dS \geq \delta Q/T$, be satisfied for the process, giving

$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}. \tag{3.431}$$

For this isothermal process, this reduces to

$$S_2 - S_1 \geq \frac{Q}{T}, \tag{3.432}$$

$$(n_{N_2}\overline{s}_{N_2} + n_N\overline{s}_N)|_2$$
$$- (n_{N_2}\overline{s}_{N_2} + n_N\overline{s}_N)|_1 \geq \frac{Q}{T}, \tag{3.433}$$

$$\left(n_{N_2}\left(\overline{s}_{T,N_2}^o - \overline{R}\ln\left(\frac{y_{N_2}P}{P_o}\right)\right) + n_N\left(\overline{s}_{T,N}^o - \overline{R}\ln\left(\frac{y_N P}{P_o}\right)\right)\right)\Big|_2$$
$$- \left(n_{N_2}\left(\overline{s}_{T,N_2}^o - \overline{R}\ln\left(\frac{y_{N_2}P}{P_o}\right)\right) + n_N\left(\overline{s}_{T,N}^o - \overline{R}\ln\left(\frac{y_N P}{P_o}\right)\right)\right)\Big|_1 \geq \frac{Q}{T}, \tag{3.434}$$

$$\left(n_{N_2}\left(\overline{s}_{T,N_2}^o - \overline{R}\ln\left(\frac{P_{N_2}}{P_o}\right)\right) + n_N\left(\overline{s}_{T,N}^o - \overline{R}\ln\left(\frac{P_N}{P_o}\right)\right)\right)\Big|_2$$
$$- \left(n_{N_2}\left(\overline{s}_{T,N_2}^o - \overline{R}\ln\left(\frac{P_{N_2}}{P_o}\right)\right) + n_N\left(\overline{s}_{T,N}^o - \overline{R}\ln\left(\frac{P_N}{P_o}\right)\right)\right)\Big|_1 \geq \frac{Q}{T}, \tag{3.435}$$

$$\left(n_{N_2}\left(\overline{s}_{T,N_2}^o - \overline{R}\ln\left(\frac{n_{N_2}\overline{R}T}{P_o V}\right)\right) + n_N\left(\overline{s}_{T,N}^o - \overline{R}\ln\left(\frac{n_N\overline{R}T}{P_o V}\right)\right)\right)\Big|_2$$
$$- \left(n_{N_2}\left(\overline{s}_{T,N_2}^o - \overline{R}\ln\left(\frac{n_{N_2}\overline{R}T}{P_o V}\right)\right) + \underbrace{n_N}_{=0}\left(\overline{s}_{T,N}^o - \overline{R}\ln\left(\frac{n_N\overline{R}T}{P_o V}\right)\right)\right)\Big|_1 \geq \frac{Q}{T}. \tag{3.436}$$

Now, at the initial state $n_N = 0 \ kmole$, and $\overline{R}T/P_o/V$ has a constant value of

$$\frac{\overline{R}T}{P_oV} = \frac{\left(8.314 \ \frac{kJ}{kmole \ K}\right)(6000 \ K)}{(100 \ kPa)(498.84 \ m^3)} = 1 \ \frac{1}{kmole}, \tag{3.437}$$

so Eq. (3.436) reduces to

$$\left(n_{N_2} \left(\overline{s}_{T,N_2}^o - \overline{R}\ln\left(\frac{n_{N_2}}{1 \ kmole}\right)\right) + n_N \left(\overline{s}_{T,N}^o - \overline{R}\ln\left(\frac{n_N}{1 \ kmole}\right)\right)\right)\Big|_2$$
$$- \left(n_{N_2} \left(\overline{s}_{T,N_2}^o - \overline{R}\ln\left(\frac{n_{N_2}}{1 \ kmole}\right)\right)\right)\Big|_1 \ \geq \ \frac{Q}{T}, \tag{3.438}$$

$$((0.888143) \, (292.984 - 8.314 \ln{(0.88143)}) + (0.223714) \, (216.926 - 8.314 \ln{(0.223714)}))|_2$$
$$- \, ((1) \, (292.984 - 8.314 \ln{(1)}))|_1 \ \geq \ \frac{105002}{6000},$$
$$19.4181 \ \frac{kJ}{K} \geq 17.5004 \ \frac{kJ}{K}. \tag{3.439}$$

Indeed, the second law is satisfied. Moreover, the irreversibility of the chemical reaction is $19.4181 - 17.5004 = +1.91772 \ kJ/K$.

For the isochoric, isothermal process, it is also appropriate to use Eq. (3.356), $dA|_{T,V} \leq 0$, to check for second law satisfaction. This turns out to give an identical result. Since by Eq. (3.235), $A = U - TS$, $A_2 - A_1 = (E_2 - T_2S_2) - (E_1 - T_1S_1)$. Since the process is isothermal, $A_2 - A_1 = E_2 - E_1 - T(S_2 - S_1)$. For $A_2 - A_1 \leq 0$, one must demand $E_2 - E_1 - T(S_2 - S_1) \leq 0$, or $E_2 - E_1 \leq T(S_2 - S_1)$, or $S_2 - S_1 \geq (E_2 - E_1)/T$. Since $Q = E_2 - E_1$ for this isochoric process, one then recovers $S_2 - S_1 \geq Q/T$.

3.11.2.2   Isothermal, isobaric system

Allowing for isobaric rather than isochoric equilibration introduces small variation in the analysis.

Example 3.14

Consider the same reaction

$$N_2 + N_2 \leftrightharpoons 2N + N_2. \tag{3.440}$$

for an *isobaric* and *isothermal* process. That is, consider 1 $kmole$ of N_2 and 0 $kmole$ of N at a pressure of 100 kPa and a temperature of 6000 K. Using the ideal gas tables, find the equilibrium concentrations of N and N_2 if the equilibration process is isothermal and isobaric.

The initial volume is the same as from the previous example:

$$V_1 \ = \ 498.84 \ m^3. \tag{3.441}$$

Note the volume will change in this isobaric process. Initially, the mixture is all N_2, so its partial pressure is the total pressure, and the initial partial pressure of N is 0.

A few other key results are identical to the previous example:

$$n_N = 2\left(n_{N_2}\big|_{t=0} - n_{N_2}\right), \tag{3.442}$$

and

$$2\overline{g}_N \leq \overline{g}_{N_2}. \tag{3.443}$$

Substituting using the definitions of Gibbs free energy, one gets

$$2\left(\overline{h}_N - T\,\overline{s}_N\right) \quad \leq \quad \overline{h}_{N_2} - T\,\overline{s}_{N_2}, \tag{3.444}$$

$$2\left(\overline{h}_N - T\left(\overline{s}^o_{T,N} - \overline{R}\ln\left(\frac{y_N P}{P_o}\right)\right)\right) \quad \leq \quad \overline{h}_{N_2} - T\left(\overline{s}^o_{T,N_2} - \overline{R}\ln\left(\frac{y_{N_2} P}{P_o}\right)\right), \tag{3.445}$$

$$2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) - \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) \quad \leq \quad -2\overline{R}T\ln\left(\frac{y_N P}{P_o}\right) + \overline{R}T\ln\left(\frac{y_{N_2} P}{P_o}\right), \tag{3.446}$$

$$-2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) + \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) \quad \geq \quad 2\overline{R}T\ln\left(\frac{y_N P}{P_o}\right) - \overline{R}T\ln\left(\frac{y_{N_2} P}{P_o}\right), \tag{3.447}$$

$$-2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) + \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) \quad \geq \quad \overline{R}T\ln\left(\frac{y_N^2 P^2}{P_o^2}\frac{P_o}{P y_{N_2}}\right). \tag{3.448}$$

In this case $P_o = P$, so one gets

$$-2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) + \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) \quad \geq \quad \overline{R}T\ln\left(\frac{y_N^2}{y_{N_2}}\right). \tag{3.449}$$

At the initial state, one has $y_N = 0$, so the right hand side approaches $-\infty$, and the inequality holds. At equilibrium, one has equality.

$$-2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) + \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) \quad = \quad \overline{R}T\ln\left(\frac{y_N^2}{y_{N_2}}\right). \tag{3.450}$$

Taking numerical values from Borgnakke and Sonntag's Table A.9:

$$-2\left(5.9727 \times 10^5\,\frac{kJ}{kmole} - (6000\ K)\left(216.926\,\frac{kJ}{kg\ K}\right)\right) +$$

$$\left(2.05848 \times 10^5\,\frac{kJ}{kmole} - (6000\ K)\left(292.984\,\frac{kJ}{kg\ K}\right)\right)$$

$$= \quad \left(8.314\,\frac{kJ}{kmole\ K}\right)(6000\ K)\ln\left(\frac{y_N^2}{y_{N_2}}\right),$$

$$\underbrace{-2.87635}_{\equiv \ln K_P} \quad = \quad \ln\left(\frac{y_N^2}{y_{N_2}}\right), \tag{3.451}$$

$$\underbrace{0.0563399}_{\equiv K_P} \quad = \quad \frac{y_N^2}{y_{N_2}}, \tag{3.452}$$

$$= \quad \frac{\left(\frac{n_N}{n_N + n_{N_2}}\right)^2}{\left(\frac{n_{N_2}}{n_N + n_{N_2}}\right)}, \tag{3.453}$$

$$= \quad \frac{n_N^2}{n_{N_2}(n_N + n_{N_2})}, \tag{3.454}$$

$$= \quad \frac{\left(2\left(n_{N_2}|_{t=0} - n_{N_2}\right)\right)^2}{n_{N_2}(2\left(n_{N_2}|_{t=0} - n_{N_2}\right) + n_{N_2})}, \tag{3.455}$$

$$= \quad \frac{\left(2\left(1\ kmole - n_{N_2}\right)\right)^2}{n_{N_2}(2\left(1\ kmole - n_{N_2}\right) + n_{N_2})}. \tag{3.456}$$

This is a quadratic equation for n_{N_2}. It has two roots

$$n_{N_2} = 0.882147 \ kmole \qquad \text{physical;} \qquad n_{N_2} = 1.11785 \ kmole, \qquad \text{non-physical} \tag{3.457}$$

The second root generates more N_2 than at the start, and also yields non-physically negative $n_N = -0.235706 \ kmole$. So, at equilibrium the physical root is

$$n_N = 2(1 - n_{N_2}) = 2(1 - 0.882147) = 0.235706 \ kmole. \tag{3.458}$$

Again, the diatomic species is preferred. As the temperature is raised, one could show that the monatomic species would come to dominate.

The volume at equilibrium is

$$V_2 = \frac{(n_{N_2} + n_N)\overline{R}T}{P}, \tag{3.459}$$

$$= \frac{(0.882147 \ kmole + 0.235706 \ kmole)\left(8.314 \ \frac{kJ}{kmole \ K}\right)(6000 \ K)}{100 \ kPa}, \tag{3.460}$$

$$= 557.630 \ m^3. \tag{3.461}$$

The volume has increased because there are more molecules with the pressure and temperature being equal.

The molar concentrations $\overline{\rho}_i$ at equilibrium, are

$$\overline{\rho}_N = \frac{0.235706 \ kmole}{557.636 \ m^3} = 4.227 \times 10^{-4} \ \frac{kmole}{m^3} = 4.227 \times 10^{-7} \ \frac{mole}{cm^3}, \tag{3.462}$$

$$\overline{\rho}_{N_2} = \frac{0.882147 \ kmole}{557.636 \ m^3} = 1.58196 \times 10^{-3} \ \frac{kmole}{m^3} = 1.58196 \times 10^{-6} \ \frac{mole}{cm^3}. \tag{3.463}$$

The molar concentrations are a little smaller than for the isochoric case, mainly because the volume is larger at equilibrium.

Now, consider the heat transfer. One knows for the isobaric process that $Q = H_2 - H_1$. The initial enthalpy is given by

$$H_1 = n_{N_2}\overline{h}_{N_2} = (1 \ kmole)\left(2.05848 \times 10^5 \ \frac{kJ}{kmole}\right) = 2.05848 \times 10^5 \ kJ. \tag{3.464}$$

The enthalpy at the final state is

$$H_2 = n_{N_2}\overline{h}_{N_2} + n_N\overline{h}_N, \tag{3.465}$$

$$= (0.882147 \ kmole)\left(2.05848 \times 10^5 \ \frac{kJ}{kmole}\right) + (0.235706 \ kmole)\left(5.9727 \times 10^5 \ \frac{kJ}{kmole}\right) \tag{3.466}$$

$$= 3.22368 \times 10^5 \ kJ. \tag{3.467}$$

So,

$$Q = H_2 - H_1 = 3.22389 \times 10^5 \ kJ - 2.05848 \times 10^5 \ kJ = 1.16520 \times 10^5 \ kJ. \tag{3.468}$$

Heat needed to be added to keep the system at the constant temperature. This is because the nitrogen dissociation process is *endothermic*. Relative to the isochoric process, *more* heat had to be added to maintain the temperature. This to counter the cooling effect of the expansion.

Lastly, it is a straightforward exercise to show that the second law is satisfied for this process.

3.11.3   Equilibrium condition

The results of both of the previous examples, in which a functional form of a progress variable's time variation, $d\zeta/dt$, was postulated in order to satisfy the second law, gave a condition for equilibrium. This can be generalized so as to require at equilibrium that

$$\underbrace{\sum_{i=1}^{N} \overline{\mu}_i \nu_i}_{\equiv -\overline{\alpha}} = 0. \tag{3.469}$$

Here, ν_i represents the *net* number of moles of species i generated in the forward reaction. This will be discussed in detail in the following Sec. 4.4. So, in the phase equilibrium example, Eq. (3.469) becomes

$$\overline{\mu}_l(-1) + \overline{\mu}_g(1) = 0. \tag{3.470}$$

In the nitrogen chemistry example, Eq. (3.469) becomes

$$\overline{\mu}_{N_2}(-1) + \overline{\mu}_N(2) = 0. \tag{3.471}$$

The negation of the term on the left side of Eq (3.469) is sometimes defined as the *chemical affinity*, $\overline{\alpha}$:

$$\overline{\alpha} \equiv -\sum_{i=1}^{N} \overline{\mu}_i \nu_i. \tag{3.472}$$

Chapter 4

Thermochemistry of a single reaction

These four bodies are fire, air, water, earth. Fire occupies the highest place among them all...

Aristotle (384 BC-322 BC), *Meteorology*, Book 1, § 2.

——————————-

This chapter will further develop notions associated with the thermodynamics of chemical reactions. The focus will be on chemical reaction of N species composed of L elements reacting in $J = 1$ reaction. Several sources can be consulted as references.[1][2][3][4][5]

4.1 Molecular mass

The molecular mass of a molecule is a straightforward notion from chemistry. One simply sums the product of the number of atoms and each atom's atomic mass to form the molecular mass. If one defines L as the number of elements present in species i, ϕ_{li} as the number of moles of atomic element l in species i, and $\mathcal{M}_l$ as the atomic mass of element l, the molecular mass M_i of species i

$$M_i = \sum_{l=1}^{L} \mathcal{M}_l \phi_{li}. \tag{4.1}$$

In vector form, one would say

$$\mathbf{M}^T = \mathcal{M}^T \cdot \boldsymbol{\phi}, \qquad \text{or} \qquad \mathbf{M} = \boldsymbol{\phi}^T \cdot \mathcal{M}. \tag{4.2}$$

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[1] Borgnakke, C., and Sonntag, R. E., 2009, *Fundamentals of Thermodynamics*, Seventh Edition, John Wiley, New York. See Chapters 14 and 15.

[2] Abbott, M. M., and Van Ness, H. C., 1972, *Thermodynamics*, Schaum's Outline Series in Engineering, McGraw-Hill, New York. See Chapter 7.

[3] Kondepudi, D., and Prigogine, I., 1998, *Modern Thermodynamics: From Heat Engines to Dissipative Structures*, John Wiley, New York. See Chapters 4, 5, 7, and 9.

[4] Turns, S. R., 2011, *An Introduction to Combustion*, Third Edition, McGraw-Hill, Boston. See Chapter 2.

[5] Kuo, K. K., 2005, *Principles of Combustion*, Second Edition, John Wiley, New York. See Chapters 1, 2.

Here, $\mathbf{M}$ is the vector of length N containing the molecular masses, $\mathcal{M}$ is the vector of length L containing the elemental masses, and $\boldsymbol{\phi}$ is the matrix of dimension $L \times N$ containing the number of moles of each element in each species. Generally, $\boldsymbol{\phi}$ is full rank. If $N > L$, $\boldsymbol{\phi}$ has rank L. If $N < L$, $\boldsymbol{\phi}$ has rank N. In any problem involving an actual chemical reaction, one will find $N \geq L$, and in most cases $N > L$. In isolated problems not involving a reaction, one may have $N < L$. In any case, $\mathbf{M}$ lies in the column space of $\boldsymbol{\phi}^T$, which is the row space of $\boldsymbol{\phi}$.

Example 4.1

   Find the molecular mass of H_2O.

   Here, one has two elements H and O, so $L = 2$, and one species, so $N = 1$; thus, in this isolated problem, $N < L$. Take $i = 1$ for species H_2O. Take $l = 1$ for element H. Take $l = 2$ for element O. From the periodic table, one gets $\mathcal{M}_1 = 1 \ g/mole$ for H, $\mathcal{M}_2 = 16 \ g/mole$ for O. For element 1, there are 2 atoms, so $\phi_{11} = 2$. For element 2, there is 1 atom so $\phi_{21} = 1$. So, the molecular mass of species 1, H_2O is

$$M_1 \quad = \quad (\, \mathcal{M}_1 \quad \mathcal{M}_2 \,) \cdot \begin{pmatrix} \phi_{11} \\ \phi_{21} \end{pmatrix}, \tag{4.3}$$

$$= \quad \mathcal{M}_1 \phi_{11} + \mathcal{M}_2 \phi_{21}, \tag{4.4}$$

$$= \quad \left(1 \ \frac{g}{mole} \right) (2) + \left(16 \ \frac{g}{mole} \right) (1), \tag{4.5}$$

$$= \quad 18 \ \frac{g}{mole}. \tag{4.6}$$

Example 4.2

   Find the molecular masses of the two species C_8H_{18} and CO_2.

   Here, the vector matrix notation is exercised. In a certain sense this is overkill, but it is useful to be able to understand a general notation.

   One has $N = 2$ species, and takes $i = 1$ for C_8H_{18} and $i = 2$ for CO_2. One also has $L = 3$ elements and takes $l = 1$ for C, $l = 2$ for H, and $l = 3$ for O. Now, for each element, one has $\mathcal{M}_1 = 12 \ g/mole$, $\mathcal{M}_2 = 1 \ g/mole$, $\mathcal{M}_3 = 16 \ g/mole$. The molecular masses are then given by

$$(\, M_1 \quad M_2 \,) \quad = \quad (\, \mathcal{M}_1 \quad \mathcal{M}_2 \quad \mathcal{M}_3 \,) \cdot \begin{pmatrix} \phi_{11} & \phi_{12} \\ \phi_{21} & \phi_{22} \\ \phi_{31} & \phi_{32} \end{pmatrix}, \tag{4.7}$$

$$= \quad (\, 12 \quad 1 \quad 16 \,) \cdot \begin{pmatrix} 8 & 1 \\ 18 & 0 \\ 0 & 2 \end{pmatrix}, \tag{4.8}$$

$$= \quad (\, 114 \quad 44 \,). \tag{4.9}$$

That is, for C_8H_{18}, one has molecular mass $M_1 = 114 \ g/mole$. For CO_2, one has molecular mass $M_2 = 44 \ g/mole$.

4.2 Stoichiometry

4.2.1 General development

Stoichiometry represents a mass balance on each element in a chemical reaction. For example, in the simple global reaction

$$2H_2 + O_2 \leftrightharpoons 2H_2O, \tag{4.10}$$

one has 4 H atoms in both the reactant and product sides and 2 O atoms in both the reactant and product sides. In this section stoichiometry will be systematized.

Consider now a general reaction with N species. This reaction can be represented by

$$\sum_{i=1}^{N} \nu_i' \chi_i \leftrightharpoons \sum_{i=1}^{N} \nu_i'' \chi_i. \tag{4.11}$$

Here, χ_i is the ith chemical species, ν_i' is the *forward stoichiometric coefficient* of the ith reaction, and ν_i'' is the *reverse stoichiometric coefficient* of the ith reaction. Both ν_i' and ν_i'' are to be interpreted as pure dimensionless numbers.

In Equation (4.10), one has $N = 3$ species. One might take $\chi_1 = H_2$, $\chi_2 = O_2$, and $\chi_3 = H_2O$. The reaction is written in more general form as

$$(2)\chi_1 + (1)\chi_2 + (0)\chi_3 \leftrightharpoons (0)\chi_1 + (0)\chi_2 + (2)\chi_3, \tag{4.12}$$

$$(2)H_2 + (1)O_2 + (0)H_2O \leftrightharpoons (0)H_2 + (0)O_2 + (2)H_2O. \tag{4.13}$$

Here, one has

$$\nu_1' = 2, \qquad \nu_1'' = 0, \tag{4.14}$$

$$\nu_2' = 1, \qquad \nu_2'' = 0, \tag{4.15}$$

$$\nu_3' = 0, \qquad \nu_3'' = 2. \tag{4.16}$$

It is common and useful to define another pure dimensionless number, the *net stoichiometric coefficients* for species i, ν_i. Here, ν_i represents the net production of number if the reaction goes forward. It is given by

$$\nu_i = \nu_i'' - \nu_i'. \tag{4.17}$$

For the reaction $2H_2 + O_2 \leftrightharpoons 2H_2O$, one has

$$\nu_1 = \nu_1'' - \nu_1' = 0 - 2 = -2, \tag{4.18}$$

$$\nu_2 = \nu_2'' - \nu_2' = 0 - 1 = -1, \tag{4.19}$$

$$\nu_3 = \nu_3'' - \nu_3' = 2 - 0 = 2. \tag{4.20}$$

With these definitions, it is possible to summarize a chemical reaction as

$$\sum_{i=1}^{N} \nu_i \chi_i = 0. \tag{4.21}$$

In vector notation, one would say

$$\boldsymbol{\nu}^T \cdot \boldsymbol{\chi} = 0. \tag{4.22}$$

For the reaction of this section, one might write the non-traditional form

$$-2H_2 - O_2 + 2H_2O = 0. \tag{4.23}$$

It remains to enforce a stoichiometric balance. This is achieved if, for each element, $l = 1, \ldots, L$, one has the following equality:

$$\sum_{i=1}^{N} \phi_{li}\nu_i = 0, \qquad l = 1, \ldots, L. \tag{4.24}$$

That is to say, for each element, the sum of the product of the net species production and the number of elements in the species must be zero. In vector notation, this becomes

$$\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \mathbf{0}. \tag{4.25}$$

One may recall from linear algebra that this demands that $\boldsymbol{\nu}$ lie in the *right null space* of $\boldsymbol{\phi}$.

Example 4.3
   Show stoichiometric balance is achieved for $-2H_2 - O_2 + 2H_2O = 0$.

   Here again, the number of elements $L = 2$, and one can take $l = 1$ for H and $l = 2$ for O. Also the number of species $N = 3$, and one takes $i = 1$ for H_2, $i = 2$ for O_2, and $i = 3$ for H_2O. Then, for element 1, H, in species 1, H_2, one has

$$\phi_{11} = 2, H \text{ in } H_2. \tag{4.26}$$

   Similarly, one gets

$$\begin{aligned}
\phi_{12} &= 0, & H \text{ in } O_2, & \tag{4.27} \\
\phi_{13} &= 2, & H \text{ in } H_2O, & \tag{4.28} \\
\phi_{21} &= 0, & O \text{ in } H_2, & \tag{4.29} \\
\phi_{22} &= 2, & O \text{ in } O_2, & \tag{4.30} \\
\phi_{23} &= 1, & O \text{ in } H_2O. & \tag{4.31}
\end{aligned}$$

In matrix form then, $\sum_{i=1}^{N} \phi_{li}\nu_i = 0$ gives

$$\begin{pmatrix} 2 & 0 & 2 \\ 0 & 2 & 1 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{4.32}$$

   This is two equations in three unknowns. Thus, it is formally underconstrained. Certainly the trivial solution $\nu_1 = \nu_2 = \nu_3 = 0$ will satisfy, but one seeks non-trivial solutions. Assume ν_3 has a known value $\nu_3 = \xi$. Then, the system reduces to

$$\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \end{pmatrix} = \begin{pmatrix} -2\xi \\ -\xi \end{pmatrix}. \tag{4.33}$$

The inversion here is easy, and one finds $\nu_1 = -\xi$, $\nu_2 = -\frac{1}{2}\xi$. Or in vector form,

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} -\xi \\ -\frac{1}{2}\xi \\ \xi \end{pmatrix}, \tag{4.34}$$

$$= \xi \begin{pmatrix} -1 \\ -\frac{1}{2} \\ 1 \end{pmatrix}, \qquad \xi \in \mathbb{R}^1 \tag{4.35}$$

Again, this amounts to saying the solution vector $(\nu_1, \nu_2, \nu_3)^T$ lies in the right null space of the coefficient matrix ϕ_{li}.

Here, ξ is any real scalar. If one takes $\xi = 2$, one gets

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} -2 \\ -1 \\ 2 \end{pmatrix}, \tag{4.36}$$

This simply corresponds to

$$-2H_2 - O_2 + 2H_2O = 0. \tag{4.37}$$

If one takes $\xi = -4$, one still achieves stoichiometric balance, with

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} 4 \\ 2 \\ -4 \end{pmatrix}, \tag{4.38}$$

which corresponds to the equally valid

$$4H_2 + 2O_2 - 4H_2O = 0. \tag{4.39}$$

In summary, *the stoichiometric coefficients are non-unique but partially constrained by mass conservation.* Which set is chosen is to some extent arbitrary, and often based on traditional conventions from chemistry. But others are equally valid.

There is a small issue with units here, which will be seen to be difficult to reconcile. In practice, it will have little to no importance. In the previous example, one might be tempted to ascribe units of *moles* to ν_i. Later, it will be seen that in classical reaction kinetics, ν_i is best interpreted as a pure dimensionless number, consistent with the definition of this section. So, in the context of the previous example, one would then take ξ to be dimensionless as well, which is perfectly acceptable for the example. In later problems, it will be more useful to give ξ the units of *moles*. Note that multiplication of ξ by any scalar, *e.g. mole*$/(6.02 \times 10^{23})$, still yields an acceptable result.

Example 4.4

Balance an equation for hypothesized ethane combustion

$$\nu_1' C_2H_6 + \nu_2' O_2 \rightleftharpoons \nu_3'' CO_2 + \nu_4'' H_2O. \tag{4.40}$$
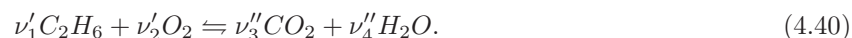
One could also say in terms of the net stoichiometric coefficients

$$\nu_1 C_2 H_6 + \nu_2 O_2 + \nu_3 CO_2 + \nu_4 H_2 O = 0. \tag{4.41}$$

Here, one takes $\chi_1 = C_2 H_6$, $\chi_2 = O_2$, $\chi_3\ CO_2$, $\chi_4 = H_2 O$. So, there are $N = 4$ species. There are also $L = 3$ elements: $l = 1 : C$, $l = 2 : H$, $l = 3 : O$. One then has

$$
\begin{aligned}
\phi_{11} &= 2, & C \text{ in } C_2 H_6, & \tag{4.42}\\
\phi_{12} &= 0, & C \text{ in } O_2, & \tag{4.43}\\
\phi_{13} &= 1, & C \text{ in } CO_2, & \tag{4.44}\\
\phi_{14} &= 0, & C \text{ in } H_2 O, & \tag{4.45}\\
\phi_{21} &= 6, & H \text{ in } C_2 H_6, & \tag{4.46}\\
\phi_{22} &= 0, & H \text{ in } O_2, & \tag{4.47}\\
\phi_{23} &= 0, & H \text{ in } CO_2, & \tag{4.48}\\
\phi_{24} &= 2, & H \text{ in } H_2 O, & \tag{4.49}\\
\phi_{31} &= 0, & O \text{ in } C_2 H_6, & \tag{4.50}\\
\phi_{32} &= 2, & O \text{ in } O_2, & \tag{4.51}\\
\phi_{33} &= 2, & O \text{ in } CO_2, & \tag{4.52}\\
\phi_{34} &= 1, & O \text{ in } H_2 O, & \tag{4.53}\\
& & & \tag{4.54}
\end{aligned}
$$

So, the stoichiometry equation, $\sum_{i=1}^{N} \phi_{li} \nu_i = 0$, is given by

$$
\begin{pmatrix} 2 & 0 & 1 & 0 \\ 6 & 0 & 0 & 2 \\ 0 & 2 & 2 & 1 \end{pmatrix}
\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{pmatrix}
= \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{4.55}
$$

Here, there are three equations in four unknowns, so the system is underconstrained. There are many ways to address this problem. Here, choose the robust way of casting the system into *row echelon form*. This is easily achieved by Gaussian elimination. Row echelon form seeks to have zeros in the lower left part of the matrix. The lower left corner has a zero already, so that is useful. Now, multiply the top equation by 3 and subtract the result from the second to get

$$
\begin{pmatrix} 2 & 0 & 1 & 0 \\ 0 & 0 & -3 & 2 \\ 0 & 2 & 2 & 1 \end{pmatrix}
\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{pmatrix}
= \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{4.56}
$$

Next switch the last two equations to get

$$
\begin{pmatrix} 2 & 0 & 1 & 0 \\ 0 & 2 & 2 & 1 \\ 0 & 0 & -3 & 2 \end{pmatrix}
\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{pmatrix}
= \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{4.57}
$$

Now, divide the first by 2, the second by 2 and the third by -3 to get unity in the diagonal:

$$
\begin{pmatrix} 1 & 0 & \frac{1}{2} & 0 \\ 0 & 1 & 1 & \frac{1}{2} \\ 0 & 0 & 1 & -\frac{2}{3} \end{pmatrix}
\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{pmatrix}
= \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{4.58}
$$

So-called *bound variables* have non-zero coefficients on the diagonal, so one can take the bound variables to be ν_1, ν_2, and ν_3. The remaining variables are *free variables.* Here, one takes the free variable to be ν_4. So, set $\nu_4 = \xi$, and rewrite the system as

$$
\begin{pmatrix} 1 & 0 & \frac{1}{2} \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} 0 \\ -\frac{1}{2}\xi \\ \frac{2}{3}\xi \end{pmatrix}. \tag{4.59}
$$

Solving, one finds

$$
\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{pmatrix} = \begin{pmatrix} -\frac{1}{3}\xi \\ -\frac{7}{6}\xi \\ \frac{2}{3}\xi \\ \xi \end{pmatrix} = \xi \begin{pmatrix} -\frac{1}{3} \\ -\frac{7}{6} \\ \frac{2}{3} \\ 1 \end{pmatrix}, \qquad \xi \in \mathbb{R}^1. \tag{4.60}
$$

Again one finds a non-unique solution in the right null space of ϕ. If one chooses $\xi = 6$, then one gets

$$
\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{pmatrix} = \begin{pmatrix} -2 \\ -7 \\ 4 \\ 6 \end{pmatrix}, \tag{4.61}
$$

which corresponds to the stoichiometrically balanced reaction

$$
2C_2H_6 + 7O_2 \rightleftharpoons 4CO_2 + 6H_2O. \tag{4.62}
$$

In this example, ξ is dimensionless.

Example 4.5

Consider stoichiometric balance for a propane oxidation reaction which may produce carbon monoxide and hydroxyl in addition to carbon dioxide and water.

The hypothesized reaction takes the form

$$
\nu_1' C_3H_8 + \nu_2' O_2 \rightleftharpoons \nu_3'' CO_2 + \nu_4'' CO + \nu_5'' H_2O + \nu_6'' OH. \tag{4.63}
$$
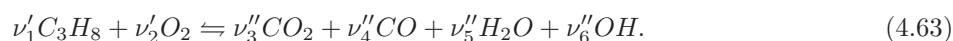
In terms of net stoichiometric coefficients, this becomes

$$
\nu_1 C_3H_8 + \nu_2 O_2 + \nu_3 CO_2 + \nu_4 CO + \nu_5 H_2O + \nu_6 OH = 0. \tag{4.64}
$$

There are $N = 6$ species and $L = 3$ elements. One then has

$$
\begin{array}{rclll}
\phi_{11} & = & 3, & C \text{ in } C_3H_8, & (4.65) \\
\phi_{12} & = & 0, & C \text{ in } O_2, & (4.66) \\
\phi_{13} & = & 1, & C \text{ in } CO_2, & (4.67) \\
\phi_{14} & = & 1, & C \text{ in } CO, & (4.68) \\
\phi_{15} & = & 0, & C \text{ in } H_2O, & (4.69) \\
\phi_{16} & = & 0, & C \text{ in } OH, & (4.70) \\
\phi_{21} & = & 8, & H \text{ in } C_3H_8, & (4.71)
\end{array}
$$

$$\phi_{22} = 0, \qquad H \text{ in } O_2, \tag{4.72}$$

$$\phi_{23} = 0, \qquad H \text{ in } CO_2, \tag{4.73}$$

$$\phi_{24} = 0, \qquad H \text{ in } CO, \tag{4.74}$$

$$\phi_{25} = 2, \qquad H \text{ in } H_2O, \tag{4.75}$$

$$\phi_{26} = 1, \qquad H \text{ in } OH, \tag{4.76}$$

$$\phi_{31} = 0, \qquad O \text{ in } C_3H_8, \tag{4.77}$$

$$\phi_{32} = 2, \qquad O \text{ in } O_2, \tag{4.78}$$

$$\phi_{33} = 2, \qquad O \text{ in } CO_2, \tag{4.79}$$

$$\phi_{34} = 1, \qquad O \text{ in } CO, \tag{4.80}$$

$$\phi_{35} = 1, \qquad O \text{ in } H_2O, \tag{4.81}$$

$$\phi_{36} = 1, \qquad O \text{ in } OH. \tag{4.82}$$

The equation $\boldsymbol{\phi} \cdot \boldsymbol{\nu} = 0$, then becomes

$$\begin{pmatrix} 3 & 0 & 1 & 1 & 0 & 0 \\ 8 & 0 & 0 & 0 & 2 & 1 \\ 0 & 2 & 2 & 1 & 1 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \\ \nu_6 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{4.83}$$

Multiplying the first equation by $-8/3$ and adding it to the second gives

$$\begin{pmatrix} 3 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & -\frac{8}{3} & -\frac{8}{3} & 2 & 1 \\ 0 & 2 & 2 & 1 & 1 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \\ \nu_6 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{4.84}$$

Trading the second and third rows gives

$$\begin{pmatrix} 3 & 0 & 1 & 1 & 0 & 0 \\ 0 & 2 & 2 & 1 & 1 & 1 \\ 0 & 0 & -\frac{8}{3} & -\frac{8}{3} & 2 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \\ \nu_6 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{4.85}$$

Dividing the first row by 3, the second by 2 and the third by $-8/3$ gives

$$\begin{pmatrix} 1 & 0 & \frac{1}{3} & \frac{1}{3} & 0 & 0 \\ 0 & 1 & 1 & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ 0 & 0 & 1 & 1 & -\frac{3}{4} & -\frac{3}{8} \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \\ \nu_6 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{4.86}$$

Take bound variables to be ν_1, ν_2, and ν_3 and free variables to be ν_4, ν_5, and ν_6. So, set $\nu_4 = \xi_1$, $\nu_5 = \xi_2$, and $\nu_6 = \xi_3$, and get

$$\begin{pmatrix} 1 & 0 & \frac{1}{3} \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} -\frac{\xi_1}{3} \\ -\frac{\xi_1}{2} - \frac{\xi_2}{2} - \frac{\xi_3}{2} \\ -\xi_1 + \frac{3}{4}\xi_2 + \frac{3}{8}\xi_3 \end{pmatrix}. \tag{4.87}$$

Solving, one finds

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} \frac{1}{8}(-2\xi_2 - \xi_3) \\ \frac{1}{8}(4\xi_1 - 10\xi_2 - 7\xi_3) \\ \frac{1}{8}(-8\xi_1 + 6\xi_2 + 3\xi_3) \end{pmatrix}. \tag{4.88}$$

For all the coefficients, one then has

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \\ \nu_6 \end{pmatrix} = \begin{pmatrix} \frac{1}{8}(-2\xi_2 - \xi_3) \\ \frac{1}{8}(4\xi_1 - 10\xi_2 - 7\xi_3) \\ \frac{1}{8}(-8\xi_1 + 6\xi_2 + 3\xi_3) \\ \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix} = \frac{\xi_1}{8}\begin{pmatrix} 0 \\ 4 \\ -8 \\ 8 \\ 0 \\ 0 \end{pmatrix} + \frac{\xi_2}{8}\begin{pmatrix} -2 \\ -10 \\ 6 \\ 0 \\ 8 \\ 0 \end{pmatrix} + \frac{\xi_3}{8}\begin{pmatrix} -1 \\ -7 \\ 3 \\ 0 \\ 0 \\ 8 \end{pmatrix}. \tag{4.89}$$

Here, one finds *three* independent vectors in the right null space. To simplify the notation, take $\hat{\xi}_1 = \xi_1/8$, $\hat{\xi}_2 = \xi_2/8$, and $\hat{\xi}_3 = \xi_3/8$. Then,

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \\ \nu_6 \end{pmatrix} = \hat{\xi}_1\begin{pmatrix} 0 \\ 4 \\ -8 \\ 8 \\ 0 \\ 0 \end{pmatrix} + \hat{\xi}_2\begin{pmatrix} -2 \\ -10 \\ 6 \\ 0 \\ 8 \\ 0 \end{pmatrix} + \hat{\xi}_3\begin{pmatrix} -1 \\ -7 \\ 3 \\ 0 \\ 0 \\ 8 \end{pmatrix}. \tag{4.90}$$

The most general reaction that can achieve a stoichiometric balance is given by

$$(-2\hat{\xi}_2 - \hat{\xi}_3)C_3H_8 + (4\hat{\xi}_1 - 10\hat{\xi}_2 - 7\hat{\xi}_3)O_2 + (-8\hat{\xi}_1 + 6\hat{\xi}_2 + 3\hat{\xi}_3)CO_2 + 8\hat{\xi}_1\,CO + 8\hat{\xi}_2\,H_2O + 8\hat{\xi}_3\,OH = 0. \tag{4.91}$$

Rearranging, one gets

$$(2\hat{\xi}_2 + \hat{\xi}_3)C_3H_8 + (-4\hat{\xi}_1 + 10\hat{\xi}_2 + 7\hat{\xi}_3)O_2 \rightleftharpoons (-8\hat{\xi}_1 + 6\hat{\xi}_2 + 3\hat{\xi}_3)CO_2 + 8\hat{\xi}_1\,CO + 8\hat{\xi}_2\,H_2O + 8\hat{\xi}_3\,OH. \tag{4.92}$$

This will be balanced for all $\hat{\xi}_1$, $\hat{\xi}_2$, and $\hat{\xi}_3$. The values that are actually achieved in practice depend on the thermodynamics of the problem. Stoichiometry only provides some limitations.

A slightly more familiar form is found by taking $\hat{\xi}_2 = 1/2$ and rearranging, giving

$$(1 + \hat{\xi}_3)\,C_3H_8 + (5 - 4\hat{\xi}_1 + 7\hat{\xi}_3)\,O_2 \rightleftharpoons (3 - 8\hat{\xi}_1 + 3\hat{\xi}_3)\,CO_2 + 4\,H_2O + 8\hat{\xi}_1\,CO + 8\hat{\xi}_3\,OH. \tag{4.93}$$

One notes that often the production of CO and OH will be small. If there is no production of CO or OH, $\hat{\xi}_1 = \hat{\xi}_3 = 0$ and one recovers the familiar balance of

$$C_3H_8 + 5\,O_2 \rightleftharpoons 3\,CO_2 + 4\,H_2O. \tag{4.94}$$

One also notes that stoichiometry alone admits unusual solutions. For instance, if $\hat{\xi}_1 = 100$ $\hat{\xi}_2 = 1/2$, and $\hat{\xi}_3 = 1$, one has

$$2\,C_3H_8 + 794\,CO_2 \rightleftharpoons 388\,O_2 + 4\,H_2O + 800\,CO + 8\,OH. \tag{4.95}$$

This reaction is certainly admitted by stoichiometry but is not observed in nature. To determine precisely which of the infinitely many possible final states are realized requires a consideration of the equilibrium condition $\sum_{i=1}^{N} \nu_i \overline{\mu}_i = 0$.

Looked at in another way, we can think of three independent classes of reactions admitted by the stoichiometry, one for each of the linearly independent null space vectors. Taking first $\hat{\xi}_1 = 1/4$, $\hat{\xi}_2 = 0$, $\hat{\xi}_3 = 0$, one gets, after rearrangement

$$2CO + O_2 \rightleftharpoons 2CO_2, \tag{4.96}$$

as one class of reaction admitted by stoichiometry. Taking next $\hat{\xi}_1 = 0$, $\hat{\xi}_2 = 1/2$, $\hat{\xi}_3 = 0$, one gets

$$C_3H_8 + 5O_2 \leftrightharpoons 3CO_2 + 4H_2O, \tag{4.97}$$

as the second class admitted by stoichiometry. The third class is given by taking $\hat{\xi}_1 = 0$, $\hat{\xi}_2 = 0$, $\hat{\xi}_3 = 1$, and is

$$C_3H_8 + 7O_2 \leftrightharpoons 3CO_2 + 8OH. \tag{4.98}$$

In this example, both ξ and $\hat{\xi}$ are dimensionless.

In general, one can expect to find the stoichiometric coefficients for N species composed of L elements to be of the following form:

$$\nu_i = \sum_{k=1}^{N-L} \mathcal{D}_{ik}\xi_k, \qquad i = 1, \ldots, N. \tag{4.99}$$

Here, $\mathcal{D}_{ik}$ is a dimensionless component of a full rank matrix of dimension $N \times (N - L)$ and rank $N - L$, and ξ_k is a dimensionless component of a vector of parameters of length $N - L$. The matrix whose components are $\mathcal{D}_{ik}$ are constructed by populating its columns with vectors which lie in the right null space of ϕ_{li}. Note that multiplication of ξ_k by any constant gives another set of ν_i, and mass conservation for each element is still satisfied.

4.2.2 Fuel-air mixtures

In combustion with air, one often models air as a simple mixture of diatomic oxygen and inert diatomic nitrogen in the

$$\text{air:} \qquad \nu'_{air}(O_2 + 3.76N_2). \tag{4.100}$$

The *air-fuel ratio*, $\mathcal{A}$ and its reciprocal, the *fuel-air ratio*, $\mathcal{F}$, can be defined on a mass and mole basis.

$$\mathcal{A}_{mass} = \frac{m_{air}}{m_{fuel}}, \qquad \mathcal{A}_{mole} = \frac{n_{air}}{n_{fuel}}. \tag{4.101}$$

Via the molecular masses, one has

$$\mathcal{A}_{mass} = \frac{m_{air}}{m_{fuel}} = \frac{n_{air}M_{air}}{n_{fuel}M_{fuel}} = \mathcal{A}_{mole}\frac{M_{air}}{M_{fuel}}. \tag{4.102}$$

If there is not enough air to burn all the fuel, the mixture is said to be *rich*. If there is excess air, the mixture is said to be *lean*. If there is just enough, the mixture is said to be *stoichiometric*. The *equivalence ratio*, Φ, is defined as the actual fuel-air ratio scaled by the stoichiometric fuel-air ratio:

$$\Phi \equiv \frac{\mathcal{F}_{actual}}{\mathcal{F}_{stoichiometric}} = \frac{\mathcal{A}_{stoichiometric}}{\mathcal{A}_{actual}}. \tag{4.103}$$

The ratio Φ is the same whether $\mathcal{F}$'s are taken on a mass or mole basis, because the ratio of molecular masses cancel.

Example 4.6

Calculate the stoichiometry of the combustion of methane with air with an equivalence ratio of $\Phi = 0.5$. If the pressure is $0.1 \, MPa$, find the dew point of the products.

First calculate the coefficients for stoichiometric combustion:

$$\nu_1' CH_4 + \nu_2'(O_2 + 3.76 N_2) \rightleftharpoons \nu_3'' CO_2 + \nu_4'' H_2 O + \nu_5'' N_2. \tag{4.104}$$
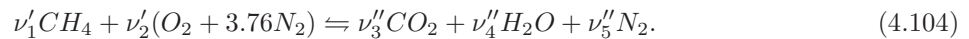
Or

$$\nu_1 CH_4 + \nu_2 O_2 + \nu_3 CO_2 + \nu_4 H_2 O + (\nu_5 + 3.76\nu_2) N_2 = 0. \tag{4.105}$$

Here, one has $N = 5$ species and $L = 4$ elements. Adopting a slightly more intuitive procedure for variety, one writes a conservation equation for each element to get

$$\begin{aligned}
\nu_1 + \nu_3 &= 0, & C, & \tag{4.106} \\
4\nu_1 + 2\nu_4 &= 0, & H, & \tag{4.107} \\
2\nu_2 + 2\nu_3 + \nu_4 &= 0, & O, & \tag{4.108} \\
3.76\nu_2 + \nu_5 &= 0, & N. & \tag{4.109}
\end{aligned}$$

In matrix form this becomes

$$\begin{pmatrix} 1 & 0 & 1 & 0 & 0 \\ 4 & 0 & 0 & 2 & 0 \\ 0 & 2 & 2 & 1 & 0 \\ 0 & 3.76 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \tag{4.110}$$

Now, one might expect to have one free variable, since one has five unknowns in four equations. While casting the equation in row echelon form is guaranteed to yield a proper solution, one can often use intuition to get a solution more rapidly. One certainly expects that CH_4 will need to be present for the reaction to take place. One might also expect to find an answer if there is one mole of CH_4. So take $\nu_1 = -1$. Realize that one could also get a physically valid answer by assuming ν_1 to be equal to *any* scalar. With $\nu_1 = -1$, one gets

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 2 & 2 & 1 & 0 \\ 3.76 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \end{pmatrix} = \begin{pmatrix} 1 \\ 4 \\ 0 \\ 0 \end{pmatrix}. \tag{4.111}$$

One easily finds the unique inverse does exist, and that the solution is

$$\begin{pmatrix} \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \end{pmatrix} = \begin{pmatrix} -2 \\ 1 \\ 2 \\ 7.52 \end{pmatrix}. \tag{4.112}$$

If there had been more than one free variable, the 4×4 matrix would have been singular, and no unique inverse would have existed.

In any case, the reaction under stoichiometric conditions is

$$-CH_4 - 2O_2 + CO_2 + 2H_2O + (7.52 + (3.76)(-2))N_2 \;\; = \;\; 0, \tag{4.113}$$
$$CH_4 + 2(O_2 + 3.76N_2) \;\; \leftrightharpoons \;\; CO_2 + 2H_2O + 7.52N_2. \tag{4.114}$$

For the stoichiometric reaction, the fuel-air ratio on a mole basis is

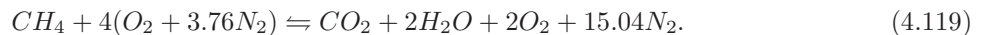$$\mathcal{F}_{stoichiometric} = \frac{1}{2 + 2(3.76)} = 0.1050. \tag{4.115}$$

Now, $\Phi = 0.5$, so

$$\mathcal{F}_{actual} \;\; = \;\; \Phi \mathcal{F}_{stoichiometric}, \tag{4.116}$$
$$= \;\; (0.5)(0.1050), \tag{4.117}$$
$$= \;\; 0.0525. \tag{4.118}$$

By inspection, one can write the *actual* reaction equation as

$$CH_4 + 4(O_2 + 3.76N_2) \leftrightharpoons CO_2 + 2H_2O + 2O_2 + 15.04N_2. \tag{4.119}$$

Check:

$$\mathcal{F}_{actual} = \frac{1}{4 + 4(3.76)} = 0.0525. \tag{4.120}$$

For the dew point of the products, one needs the partial pressure of H_2O. The mole fraction of H_2O is

$$y_{H_2O} = \frac{2}{1 + 2 + 2 + 15.04} = 0.0499 \tag{4.121}$$

So, the partial pressure of H_2O is

$$P_{H_2O} = y_{H_2O}P = 0.0499(100 \; kPa) = 4.99 \; kPa. \tag{4.122}$$

From the steam tables, the saturation temperature at this pressure is $T_{sat} = T_{dew \; point} = 32.88°C$. If the products cool to this temperature in an exhaust device, the water could condense in the apparatus.

4.3   First law analysis of reacting systems

One can easily use the first law to learn much about chemically reacting systems.

4.3.1   Enthalpy of formation

The enthalpy of formation is the enthalpy that is required to form a molecule from combining its constituents at $P = 0.1 \; MPa$ and $T = 298 \; K$. Consider the reaction (taken here to be irreversible)

$$C + O_2 \rightarrow CO_2. \tag{4.123}$$

In order to maintain the process at constant temperature, it is found that heat transfer to the volume is necessary. For the steady constant pressure process, one has

$$E_2 - E_1 = {}_1Q_2 - {}_1W_2, \tag{4.124}$$

$$= {}_1Q_2 - \int_1^2 PdV, \tag{4.125}$$

$$= {}_1Q_2 - P(V_2 - V_1), \tag{4.126}$$

$${}_1Q_2 = E_2 - E_1 + P(V_2 - V_1), \tag{4.127}$$

$$= H_2 - H_1, \tag{4.128}$$

$${}_1Q_2 = H_{products} - H_{reactants}, \tag{4.129}$$

$$= \sum_{products} n_i \overline{h}_i - \sum_{reactants} n_i \overline{h}_i. \tag{4.130}$$

In this reaction, one measures that ${}_1Q_2 = -393522 \ kJ$ for the reaction of 1 $kmole$ of C and O_2. That is, the reaction liberates such energy to the environment. So, measuring the heat transfer can give a measure of the enthalpy difference between reactants and products. Assign a value of enthalpy zero to elements in their standard state at the reference state. Thus, C and O_2 both have enthalpies of 0 $kJ/kmole$ at $T = 298 \ K$, $P = 0.1 \ MPa$. This enthalpy is designated, for species i,

$$\overline{h}_{f,i}^o = \overline{h}_{T_o,i}^o, \tag{4.131}$$

and is called the *enthalpy of formation*. So, the energy balance for the products and reactants, here both at the standard state, becomes

$${}_1Q_2 = n_{CO_2} \overline{h}_{f,CO_2}^o - n_C \overline{h}_{f,C}^o - n_{O_2} \overline{h}_{f,O_2}^o, \tag{4.132}$$

$$-393522 \ kJ = (1 \ kmole)\overline{h}_{f,CO_2}^o - (1 \ kmole)\left(0 \ \frac{kJ}{kmole}\right) - (1 \ kmole)\left(0 \ \frac{kJ}{kmole}\right). \tag{4.133}$$

Thus, the enthalpy of formation of CO_2 is $\overline{h}_{f,CO_2}^o = -393522 \ kJ/kmole$, since the reaction involved creation of 1 $kmole$ of CO_2.

Often values of enthalpy are tabulated in the forms of enthalpy differences $\Delta \overline{h}_i$. These are defined such that

$$\overline{h}_i = \overline{h}_{f,i}^o + \underbrace{(\overline{h}_i - \overline{h}_{f,i}^o)}_{=\Delta \overline{h}_i}, \tag{4.134}$$

$$= \overline{h}_{f,i}^o + \Delta \overline{h}_i. \tag{4.135}$$

Lastly, one notes for an ideal gas that the enthalpy is a function of temperature only, and so does not depend on the reference pressure; hence

$$\overline{h}_i = \overline{h}_i^o, \qquad \Delta \overline{h}_i = \Delta \overline{h}_i^o, \qquad \text{if ideal gas.} \tag{4.136}$$

Example 4.7

(Borgnakke and Sonntag, p. 575). Consider the following irreversible reaction in a steady state, steady flow process confined to the standard state of $P = 0.1 \ MPa$, $T = 298 \ K$:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(\ell). \tag{4.137}$$
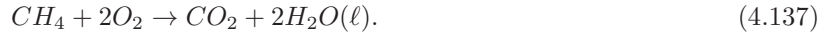
The first law holds that

$$Q_{cv} = \sum_{products} n_i \overline{h}_i - \sum_{reactants} n_i \overline{h}_i. \tag{4.138}$$

All components are at their reference states. Borgnakke and Sonntag's Table A.10 gives properties, and one finds

$$
\begin{aligned}
Q_{cv} &= n_{CO_2}\overline{h}_{CO_2} + n_{H_2O}\overline{h}_{H_2O} - n_{CH_4}\overline{h}_{CH_4} - n_{O_2}\overline{h}_{O_2}, \tag{4.139} \\
&= (1 \ kmole)\left(-393522 \ \frac{kJ}{kmole}\right) + (2 \ kmole)\left(-285830 \ \frac{kJ}{kmole}\right) \\
&\quad -(1 \ kmole)\left(-74873 \ \frac{kJ}{kmole}\right) - (2 \ kmole)\left(0 \ \frac{kJ}{kmole}\right), \tag{4.140} \\
&= -890309 \ kJ. \tag{4.141}
\end{aligned}
$$

A more detailed analysis is required in the likely case in which the system is not at the reference state.

Example 4.8

(adopted from Moran and Shapiro[6]) A mixture of 1 *kmole* of gaseous methane and 2 *kmole* of oxygen initially at 298 K and 101.325 kPa burns completely in a closed, rigid, container. Heat transfer occurs until the final temperature is 900 K. Find the heat transfer and the final pressure.

The combustion is stoichiometric. Assume that no small concentration species are generated. The global reaction is given by

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O. \tag{4.142}$$

The first law analysis for the closed system is slightly different:

$$E_2 - E_1 = {}_1Q_2 - {}_1W_2. \tag{4.143}$$

Since the process is isochoric, ${}_1W_2 = 0$. So

$$
\begin{aligned}
{}_1Q_2 &= E_2 - E_1, \tag{4.144} \\
&= n_{CO_2}\overline{e}_{CO_2} + n_{H_2O}\overline{e}_{H_2O} - n_{CH_4}\overline{e}_{CH_4} - n_{O_2}\overline{e}_{O_2}, \tag{4.145}
\end{aligned}
$$

---

[6]Moran, M. J., and Shapiro, H. N., 2003, *Fundamentals of Engineering Thermodynamics*, Fifth Edition, John Wiley, New York. p. 619.

$$
\begin{align}
&= n_{CO_2}(\overline{h}_{CO_2} - \overline{R}T_2) + n_{H_2O}(\overline{h}_{H_2O} - \overline{R}T_2) - n_{CH_4}(\overline{h}_{CH_4} - \overline{R}T_1) - n_{O_2}(\overline{h}_{O_2} - \overline{R}T_1), \tag{4.146} \\
&= \overline{h}_{CO_2} + 2\overline{h}_{H_2O} - \overline{h}_{CH_4} - 2\overline{h}_{O_2} - 3\overline{R}(T_2 - T_1), \tag{4.147} \\
&= (\overline{h}^o_{CO_2,f} + \Delta\overline{h}_{CO_2}) + 2(\overline{h}^o_{H_2O,f} + \Delta\overline{h}_{H_2O}) - (\overline{h}^o_{CH_4,f} + \Delta\overline{h}_{CH_4}) - 2(\overline{h}^o_{O_2,f} + \Delta\overline{h}_{O_2}) \\
&\quad\, -3\overline{R}(T_2 - T_1), \tag{4.148} \\
&= (-393522 + 28030) + 2(-241826 + 21937) - (-74873 + 0) - 2(0 + 0) \\
&\quad\, -3(8.314)(900 - 298), \tag{4.149} \\
&= -745412 \ kJ. \tag{4.150}
\end{align}
$$

For the pressures, one has

$$
\begin{align}
P_1 V_1 &= (n_{CH_4} + n_{O_2})\overline{R}T_1, \tag{4.151} \\
V_1 &= \frac{(n_{CH_4} + n_{O_2})\overline{R}T_1}{P_1}, \tag{4.152} \\
&= \frac{(1 \ kmole + 2 \ kmole)\left(8.314 \ \frac{kJ}{kg \ K}\right)(298 \ K)}{101.325 \ kPa}, \tag{4.153} \\
&= 73.36 \ m^3. \tag{4.154}
\end{align}
$$

Now, $V_2 = V_1$, so

$$
\begin{align}
P_2 &= \frac{(n_{CO_2} + n_{H_2O})\overline{R}T_2}{V_2}, \tag{4.155} \\
&= \frac{(1 \ kmole + 2 \ kmole)\left(8.314 \ \frac{kJ}{kg \ K}\right)(900 \ K)}{73.36 \ m^3}, \tag{4.156} \\
&= 306.0 \ kPa. \tag{4.157}
\end{align}
$$

The pressure increased in the reaction. This is entirely attributable to the temperature rise, as the number of moles remained constant here.

4.3.2 Enthalpy and internal energy of combustion

The *enthalpy of combustion* is the difference between the enthalpy of products and reactants when complete combustion occurs at a given pressure and temperature. It is also known as the *heating value* or the *heat of reaction*. The *internal energy of combustion* is related and is the difference between the internal energy of products and reactants when complete combustion occurs at a given volume and temperature.

The term *higher heating value* refers to the energy of combustion when liquid water is in the products. *Lower heating value* refers to the energy of combustion when water vapor is in the product.

4.3.3 Adiabatic flame temperature in isochoric stoichiometric systems

The *adiabatic flame temperature* refers to the temperature which is achieved when a fuel and oxidizer are combined with no loss of work or heat energy. Thus, it must occur in a closed, insulated, fixed volume. It is generally the highest temperature that one can expect to achieve in a combustion process. It generally requires an iterative solution. Of all mixtures, stoichiometric mixtures will yield the highest adiabatic flame temperatures because there is no need to heat the excess fuel or oxidizer.

Here, four examples will be presented to illustrate the following points.

- The adiabatic flame temperature can be well over 5000 K for seemingly ordinary mixtures.

- Dilution of the mixture with an inert diluent lowers the adiabatic flame temperature. The same effect would happen in rich and lean mixtures.

- Preheating the mixture, such as one might find in the compression stroke of an engine, increases the adiabatic flame temperature.

- Consideration of the presence of minor species lowers the adiabatic flame temperature.

4.3.3.1 Undiluted, cold mixture

Example 4.9

   A closed, fixed, adiabatic volume contains a stoichiometric mixture of 2 *kmole* of H_2 and 1 *kmole* of O_2 at 100 *kPa* and 298 *K*. Find the adiabatic flame temperature assuming the irreversible reaction

$$2H_2 + O_2 \rightarrow 2H_2O. \tag{4.158}$$

The volume is given by

$$V = \frac{(n_{H_2} + n_{O_2})\overline{R}T_1}{P_1}, \tag{4.159}$$

$$= \frac{(2\ kmole + 1\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(298\ K)}{100\ kPa}, \tag{4.160}$$

$$= 74.33\ m^3. \tag{4.161}$$

The first law gives

$$E_2 - E_1 = {}_1Q_2 - {}_1W_2, \tag{4.162}$$

$$E_2 - E_1 = 0, \tag{4.163}$$

$$n_{H_2O}\overline{e}_{H_2O} - n_{H_2}\overline{e}_{H_2} - n_{O_2}\overline{e}_{O_2} = 0, \tag{4.164}$$

$$n_{H_2O}(\overline{h}_{H_2O} - \overline{R}T_2) - n_{H_2}(\overline{h}_{H_2} - \overline{R}T_1) - n_{O_2}(\overline{h}_{O_2} - \overline{R}T_1) = 0, \tag{4.165}$$

$$2\overline{h}_{H_2O} - 2\underbrace{\overline{h}_{H_2}}_{=0} - \underbrace{\overline{h}_{O_2}}_{=0} + \overline{R}(-2T_2 + 3T_1) \quad = \quad 0, \tag{4.166}$$

$$2\overline{h}_{H_2O} + (8.314)\left((-2)\,T_2 + (3)\,(298)\right) \quad = \quad 0, \tag{4.167}$$

$$\overline{h}_{H_2O} - 8.314T_2 + 3716.4 \quad = \quad 0, \tag{4.168}$$

$$\overline{h}^o_{f,H_2O} + \Delta\overline{h}_{H_2O} - 8.314T_2 + 3716.4 \quad = \quad 0, \tag{4.169}$$

$$-241826 + \Delta\overline{h}_{H_2O} - 8.314T_2 + 3716.4 \quad = \quad 0, \tag{4.170}$$

$$-238110 + \Delta\overline{h}_{H_2O} - 8.314T_2 \quad = \quad 0. \tag{4.171}$$

At this point, one begins an iteration process, guessing a value of T_2 and an associated $\Delta\overline{h}_{H_2O}$. When T_2 is guessed at 5600 K, the left side becomes -6507.04. When T_2 is guessed at 6000 K, the left side becomes 14301.4. Interpolate then to arrive at

$$T_2 = 5725\ K. \tag{4.172}$$

This is an extremely high temperature. At such temperatures, in fact, one can expect other species to co-exist in the equilibrium state in large quantities. These may include H, OH, O, HO_2, and H_2O_2, among others.

The final pressure is given by

$$P_2 \quad = \quad \frac{n_{H_2O}\overline{R}T_2}{V}, \tag{4.173}$$

$$= \quad \frac{(2\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(5725\ K)}{74.33\ m^3}, \tag{4.174}$$

$$= \quad 1280.71\ kPa. \tag{4.175}$$

The final concentration of H_2O is

$$\overline{\rho}_{H_2O} = \frac{2\ kmole}{74.33\ m^3} = 2.69 \times 10^{-2}\ \frac{kmole}{m^3}. \tag{4.176}$$

4.3.3.2   Dilute, cold mixture

Example 4.10

Consider a variant on the previous example in which the mixture is diluted with an inert, taken here to be N_2. A closed, fixed, adiabatic volume contains a stoichiometric mixture of 2 $kmole$ of H_2, 1 $kmole$ of O_2, and 8 $kmole$ of N_2 at 100 kPa and 298 K. Find the adiabatic flame temperature and the final pressure, assuming the irreversible reaction

$$2H_2 + O_2 + 8N_2 \rightarrow 2H_2O + 8N_2. \tag{4.177}$$

The volume is given by

$$V \quad = \quad \frac{(n_{H_2} + n_{O_2} + n_{N_2})\overline{R}T_1}{P_1}, \tag{4.178}$$

$$= \quad \frac{(2\ kmole + 1\ kmole + 8\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(298\ K)}{100\ kPa}, \tag{4.179}$$

$$= \quad 272.533\ m^3. \tag{4.180}$$

The first law gives

$$
\begin{aligned}
E_2 - E_1 &= {}_1Q_2 - {}_1W_2, \\
E_2 - E_1 &= 0, \\
n_{H_2O}\overline{e}_{H_2O} - n_{H_2}\overline{e}_{H_2} - n_{O_2}\overline{e}_{O_2} + n_{N_2}(\overline{e}_{N_{2_2}} - \overline{e}_{N_{2_1}}) &= 0, \\
n_{H_2O}(\overline{h}_{H_2O} - \overline{R}T_2) - n_{H_2}(\overline{h}_{H_2} - \overline{R}T_1) - n_{O_2}(\overline{h}_{O_2} - \overline{R}T_1) + n_{N_2}((\overline{h}_{N_{2_2}} - \overline{R}T_2) - (\overline{h}_{N_{2_1}} - \overline{R}T_1)) &= 0, \\
2\overline{h}_{H_2O} - 2\underbrace{\overline{h}_{H_2}}_{=0} - \underbrace{\overline{h}_{O_2}}_{=0} + \overline{R}(-10T_2 + 11T_1) + 8(\underbrace{\overline{h}_{N_{2_2}}}_{=\Delta\overline{h}_{N_2}} - \underbrace{\overline{h}_{N_{2_1}}}_{=0}) &= 0, \\
2\overline{h}_{H_2O} + (8.314)(-10T_2 + (11)(298)) + 8\Delta\overline{h}_{N_{2_2}} &= 0, \\
2\overline{h}_{H_2O} - 83.14T_2 + 27253.3 + 8\Delta\overline{h}_{N_{2_2}} &= 0, \\
2\overline{h}^o_{f,H_2O} + 2\Delta\overline{h}_{H_2O} - 83.14T_2 + 27253.3 + 8\Delta\overline{h}_{N_{2_2}} &= 0, \\
2(-241826) + 2\Delta\overline{h}_{H_2O} - 83.14T_2 + 27253.3 + 8\Delta\overline{h}_{N_{2_2}} &= 0, \\
-456399 + 2\Delta\overline{h}_{H_2O} - 83.14T_2 + 8\Delta\overline{h}_{N_{2_2}} &= 0,
\end{aligned}
$$

At this point, one begins an iteration process, guessing a value of T_2 and an associated $\Delta\overline{h}_{H_2O}$. When T_2 is guessed at 2000 K, the left side becomes -28006.7. When T_2 is guessed at 2200 K, the left side becomes 33895.3. Interpolate then to arrive at

$$T_2 = 2090.5 \ K. \tag{4.181}$$

The inert diluent significantly lowers the adiabatic flame temperature. This is because the N_2 serves as a heat sink for the energy of reaction. If the mixture were at non-stoichiometric conditions, the excess species would also serve as a heat sink, and the adiabatic flame temperature would be lower than that of the stoichiometric mixture.

The final pressure is given by

$$
\begin{aligned}
P_2 &= \frac{(n_{H_2O} + n_{N_2})\overline{R}T_2}{V}, \tag{4.182} \\
&= \frac{(2 \ kmole + 8 \ kmole)\left(8.314 \ \frac{kJ}{kmole \ K}\right)(2090.5 \ K)}{272.533 \ m^3}, \tag{4.183} \\
&= 637.74 \ kPa. \tag{4.184}
\end{aligned}
$$

The final concentrations of H_2O and N_2 are

$$
\begin{aligned}
\overline{\rho}_{H_2O} &= \frac{2 \ kmole}{272.533 \ m^3} = 7.34 \times 10^{-3} \ \frac{kmole}{m^3}, \tag{4.185} \\
\overline{\rho}_{N_2} &= \frac{8 \ kmole}{272.533 \ m^3} = 2.94 \times 10^{-2} \ \frac{kmole}{m^3}. \tag{4.186}
\end{aligned}
$$

4.3.3.3 Dilute, preheated mixture

Example 4.11

Consider a variant on the previous example in which the diluted mixture is preheated to 1000 K. One can achieve this via an isentropic compression of the cold mixture, such as might occur in an engine.

To simplify the analysis here, the temperature of the mixture will be increased, while the pressure will be maintained. A closed, fixed, adiabatic volume contains a stoichiometric mixture of 2 $kmole$ of H_2, 1 $kmole$ of O_2, and 8 $kmole$ of N_2 at 100 kPa and 1000 K. Find the adiabatic flame temperature and the final pressure, assuming the irreversible reaction

$$2H_2 + O_2 + 8N_2 \rightarrow 2H_2O + 8N_2. \tag{4.187}$$

The volume is given by

$$V = \frac{(n_{H_2} + n_{O_2} + n_{N_2})\overline{R}T_1}{P_1}, \tag{4.188}$$

$$= \frac{(2\ kmole + 1\ kmole + 8\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(1000\ K)}{100\ kPa}, \tag{4.189}$$

$$= 914.54\ m^3. \tag{4.190}$$

The first law gives

$$E_2 - E_1 = {}_1Q_2 - {}_1W_2,$$

$$E_2 - E_1 = 0,$$

$$n_{H_2O}\overline{e}_{H_2O} - n_{H_2}\overline{e}_{H_2} - n_{O_2}\overline{e}_{O_2} + n_{N_2}(\overline{e}_{N_2 2} - \overline{e}_{N_2 1}) = 0,$$

$$n_{H_2O}(\overline{h}_{H_2O} - \overline{R}T_2) - n_{H_2}(\overline{h}_{H_2} - \overline{R}T_1) - n_{O_2}(\overline{h}_{O_2} - \overline{R}T_1) + n_{N_2}((\overline{h}_{N_2 1} - \overline{R}T_2) - (\overline{h}_{N_2 1} - \overline{R}T_1)) = 0,$$

$$2\overline{h}_{H_2O} - 2\overline{h}_{H_2} - \overline{h}_{O_2} + \overline{R}(-10T_2 + 11T_1) + 8(\overline{h}_{N_2 2} - \overline{h}_{N_2 1}) = 0,$$

$$2(-241826 + \Delta\overline{h}_{H_2O}) - 2(20663) - 22703 + (8.314)(-10T_2 + (11)(1000)) + 8\Delta\overline{h}_{N_2 2} - 8(21463) = 0,$$

$$2\Delta\overline{h}_{H_2O} - 83.14T_2 - 627931 + 8\Delta\overline{h}_{N_2 2} = 0,$$

At this point, one begins an iteration process, guessing a value of T_2 and an associated $\Delta\overline{h}_{H_2O}$. When T_2 is guessed at 2600 K, the left side becomes -11351. When T_2 is guessed at 2800 K, the left side becomes 52787. Interpolate then to arrive at

$$T_2 = 2635.4\ K. \tag{4.191}$$

The preheating raised the adiabatic flame temperature. Note that the preheating was by 1000 K − 298 K = 702 K. The new adiabatic flame temperature is only 2635.4 K − 2090.5 K = 544.9 K greater.

The final pressure is given by

$$P_2 = \frac{(n_{H_2O} + n_{N_2})\overline{R}T_2}{V}, \tag{4.192}$$

$$= \frac{(2\ kmole + 8\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(2635.4\ K)}{914.54\ m^3}, \tag{4.193}$$

$$= 239.58\ kPa. \tag{4.194}$$

The final concentrations of H_2O and N_2 are

$$\overline{\rho}_{H_2O} = \frac{2\ kmole}{914.54\ m^3} = 2.19 \times 10^{-3}\ \frac{kmole}{m^3}, \tag{4.195}$$

$$\overline{\rho}_{N_2} = \frac{8\ kmole}{914.54\ m^3} = 8.75 \times 10^{-3}\ \frac{kmole}{m^3}. \tag{4.196}$$

4.3.3.4 Dilute, preheated mixture with minor species

Example 4.12

Consider a variant on the previous example. Here, allow for minor species to be present at equilibrium. A closed, fixed, adiabatic volume contains a stoichiometric mixture of 2 $kmole$ of H_2, 1 $kmole$ of O_2, and 8 $kmole$ of N_2 at 100 kPa and 1000 K. Find the adiabatic flame temperature and the final pressure, assuming reversible reactions.

Here, the details of the analysis are omitted, but the result is given which is the consequence of a calculation involving detailed reactions rates involving equations of the form to be studied in Sec. 5.1. One can also solve an optimization problem to minimize the Gibbs free energy of a wide variety of products to get the same answer; for a general discussion, see Sec. 5.2.1. In this case, the equilibrium temperature and pressure are found to be

$$T = 2484.8 \ K, \qquad P = 227.89 \ kPa. \tag{4.197}$$

Equilibrium species concentrations are found to be

$$\text{minor product} \quad \overline{\rho}_{H_2} \ = \ 1.3 \times 10^{-4} \ \frac{kmole}{m^3}, \tag{4.198}$$

$$\text{minor product} \quad \overline{\rho}_{H} \ = \ 1.9 \times 10^{-5} \ \frac{kmole}{m^3}, \tag{4.199}$$

$$\text{minor product} \quad \overline{\rho}_{O} \ = \ 5.7 \times 10^{-6} \ \frac{kmole}{m^3}, \tag{4.200}$$

$$\text{minor product} \quad \overline{\rho}_{O_2} \ = \ 3.6 \times 10^{-5} \ \frac{kmole}{m^3}, \tag{4.201}$$

$$\text{minor product} \quad \overline{\rho}_{OH} \ = \ 5.9 \times 10^{-5} \ \frac{kmole}{m^3}, \tag{4.202}$$

$$\textbf{major} \text{ product} \quad \overline{\rho}_{H_2O} \ = \ 2.0 \times 10^{-3} \ \frac{kmole}{m^3}, \tag{4.203}$$

$$\text{trace product} \quad \overline{\rho}_{HO_2} \ = \ 1.1 \times 10^{-8} \ \frac{kmole}{m^3}, \tag{4.204}$$

$$\text{trace product} \quad \overline{\rho}_{H_2O_2} \ = \ 1.2 \times 10^{-9} \ \frac{kmole}{m^3}, \tag{4.205}$$

$$\text{trace product} \quad \overline{\rho}_{N} \ = \ 1.7 \times 10^{-9} \ \frac{kmole}{m^3}, \tag{4.206}$$

$$\text{trace product} \quad \overline{\rho}_{NH} \ = \ 3.7 \times 10^{-10} \ \frac{kmole}{m^3}, \tag{4.207}$$

$$\text{trace product} \quad \overline{\rho}_{NH_2} \ = \ 1.5 \times 10^{-10} \ \frac{kmole}{m^3}, \tag{4.208}$$

$$\text{trace product} \quad \overline{\rho}_{NH_3} \ = \ 3.1 \times 10^{-10} \ \frac{kmole}{m^3}, \tag{4.209}$$

$$\text{trace product} \quad \overline{\rho}_{NNH} \ = \ 1.0 \times 10^{-10} \ \frac{kmole}{m^3}, \tag{4.210}$$

$$\text{minor product} \quad \overline{\rho}_{NO} \ = \ 3.1 \times 10^{-6} \ \frac{kmole}{m^3}, \tag{4.211}$$

$$\text{trace product} \quad \overline{\rho}_{NO_2} \ = \ 5.3 \times 10^{-9} \ \frac{kmole}{m^3}, \tag{4.212}$$

$$\text{trace product} \quad \overline{\rho}_{N_2O} \ = \ 2.6 \times 10^{-9} \ \frac{kmole}{m^3}, \tag{4.213}$$

$$\text{trace product} \quad \overline{\rho}_{HNO} \;=\; 1.7 \times 10^{-9} \, \frac{kmole}{m^3}, \tag{4.214}$$

$$\textbf{major} \text{ product} \quad \overline{\rho}_{N_2} \;=\; 8.7 \times 10^{-3} \, \frac{kmole}{m^3}. \tag{4.215}$$

Note that the concentrations of the major products went down when the minor species were considered. The adiabatic flame temperature also went down by a significant amount: $2635\ K - 2484.8\ K = 150.2\ K$. Some thermal energy was necessary to break the bonds which induce the presence of minor species.

4.4 Chemical equilibrium

Often reactions are not simply unidirectional, as alluded to in the previous example. The reverse reaction, especially at high temperature, can be important.

Consider the four species reaction

$$\nu_1' \chi_1 + \nu_2' \chi_2 \rightleftharpoons \nu_3'' \chi_3 + \nu_4'' \chi_4 \tag{4.216}$$

In terms of the net stoichiometric coefficients, this becomes

$$\nu_1 \chi_1 + \nu_2 \chi_2 + \nu_3 \chi_3 + \nu_4 \chi_4 = 0. \tag{4.217}$$

One can define a variable ζ, the *reaction progress*. Take the dimension of ζ to be *mole*. When $t = 0$, one takes $\zeta = 0$. Now, as the reaction goes forward, one takes $d\zeta > 0$. And a forward reaction will decrease the number of moles of χ_1 and χ_2 while increasing the number of moles of χ_3 and χ_4. This will occur in ratios dictated by the stoichiometric coefficients of the problem:

$$dn_1 \;=\; -\nu_1' d\zeta, \tag{4.218}$$
$$dn_2 \;=\; -\nu_2' d\zeta, \tag{4.219}$$
$$dn_3 \;=\; +\nu_3'' d\zeta, \tag{4.220}$$
$$dn_4 \;=\; +\nu_4'' d\zeta. \tag{4.221}$$

Note that if n_i is taken to have units of *mole*, ν_i', and ν_i'' are taken as dimensionless, then ζ must have units of *mole*. In terms of the net stoichiometric coefficients, one has

$$dn_1 \;=\; \nu_1 d\zeta, \tag{4.222}$$
$$dn_2 \;=\; \nu_2 d\zeta, \tag{4.223}$$
$$dn_3 \;=\; \nu_3 d\zeta, \tag{4.224}$$
$$dn_4 \;=\; \nu_4 d\zeta. \tag{4.225}$$

Again, for argument's sake, assume that at $t = 0$, one has

$$
\begin{align}
n_1|_{t=0} &= n_{1o}, & (4.226) \\
n_2|_{t=0} &= n_{2o}, & (4.227) \\
n_3|_{t=0} &= n_{3o}, & (4.228) \\
n_4|_{t=0} &= n_{4o}. & (4.229)
\end{align}
$$

Then, after integrating, one finds

$$
\begin{align}
n_1 &= \nu_1 \zeta + n_{1o}, & (4.230) \\
n_2 &= \nu_2 \zeta + n_{2o}, & (4.231) \\
n_3 &= \nu_3 \zeta + n_{3o}, & (4.232) \\
n_4 &= \nu_4 \zeta + n_{4o}. & (4.233)
\end{align}
$$

One can also eliminate the parameter ζ in a variety of fashions and parameterize the reaction by one of the species mole numbers. Choosing, for example, n_1 as a parameter, one gets

$$
\zeta = \frac{n_1 - n_{1o}}{\nu_1}. \tag{4.234}
$$

Eliminating ζ, one finds all other mole numbers in terms of n_1:

$$
\begin{align}
n_2 &= \nu_2 \frac{n_1 - n_{1o}}{\nu_1} + n_{2o}, & (4.235) \\
n_3 &= \nu_3 \frac{n_1 - n_{1o}}{\nu_1} + n_{3o}, & (4.236) \\
n_4 &= \nu_4 \frac{n_1 - n_{1o}}{\nu_1} + n_{4o}. & (4.237)
\end{align}
$$

Written another way, one has

$$
\frac{n_1 - n_{1o}}{\nu_1} = \frac{n_2 - n_{2o}}{\nu_2} = \frac{n_3 - n_{3o}}{\nu_3} = \frac{n_4 - n_{4o}}{\nu_4} = \zeta. \tag{4.238}
$$

For an N-species reaction, $\sum_{i=1}^{N} \nu_i \chi_i = 0$, one can generalize to say

$$
\begin{align}
dn_i &= \nu_i d\zeta, & (4.239) \\
n_i &= \nu_i \zeta + n_{io}, & (4.240) \\
\frac{n_i - n_{io}}{\nu_i} &= \zeta. & (4.241)
\end{align}
$$

Note that

$$
\frac{dn_i}{d\zeta} = \nu_i. \tag{4.242}
$$

Now, from the previous Chapter 3, one manifestation of the second law is Eq. (3.361):

$$dG|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i dn_i \leq 0. \tag{4.243}$$

Now, one can eliminate dn_i in Eq. (4.243) by use of Eq. (4.239) to get

$$dG|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i \nu_i d\zeta \leq 0, \tag{4.244}$$

$$\left.\frac{\partial G}{\partial \zeta}\right|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i \nu_i \leq 0, \tag{4.245}$$

$$= -\overline{\alpha} \leq 0. \tag{4.246}$$

Then, for the reaction to go forward, one must require that the affinity, defined earlier in Eq. (3.472), be positive:

$$\overline{\alpha} \geq 0. \tag{4.247}$$

One also knows from Chapter 3 that the irreversibility takes the form of Eq. (3.350):

$$-\frac{1}{T} \sum_{i=1}^{N} \overline{\mu}_i dn_i \geq 0, \tag{4.248}$$

$$-\frac{1}{T} d\zeta \sum_{i=1}^{N} \overline{\mu}_i \nu_i \geq 0, \tag{4.249}$$

$$-\frac{1}{T} \frac{d\zeta}{dt} \sum_{i=1}^{N} \overline{\mu}_i \nu_i \geq 0. \tag{4.250}$$

In terms of the chemical affinity, $\overline{\alpha} = -\sum_{i=1}^{N} \overline{\mu}_i \nu_i$, Eq. (4.250) can be written as

$$\frac{1}{T} \frac{d\zeta}{dt} \overline{\alpha} \geq 0. \tag{4.251}$$

Now, one straightforward, albeit naïve, way to guarantee positive semi-definiteness of the irreversibility and thus satisfaction of the second law is to construct the chemical kinetic rate equation so that

$$\frac{d\zeta}{dt} = -k \sum_{i=1}^{N} \overline{\mu}_i \nu_i = k\overline{\alpha}, \qquad k \geq 0, \qquad provisional, \; naïve \; assumption \tag{4.252}$$

This provisional assumption of convenience will be supplanted later in Sec. 4.5 by a form which agrees well with experiment. Here, k is a positive semi-definite scalar. In general, it is

a function of temperature, $k = k(T)$, so that reactions proceed rapidly at high temperature and slowly at low temperature. Then, certainly the reaction progress variable ζ will cease to change when the equilibrium condition

$$\sum_{i=1}^{N} \overline{\mu}_i \nu_i = 0, \tag{4.253}$$

is met. This is equivalent to requiring

$$\overline{\alpha} = 0. \tag{4.254}$$

Now, while Eq. (4.253) is the most compact form of the equilibrium condition, it is not the most commonly used form. One can perform the following analysis to obtain the form in most common usage. Start by employing Eq. (3.268) equating the chemical potential with the Gibbs free energy per unit mole for each species i: $\overline{\mu}_i = \overline{g}_i$. Then, employ the definition of Gibbs free energy for an ideal gas, and carry out a set of operations:

$$\sum_{i=1}^{N} \overline{g}_i \nu_i \;=\; 0, \qquad \text{at equilibrium,} \tag{4.255}$$

$$\sum_{i=1}^{N} (\overline{h}_i - T\overline{s}_i)\nu_i \;=\; 0, \qquad \text{at equilibrium.} \tag{4.256}$$

For the ideal gas, one can substitute for $\overline{h}_i(T)$ and $\overline{s}_i(T, P)$ and write the equilibrium condition as

$$\sum_{i=1}^{N} \left(\underbrace{\overline{h}^o_{T_o,i} + \underbrace{\int_{T_o}^{T} \overline{c}_{Pi}(\hat{T})\, d\hat{T}}_{=\Delta \overline{h}^o_{T,i}}}_{=\overline{h}^o_{T,i}=\overline{h}_{T,i}} - T \left(\underbrace{\underbrace{\overline{s}^o_{T_o,i} + \int_{T_o}^{T} \frac{\overline{c}_{Pi}(\hat{T})}{\hat{T}} d\hat{T}}_{=\overline{s}^o_{T,i}} - \overline{R} \ln\left(\frac{y_i P}{P_o}\right)}_{=\overline{s}_{T,i}} \right) \right) \nu_i \;=\; 0, \tag{4.257}$$

Now, writing the equilibrium condition in terms of the enthalpies and entropies referred to the standard pressure, one gets

$$\sum_{i=1}^{N} \left(\overline{h}^o_{T,i} - T\left(\overline{s}^o_{T,i} - \overline{R}\ln\left(\frac{y_i P}{P_o}\right) \right) \right) \nu_i \;=\; 0, \tag{4.258}$$

$$\sum_{i=1}^{N} \underbrace{\left(\overline{h}^o_{T,i} - T\overline{s}^o_{T,i} \right)}_{=\overline{g}^o_{T,i}=\overline{\mu}^o_{T,i}} \nu_i \;=\; -\sum_{i=1}^{N} \overline{R}T\nu_i \ln\left(\frac{y_i P}{P_o}\right), \tag{4.259}$$

$$-\sum_{\underbrace{i=1}_{\equiv \Delta G^o}}^{N} \overline{g}^o_{T,i} \nu_i = \overline{R}T \sum_{i=1}^{N} \ln \left(\frac{y_i P}{P_o}\right)^{\nu_i}, \qquad (4.260)$$

$$-\frac{\Delta G^o}{\overline{R}T} = \sum_{i=1}^{N} \ln \left(\frac{y_i P}{P_o}\right)^{\nu_i}, \qquad (4.261)$$

$$= \ln \left(\prod_{i=1}^{N} \left(\frac{y_i P}{P_o}\right)^{\nu_i}\right), \qquad (4.262)$$

$$\underbrace{\exp\left(-\frac{\Delta G^o}{\overline{R}T}\right)}_{\equiv K_P} = \prod_{i=1}^{N} \left(\frac{y_i P}{P_o}\right)^{\nu_i}, \qquad (4.263)$$

$$K_P = \prod_{i=1}^{N} \left(\frac{y_i P}{P_o}\right)^{\nu_i}, \qquad (4.264)$$

$$K_P = \left(\frac{P}{P_o}\right)^{\sum_{i=1}^{N} \nu_i} \prod_{i=1}^{n} y_i^{\nu_i}, \qquad (4.265)$$

$$K_P = \prod_{i=1}^{N} \left(\frac{P_i}{P_o}\right)^{\nu_i}, \quad \text{at equilibrium.} \quad (4.266)$$

Here, K_P is what is known as the pressure-based *equilibrium constant*. It is dimensionless. Despite its name, it is not a constant. It is defined in terms of thermodynamic properties, and for the ideal gas is a function of T only:

$$K_P \equiv \exp\left(-\frac{\Delta G^o}{\overline{R}T}\right), \qquad \text{generally valid.} \qquad (4.267)$$

Only at equilibrium does the property K_P also equal the product of the partial pressures as in Eq. (4.266). The subscript P for pressure comes about because it is also related to the product of the ratio of the partial pressure to the reference pressure raised to the net stoichiometric coefficients. Also, the net change in Gibbs free energy of the reaction at the reference pressure, ΔG^o, which is a function of T only, has been defined as

$$\Delta G^o \equiv \sum_{i=1}^{N} \overline{g}^o_{T,i} \nu_i. \qquad (4.268)$$

The term ΔG^o has units of $kJ/kmole$; it traditionally does not get an overbar. If $\Delta G^o > 0$, one has $0 < K_P < 1$, and reactants are favored over products. If $\Delta G^o < 0$, one gets $K_P > 1$, and products are favored over reactants. One can also deduce that higher pressures P push the equilibrium in such a fashion that fewer moles are present, all else being equal. One can also define ΔG^o in terms of the chemical affinity, referred to the reference pressure, as

$$\Delta G^o = -\overline{\alpha}^o. \qquad (4.269)$$

One can also define another convenient thermodynamic property, which for an ideal gas is a function of T alone, the equilibrium constant K_c:

$$K_c \equiv \left(\frac{P_o}{\overline{R}T} \right)^{\sum_{i=1}^{N} \nu_i} \exp \left(-\frac{\Delta G^o}{\overline{R}T} \right), \qquad \text{generally valid.} \qquad (4.270)$$

This property is dimensional, and the units depend on the stoichiometry of the reaction. The units of K_c will be $(mole/cm^3)^{\sum_{i=1}^{N} \nu_i}$.

The equilibrium condition, Eq. (4.266), is often written in terms of molar concentrations and K_c. This can be achieved by the operations, valid only at an equilibrium state:

$$K_P = \prod_{i=1}^{N} \left(\frac{\overline{\rho}_i \overline{R}T}{P_o} \right)^{\nu_i}, \qquad (4.271)$$

$$\exp \left(\frac{-\Delta G^o}{\overline{R}T} \right) = \left(\frac{\overline{R}T}{P_o} \right)^{\sum_{i=1}^{N} \nu_i} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i}, \qquad (4.272)$$

$$\underbrace{\left(\frac{P_o}{\overline{R}T} \right)^{\sum_{i=1}^{N} \nu_i} \exp \left(\frac{-\Delta G^o}{\overline{R}T} \right)}_{\equiv K_c} = \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i}, \qquad (4.273)$$

$$K_c = \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i}, \qquad \text{at equilibrium.} \qquad (4.274)$$

One must be careful to distinguish between the general definition of K_c as given in Eq. (4.270), and the fact that at equilibrium it is driven to also have the value of product of molar species concentrations, raised to the appropriate stoichiometric power, as given in Eq. (4.274).

4.5   Chemical kinetics of a single isothermal reaction

In the same fashion in ordinary mechanics that an understanding of statics enables an understanding of dynamics, an understanding of chemical equilibrium is necessary to understand to more challenging topic of chemical kinetics. Chemical kinetics describes the time-evolution of systems which may have an initial state far from equilibrium; it typically describes the path of such systems to an equilibrium state. Here, gas phase kinetics of ideal gas mixtures that obey Dalton's law will be studied. Important topics such as catalysis and solid or liquid reactions will not be considered.

Further, this section will be restricted to strictly *isothermal* systems. This simplifies the analysis greatly. It is straightforward to extend the analysis of this system to non-isothermal systems. One must then make further appeal to the energy equation to get an equation for temperature evolution.

The general form for evolution of species is taken to be

$$\frac{d}{dt}\left(\frac{\overline{\rho}_i}{\rho}\right) = \frac{\dot{\omega}_i}{\rho}. \tag{4.275}$$

Multiplying both sides of Eq. (4.275) by molecular mass M_i and using Eq. (2.43) to exchange $\overline{\rho}_i$ for mass fraction Y_i then gives the alternate form

$$\frac{dY_i}{dt} = \frac{\dot{\omega}_i M_i}{\rho}. \tag{4.276}$$

4.5.1 Isochoric systems

Consider the evolution of species concentration in a system which is isothermal, isochoric and spatially homogeneous. The system is undergoing a single chemical reaction involving N species of the familiar form of Eq. (4.21):

$$\sum_{i=1}^{N} \nu_i \chi_i = 0. \tag{4.277}$$

Because the density is constant for the isochoric system, Eq. (4.275) reduces to

$$\frac{d\overline{\rho}_i}{dt} = \dot{\omega}_i. \tag{4.278}$$

Then, experiment, as well as a more fundamental molecular collision theory, shows that the evolution of species concentration i is given by

$$\frac{d\overline{\rho}_i}{dt} = \nu_i \underbrace{\underbrace{aT^\beta \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right)}_{\equiv k(T)} \underbrace{\left(\prod_{k=1}^{N} \overline{\rho}_k^{\nu_k'}\right)}_{\text{forward reaction}} \underbrace{\left(1 - \frac{1}{K_c}\prod_{k=1}^{N} \overline{\rho}_k^{\nu_k}\right)}_{\text{reverse reaction}}}_{\equiv r}^{\equiv \dot{\omega}_i}, \qquad \text{isochoric system} \tag{4.279}$$

This relation actually holds for isochoric, non-isothermal systems as well, which will not be considered in any detail here. Here, some new variables are defined as follows:

- a: a kinetic rate constant called the *collision frequency factor*. Its units will depend on the actual reaction and could involve various combinations of length, time, and temperature. It is constructed so that $d\overline{\rho}_i/dt$ has units of $mole/cm^3/s$; this requires it to have units of $(mole/cm^3)^{(1-\nu_M' - \sum_{k=1}^{N}\nu_k')}/s/K^\beta$. Here, ν_M' is a coefficient which is present if an inert third body participates in the reaction.

- β: a dimensionless parameter whose value is set by experiments, sometimes combined with guiding theory, to account for weak temperature dependency of reaction rates.

- $\overline{\mathcal{E}}$: the *activation energy*. It has units of *cal/mole*, though others are often used, and is fit by both experiment and fundamental theory to account for the strong temperature dependency of reaction.

Note that in Eq. (4.279) that molar concentrations are raised to the ν'_k and ν_k powers. As it does not make sense to raise a physical quantity to a power with units, one traditionally interprets the values of ν_k, ν'_k, as well as ν''_k to be dimensionless pure numbers. They are also interpreted in a standard fashion: the smallest integer values that actually correspond to the underlying molecular collision which has been modelled. While stoichiometric balance can be achieved by a variety of ν_k values, the kinetic rates are linked to one particular set which is defined by the community.

Equation (4.279) is written in such a way that the species concentration production rate *increases* when

- The net number of moles generated in the reaction, measured by ν_i increases,

- The temperature increases; here, the sensitivity may be very high, as one observes in nature,

- The species concentrations of species involved in the forward reaction increase; this embodies the principle that the *collision-based* reaction rates are enhanced when there are more molecules to collide,

- The species concentrations of species involved in the reverse reaction decrease.

Here, three intermediate variables which are in common usage have been defined. First one takes the reaction rate to be

$$
r \;\equiv\; \underbrace{aT^\beta \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right)}_{\equiv k(T)} \underbrace{\left(\prod_{k=1}^{N}\overline{\rho}_k^{\;\nu'_k}\right)}_{\text{forward reaction}} \left(1 - \underbrace{\frac{1}{K_c}\prod_{k=1}^{N}\overline{\rho}_k^{\;\nu_k}}_{\text{reverse reaction}}\right), \tag{4.280}
$$

$$
=\; \underbrace{aT^\beta \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right)}_{\equiv k(T),\ \text{Arrhenius rate}} \underbrace{\left(\underbrace{\prod_{k=1}^{N}\overline{\rho}_k^{\;\nu'_k}}_{\text{forward reaction}} - \underbrace{\frac{1}{K_c}\prod_{k=1}^{N}\overline{\rho}_k^{\;\nu''_k}}_{\text{reverse reaction}}\right)}_{\text{law of mass action}}. \tag{4.281}
$$

The reaction rate r has units of $mole/cm^3/s$.

The temperature-dependency of the reaction rate is embodied in $k(T)$ is defined by what is known as an *Arrhenius*[7] *rate law*:

$$
k(T) \;\equiv\; aT^\beta \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right). \tag{4.282}
$$

---

[7]Svante Arrhenius, 1859-1927, Swedish physicist.

This equation was advocated by van't Hoff[8] in 1884; in 1889 Arrhenius gave a physical justification. The units of $k(T)$ actually depend on the reaction. This is a weakness of the theory, and precludes a clean non-dimensionalization. The units must be $(mole/cm^3)^{(1-\nu'_M-\sum_{k=1}^{N}\nu'_k)}/s$.

In terms of reaction progress, one can also take

$$r = \frac{1}{V}\frac{d\zeta}{dt}. \tag{4.283}$$

The factor of $1/V$ is necessary because r has units of molar concentration per time and ζ has units of *mole*. The over-riding importance of the temperature sensitivity is illustrated as part of the next example. The remainder of the expression involving the products of the species concentrations is the defining characteristic of systems which obey the *law of mass action*. Though the history is complex, most attribute the law of mass action to Guldberg[9] and Waage[10] in 1864.[11] Last, the overall molar production rate of species i, often written as $\dot{\omega}_i$, is defined as

$$\dot{\omega}_i \equiv \nu_i r. \tag{4.284}$$

As ν_i is considered to be dimensionless, the units of $\dot{\omega}_i$ must be $mole/cm^3/s$.

Example 4.13

Study the nitrogen dissociation problem considered in an earlier example which was confined to equilibrium analysis, see Sec. 3.11.2.1, in which at $t = 0$ s, 1 $kmole$ of N_2 exists at $P = 100$ kPa and $T = 6000$ K. Take as before the reaction to be *isothermal* and *isochoric*. Consider again the elementary nitrogen dissociation reaction

$$N_2 + N_2 \leftrightharpoons 2N + N_2, \tag{4.285}$$

which has kinetic rate parameters of

$$a = 7.0 \times 10^{21} \frac{cm^3\ K^{1.6}}{mole\ s}, \tag{4.286}$$

$$\beta = -1.6, \tag{4.287}$$

$$\overline{\mathcal{E}} = 224928.4 \frac{cal}{mole}. \tag{4.288}$$

In SI units, this becomes

$$a = \left(7.0 \times 10^{21} \frac{cm^3\ K^{1.6}}{mole\ s}\right)\left(\frac{1\ m}{100\ cm}\right)^3\left(\frac{1000\ mole}{kmole}\right) = 7.0 \times 10^{18} \frac{m^3\ K^{1.6}}{kmole\ s}, \tag{4.289}$$

$$\overline{\mathcal{E}} = \left(224928.4 \frac{cal}{mole}\right)\left(4.186 \frac{J}{cal}\right)\left(\frac{kJ}{1000\ J}\right)\left(\frac{1000\ mole}{kmole}\right) = 941550 \frac{kJ}{kmole}. \tag{4.290}$$

---

[8]Jacobus Henricus van't Hoff, 1852-1922, Dutch chemist.

[9]Cato Maximilian Guldberg, 1836-1902, Norwegian mathematician and chemist.

[10]Peter Waage, 1833-1900, Norwegian chemist.

[11]P. Waage and C. M. Guldberg, 1864, "Studies Concerning Affinity, *Forhandlinger: Videnskabs-Selskabet i Christiania*, 35. English translation: *Journal of Chemical Education*, 63(12): 1044-1047.

At the initial state, the material is all N_2, so $P_{N_2} = P = 100 \ kPa$. The ideal gas law then gives at $t = 0$

$$P|_{t=0} \quad = \quad P_{N_2}|_{t=0} = \overline{\rho}_{N_2}|_{t=0} \ \overline{R} T, \tag{4.291}$$

$$\overline{\rho}_{N_2}|_{t=0} \quad = \quad \frac{P|_{t=0}}{\overline{R}T}, \tag{4.292}$$

$$= \quad \frac{100 \ kPa}{\left(8.314 \ \frac{kJ}{kmole \ K}\right)(6000 \ K)}, \tag{4.293}$$

$$= \quad 2.00465 \times 10^{-3} \ \frac{kmole}{m^3}. \tag{4.294}$$

Thus, the volume, constant for all time in the isochoric process, is

$$V = \frac{n_{N_2}|_{t=0}}{\overline{\rho}_{N_2}|_{t=0}} = \frac{1 \ kmole}{2.00465 \times 10^{-3} \ \frac{kmole}{m^3}} = 4.9884 \times 10^2 \ m^3. \tag{4.295}$$

Now, the stoichiometry of the reaction is such that

$$-dn_{N_2} \quad = \quad \frac{1}{2} dn_N, \tag{4.296}$$

$$-(n_{N_2} - \underbrace{n_{N_2}|_{t=0}}_{=1 \ kmole}) \quad = \quad \frac{1}{2}(n_N - \underbrace{n_N|_{t=0}}_{=0}), \tag{4.297}$$

$$n_N \quad = \quad 2(1 \ kmole - n_{N_2}), \tag{4.298}$$

$$\frac{n_N}{V} \quad = \quad 2\left(\frac{1 \ kmole}{V} - \frac{n_{N_2}}{V}\right), \tag{4.299}$$

$$\overline{\rho}_N \quad = \quad 2\left(\frac{1 \ kmole}{4.9884 \times 10^2 \ m^3} - \overline{\rho}_{N_2}\right), \tag{4.300}$$

$$= \quad 2\left(2.00465 \times 10^{-3} \ \frac{kmole}{m^3} - \overline{\rho}_{N_2}\right). \tag{4.301}$$

Now, the general equation for kinetics of a single reaction, Eq. (4.279), reduces for N_2 molar concentration to

$$\frac{d\overline{\rho}_{N_2}}{dt} \quad = \quad \nu_{N_2} a T^\beta \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right) (\overline{\rho}_{N_2})^{\nu'_{N_2}} (\overline{\rho}_N)^{\nu'_N} \left(1 - \frac{1}{K_c} (\overline{\rho}_{N_2})^{\nu_{N_2}} (\overline{\rho}_N)^{\nu_N}\right) \tag{4.302}$$

Realizing that $\nu'_{N_2} = 2$, $\nu'_N = 0$, $\nu_{N_2} = -1$, and $\nu_N = 2$, one gets

$$\frac{d\overline{\rho}_{N_2}}{dt} \quad = \quad \underbrace{-a T^\beta \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right)}_{=k(T)} \overline{\rho}_{N_2}^2 \left(1 - \frac{1}{K_c} \frac{\overline{\rho}_N^2}{\overline{\rho}_{N_2}}\right) \tag{4.303}$$

Examine the primary temperature dependency of the reaction

$$k(T) \quad = \quad a T^\beta \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right), \tag{4.304}$$

$$= \quad \left(7.0 \times 10^{18} \ \frac{m^3 K^{1.6}}{kmole \ s}\right) T^{-1.6} \exp\left(\frac{-941550 \ \frac{kJ}{kmole}}{8.314 \ \frac{kJ}{kmole \ K} T}\right), \tag{4.305}$$

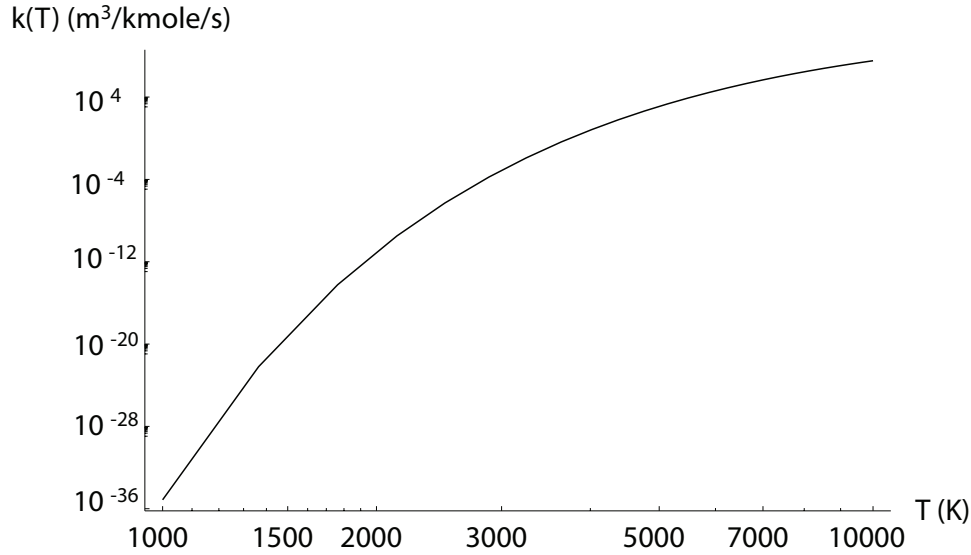$$= \quad \frac{7.0 \times 10^{18}}{T^{1.6}} \exp\left(\frac{-1.1325 \times 10^5}{T}\right) \tag{4.306}$$

Figure 4.1: $k(T)$ for Nitrogen dissociation example.

Figure 4.1 gives a plot of $k(T)$ which shows its very strong dependency on temperature. For this problem, $T = 6000 \ K$, so

$$k(6000) = \frac{7.0 \times 10^{18}}{6000^{1.6}} \exp\left(\frac{-1.1325 \times 10^5}{6000}\right), \tag{4.307}$$

$$= 40071.6 \ \frac{m^3}{kmole \ s}. \tag{4.308}$$

Now, the equilibrium constant K_c is needed. Recall

$$K_c = \left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^{N} \nu_i} \exp\left(\frac{-\Delta G^o}{\overline{R}T}\right) \tag{4.309}$$

For this system, since $\sum_{i=1}^{N} \nu_i = 1$, this reduces to

$$K_c = \left(\frac{P_o}{\overline{R}T}\right) \exp\left(\frac{-(2\overline{g}_N^o - \overline{g}_{N_2}^o)}{\overline{R}T}\right), \tag{4.310}$$

$$= \left(\frac{P_o}{\overline{R}T}\right) \exp\left(\frac{-(2(\overline{h}_N^o - Ts_{T,N}^o) - (\overline{h}_{N_2}^o - Ts_{T,N_2}^o))}{\overline{R}T}\right), \tag{4.311}$$

$$= \left(\frac{100}{(8.314)(6000)}\right) \exp\left(\frac{-(2(597270 - (6000)216.926) - (205848 - (6000)292.984))}{(8.314)(6000)}\right), \tag{4.312}$$

$$= 0.000112112 \ \frac{kmole}{m^3}. \tag{4.313}$$

The differential equation for N_2 evolution is then given by

$$\frac{d\overline{\rho}_{N_2}}{dt} = \underbrace{-\left(40071.6 \ \frac{m^3}{kmole}\right) \overline{\rho}_{N_2}^2 \left(1 - \frac{1}{0.000112112 \ \frac{kmole}{m^3}} \frac{\left(2\left(2.00465 \times 10^{-3} \ \frac{kmole}{m^3} - \overline{\rho}_{N_2}\right)\right)^2}{\overline{\rho}_{N_2}}\right)}_{\equiv f(\overline{\rho}_{N_2})},$$
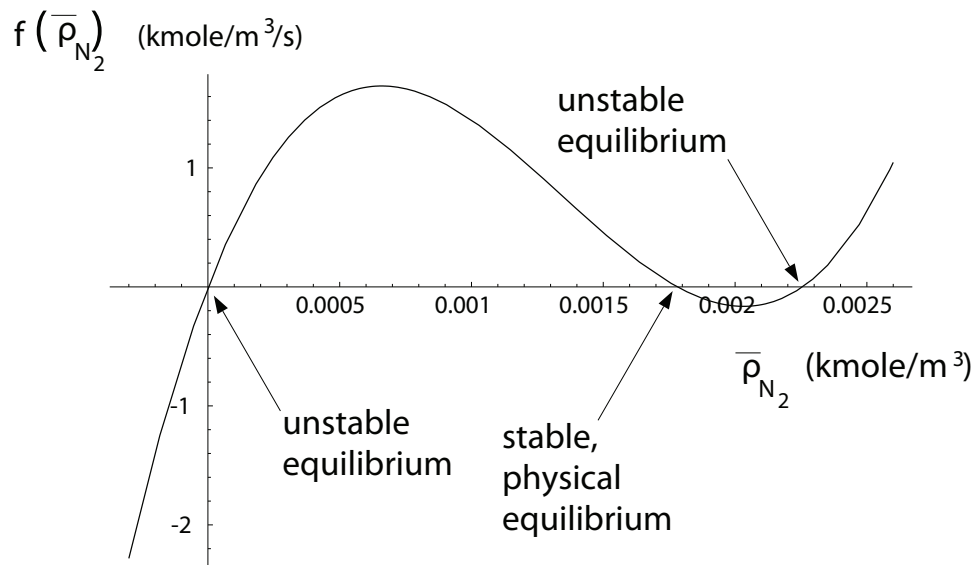
Figure 4.2: Forcing function, $f(\overline{\rho}_{N_2})$, which drives changes of $\overline{\rho}_{N_2}$ as a function of $\overline{\rho}_{N_2}$ in isothermal, isochoric problem.

$$\tag{4.314}$$

$$= \quad f(\overline{\rho}_{N_2}). \tag{4.315}$$

The system is at equilibrium when $f(\overline{\rho}_{N_2}) = 0$. This is an algebraic function of $\overline{\rho}_{N_2}$ only, and can be plotted. Figure 4.2 gives a plot of $f(\overline{\rho}_{N_2})$ and shows that it has three potential equilibrium points. It is seen there are three roots. Solving for the equilibria requires solving

$$0 \quad = \quad -\left(40071.6 \ \frac{m^3}{kmole}\right) \overline{\rho}_{N_2}^2 \left(1 - \frac{1}{0.000112112 \ \frac{kmole}{m^3}} \frac{\left(2\left(2.00465 \times 10^{-3} \ \frac{kmole}{m^3}\right) - \overline{\rho}_{N_2}\right)^2}{\overline{\rho}_{N_2}}\right). \tag{4.316}$$

The three roots are

$$\overline{\rho}_{N_2} = \underbrace{0 \ \frac{kmole}{m^3}}_{unstable}, \qquad \underbrace{0.00178121 \ \frac{kmole}{m^3}}_{stable}, \qquad \underbrace{0.00225611 \ \frac{kmole}{m^3}}_{unstable}. \tag{4.317}$$

By inspection of the topology of Fig. 4.2, the only stable root is $0.00178121 \ kmole/m^3$. This root agrees with the equilibrium value found in an earlier example for the same problem conditions. Small perturbations from this equilibrium induce the forcing function to supply dynamics which restore the system to its original equilibrium state. Small perturbations from the unstable equilibria induce non-restoring dynamics. For this root, one can then determine that the stable equilibrium value of $\overline{\rho}_N = 0.000446882 \ kmole/m^3$.

One can examine this stability more formally. Define an equilibrium concentration $\overline{\rho}_{N_2}^{eq}$ such that

$$f(\overline{\rho}_{N_2}^{eq}) = 0. \tag{4.318}$$

Now, perform a Taylor series of $f(\overline{\rho}_{N_2})$ about $\overline{\rho}_{N_2} = \overline{\rho}_{N_2}^{eq}$:

$$f(\overline{\rho}_{N_2}) \sim \underbrace{f(\overline{\rho}_{N_2}^{eq})}_{=0} + \frac{df}{d\overline{\rho}_{N_2}}\bigg|_{\overline{\rho}_{N_2}=\overline{\rho}_{N_2}^{eq}} (\overline{\rho}_{N_2} - \overline{\rho}_{N_2}^{eq}) + \frac{1}{2}\frac{d^2 f}{d\overline{\rho}_{N_2}^2}(\overline{\rho}_{N_2} - \overline{\rho}_{N_2}^{eq})^2 + \dots \tag{4.319}$$

Now, the first term of the Taylor series is zero by construction. Next, neglect all higher order terms as small so that the approximation becomes

$$f(\overline{\rho}_{N_2}) \sim \left. \frac{df}{d\overline{\rho}_{N_2}} \right|_{\overline{\rho}_{N_2}=\overline{\rho}_{N_2}^{eq}} (\overline{\rho}_{N_2} - \overline{\rho}_{N_2}^{eq}). \tag{4.320}$$

Thus, near equilibrium, one can write

$$\frac{d\overline{\rho}_{N_2}}{dt} \sim \left. \frac{df}{d\overline{\rho}_{N_2}} \right|_{\overline{\rho}_{N_2}=\overline{\rho}_{N_2}^{eq}} (\overline{\rho}_{N_2} - \overline{\rho}_{N_2}^{eq}). \tag{4.321}$$

Since the derivative of a constant is zero, one can also write the equation as

$$\frac{d}{dt}(\overline{\rho}_{N_2} - \overline{\rho}_{N_2}^{eq}) \sim \left. \frac{df}{d\overline{\rho}_{N_2}} \right|_{\overline{\rho}_{N_2}=\overline{\rho}_{N_2}^{eq}} (\overline{\rho}_{N_2} - \overline{\rho}_{N_2}^{eq}). \tag{4.322}$$

This has a solution, valid near the equilibrium point, of

$$(\overline{\rho}_{N_2} - \overline{\rho}_{N_2}^{eq}) = C \exp\left(\left. \frac{df}{d\overline{\rho}_{N_2}} \right|_{\overline{\rho}_{N_2}=\overline{\rho}_{N_2}^{eq}} t \right), \tag{4.323}$$

$$\overline{\rho}_{N_2} = \overline{\rho}_{N_2}^{eq} + C \exp\left(\left. \frac{df}{d\overline{\rho}_{N_2}} \right|_{\overline{\rho}_{N_2}=\overline{\rho}_{N_2}^{eq}} t \right). \tag{4.324}$$

$$\tag{4.325}$$

Here, C is some constant whose value is not important for this discussion. If the slope of f is positive, that is,

$$\left. \frac{df}{d\overline{\rho}_{N_2}} \right|_{\overline{\rho}_{N_2}=\overline{\rho}_{N_2}^{eq}} > 0, \qquad \text{unstable,} \tag{4.326}$$

the equilibrium will be *unstable*. That is, a perturbation will grow without bound as $t \to \infty$. If the slope is zero,

$$\left. \frac{df}{d\overline{\rho}_{N_2}} \right|_{\overline{\rho}_{N_2}=\overline{\rho}_{N_2}^{eq}} = 0, \qquad \text{neutrally stable,} \tag{4.327}$$

the solution is stable in that there is no unbounded growth, and moreover is known as *neutrally stable*. If the slope is negative,

$$\left. \frac{df}{d\overline{\rho}_{N_2}} \right|_{\overline{\rho}_{N_2}=\overline{\rho}_{N_2}^{eq}} < 0, \qquad \text{asymptotically stable,} \tag{4.328}$$

the solution is stable in that there is no unbounded growth, and moreover is known as *asymptotically stable*.

A solution via numerical integration is found for Eq. (4.314). The solution for $\overline{\rho}_{N_2}$, along with $\overline{\rho}_N$ is plotted in Fig. 4.3. Linearization of Eq. (4.314) about the equilibrium state gives rise to the locally linearly valid

$$\frac{d}{dt}\left(\overline{\rho}_{N_2} - 0.00178121 \right) = -1209.39(\overline{\rho}_{N_2} - 0.00178121) + \dots \tag{4.329}$$

This has local asymptotically stable solution

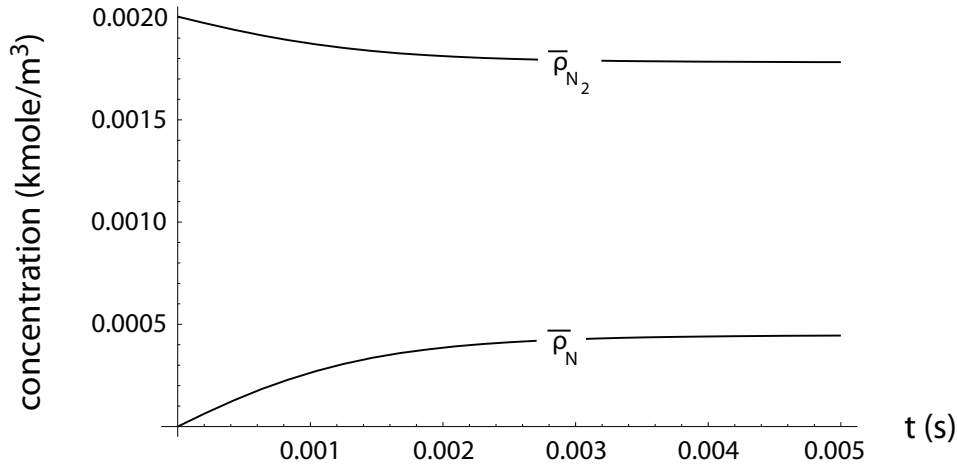$$\overline{\rho}_{N_2} = 0.00178121 + C \exp\left(-1209.39t\right). \tag{4.330}$$

Figure 4.3: $\overline{\rho}_{N_2}(t)$ and $\overline{\rho}_N(t)$ in isothermal, isochoric nitrogen dissociation problem.

Here, C is some integration constant whose value is irrelevant for this analysis. The time scale of relaxation τ is the time when the argument of the exponential is -1, which is

$$\tau = \frac{1}{1209.39 \ s^{-1}} = 8.27 \times 10^{-4} \ s. \tag{4.331}$$

One usually finds this time scale to have high sensitivity to temperature, with high temperatures giving fast time constants and thus fast reactions.

The equilibrium values agree exactly with those found in the earlier example. Here, the kinetics provide the details of *how much time it takes* to achieve equilibrium. This is one of the key questions of non-equilibrium thermodynamics.

4.5.2   Isobaric systems

The form of the previous section is the most important as it is easily extended to a computational grid with fixed volume elements in fluid flow problems. However, there is another important spatially homogeneous problem in which the formulation needs slight modification: *isobaric* reaction, with P equal to a constant. Again, in this section only *isothermal* conditions will be considered.

In an isobaric problem, there can be volume change. Consider first the problem of isobaric expansion of an inert mixture. In such a mixture, the total number of moles of each species must be constant, so one gets

$$\frac{dn_i}{dt} = 0, \qquad \text{inert, isobaric mixture.} \tag{4.332}$$

Now, carry out the sequence of operations, realizing the total mass m is also constant:

$$\frac{1}{m}\frac{d}{dt}(n_i) \;=\; 0, \tag{4.333}$$

$$\frac{d}{dt}\left(\frac{n_i}{m}\right) = 0, \tag{4.334}$$

$$\frac{d}{dt}\left(\frac{n_i}{V}\frac{V}{m}\right) = 0, \tag{4.335}$$

$$\frac{d}{dt}\left(\frac{\overline{\rho}_i}{\rho}\right) = 0, \tag{4.336}$$

$$\frac{1}{\rho}\frac{d\overline{\rho}_i}{dt} - \frac{\overline{\rho}_i}{\rho^2}\frac{d\rho}{dt} = 0, \tag{4.337}$$

$$\frac{d\overline{\rho}_i}{dt} = \frac{\overline{\rho}_i}{\rho}\frac{d\rho}{dt}. \tag{4.338}$$

So, a global density decrease of the inert material due to volume increase of a fixed mass system induces a concentration decrease of each species. Extended to a material with a single reaction rate r, one could say either

$$\frac{d\overline{\rho}_i}{dt} = \nu_i r + \frac{\overline{\rho}_i}{\rho}\frac{d\rho}{dt}, \qquad \text{or} \tag{4.339}$$

$$\frac{d}{dt}\left(\frac{\overline{\rho}_i}{\rho}\right) = \frac{1}{\rho}\nu_i r, \qquad \text{generally valid,} \tag{4.340}$$

$$= \frac{\dot{\omega}_i}{\rho}. \tag{4.341}$$

Equation (4.340) is consistent with Eq. (4.275) and is actually valid for general systems with variable density, temperature, and pressure.

However, in this section, it is required that pressure and temperature be constant. Now, differentiate the isobaric, isothermal, ideal gas law to get the density derivative.

$$P = \sum_{i=1}^{N}\overline{\rho}_i\overline{R}T, \tag{4.342}$$

$$0 = \sum_{i=1}^{N}\overline{R}T\frac{d\overline{\rho}_i}{dt}, \tag{4.343}$$

$$0 = \sum_{i=1}^{N}\frac{d\overline{\rho}_i}{dt}, \tag{4.344}$$

$$0 = \sum_{i=1}^{N}\left(\nu_i r + \frac{\overline{\rho}_i}{\rho}\frac{d\rho}{dt}\right), \tag{4.345}$$

$$0 = r\sum_{i=1}^{N}\nu_i + \frac{1}{\rho}\frac{d\rho}{dt}\sum_{i=1}^{N}\overline{\rho}_i, \tag{4.346}$$

$$\frac{d\rho}{dt} = \frac{-r\sum_{i=1}^{N}\nu_i}{\sum_{i=1}^{N}\frac{\overline{\rho}_i}{\rho}}. \tag{4.347}$$

$$= -\frac{\rho r \sum_{i=1}^{N} \nu_i}{\sum_{i=1}^{N} \overline{\rho}_i}, \tag{4.348}$$

$$= -\frac{\rho r \sum_{i=1}^{N} \nu_i}{\frac{P}{\overline{R}T}}, \tag{4.349}$$

$$= -\frac{\rho \overline{R} T r \sum_{i=1}^{N} \nu_i}{P}, \tag{4.350}$$

$$= -\frac{\rho \overline{R} T r \sum_{k=1}^{N} \nu_k}{P}. \tag{4.351}$$

Note that if there is no net number change in the reaction, $\sum_{k=1}^{N} \nu_k = 0$, the isobaric, isothermal reaction also guarantees there would be no density or volume change. It is convenient to define the net number change in the elementary reaction as $\Delta\mathsf{n}$:

$$\Delta\mathsf{n} \equiv \sum_{k=1}^{N} \nu_k. \tag{4.352}$$

Here, $\Delta\mathsf{n}$ is taken to be a dimensionless pure number. It is associated with the number change in the elementary reaction and not the actual mole change in a physical system; it is, however, proportional to the actual mole change.

Now, use Eq. (4.351) to eliminate the density derivative in Eq. (4.339) to get

$$\frac{d\overline{\rho}_i}{dt} = \nu_i r - \frac{\overline{\rho}_i}{\rho} \frac{\rho \overline{R} T r \sum_{k=1}^{N} \nu_k}{P}, \tag{4.353}$$

$$= r \left(\underbrace{\nu_i}_{\text{reaction effect}} - \underbrace{\frac{\overline{\rho}_i \overline{R} T}{P} \sum_{k=1}^{N} \nu_k}_{\text{expansion effect}} \right), \tag{4.354}$$

$$= r \left(\underbrace{\nu_i}_{\text{reaction effect}} - \underbrace{y_i \Delta\mathsf{n}}_{\text{expansion effect}} \right). \tag{4.355}$$

There are two terms dictating the rate change of species molar concentration. The first, a reaction effect, is precisely the same term that drove the isochoric reaction. The second is due to the fact that the volume can change if the number of moles change, and this induces an intrinsic change in concentration. Note that the term $\overline{\rho}_i \overline{R} T / P = y_i$, the mole fraction.

Example 4.14

> Study a variant of the nitrogen dissociation problem considered in an earlier example in which at $t = 0\ s$, 1 $kmole$ of N_2 exists at $P = 100\ kPa$ and $T = 6000\ K$. In this case, take the reaction to be *isothermal* and *isobaric*. Consider again the elementary nitrogen dissociation reaction
>
> $$N_2 + N_2 \leftrightharpoons 2N + N_2, \tag{4.356}$$

which has kinetic rate parameters of

$$a = 7.0 \times 10^{21} \frac{cm^3 \ K^{1.6}}{mole \ s}, \tag{4.357}$$

$$\beta = -1.6, \tag{4.358}$$

$$\overline{\mathcal{E}} = 224928.4 \frac{cal}{mole}. \tag{4.359}$$

In SI units, this becomes

$$a = \left(7.0 \times 10^{21} \frac{cm^3 \ K^{1.6}}{mole \ s}\right) \left(\frac{1 \ m}{100 \ cm}\right)^3 \left(\frac{1000 \ mole}{kmole}\right) = 7.0 \times 10^{18} \frac{m^3 \ K^{1.6}}{kmole \ s}, \tag{4.360}$$

$$\overline{\mathcal{E}} = \left(224928.4 \frac{cal}{mole}\right) \left(4.186 \frac{J}{cal}\right) \left(\frac{kJ}{1000 \ J}\right) \left(\frac{1000 \ mole}{kmole}\right) = 941550 \frac{kJ}{kmole}. \tag{4.361}$$

At the initial state, the material is all N_2, so $P_{N_2} = P = 100 \ kPa$. The ideal gas law then gives at $t = 0$

$$P = P_{N_2} = \overline{\rho}_{N_2} \overline{R} T, \tag{4.362}$$

$$\overline{\rho}_{N_2}\big|_{t=0} = \frac{P}{\overline{R}T}, \tag{4.363}$$

$$= \frac{100 \ kPa}{\left(8.314 \frac{kJ}{kmole \ K}\right)(6000 \ K)}, \tag{4.364}$$

$$= 2.00465 \times 10^{-3} \frac{kmole}{m^3}. \tag{4.365}$$

Thus, the initial volume is

$$V\big|_{t=0} = \frac{n_{N_2}\big|_{t=0}}{\overline{\rho}_i\big|_{t=0}} = \frac{1 \ kmole}{2.00465 \times 10^{-3} \frac{kmole}{m^3}} = 4.9884 \times 10^2 \ m^3. \tag{4.366}$$

In this isobaric process, one always has $P = 100 \ kPa$. Now, in general

$$P = \overline{R}T(\overline{\rho}_{N_2} + \overline{\rho}_N), \tag{4.367}$$

therefore one can write $\overline{\rho}_N$ in terms of $\overline{\rho}_{N_2}$:

$$\overline{\rho}_N = \frac{P}{\overline{R}T} - \overline{\rho}_{N_2}, \tag{4.368}$$

$$= \frac{100 \ kPa}{\left(8.314 \frac{kJ}{kmole \ K}\right)(6000 \ K)} - \overline{\rho}_{N_2}, \tag{4.369}$$

$$= \left(2.00465 \times 10^{-3} \frac{kmole}{m^3}\right) - \overline{\rho}_{N_2}. \tag{4.370}$$

Then, the equations for kinetics of a single isobaric isothermal reaction, Eq. (4.354) in conjunction with Eq. (4.280), reduce for N_2 molar concentration to

$$\frac{d\overline{\rho}_{N_2}}{dt} = \underbrace{\left(aT^\beta \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right)(\overline{\rho}_{N_2})^{\nu'_{N_2}}(\overline{\rho}_N)^{\nu'_N}\left(1 - \frac{1}{K_c}(\overline{\rho}_{N_2})^{\nu_{N_2}}(\overline{\rho}_N)^{\nu_N}\right)\right)}_{=r}\left(\nu_{N_2} - \frac{\overline{\rho}_{N_2}\overline{R}T}{P}(\nu_{N_2} + \nu_N)\right). \tag{4.371}$$

Realizing that $\nu'_{N_2} = 2$, $\nu'_N = 0$, $\nu_{N_2} = -1$, and $\nu_N = 2$, one gets

$$\frac{d\overline{\rho}_{N_2}}{dt} = \underbrace{aT^\beta \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right)}_{=k(T)} \overline{\rho}_{N_2}^2 \left(1 - \frac{1}{K_c}\frac{\overline{\rho}_N^2}{\overline{\rho}_{N_2}}\right)\left(-1 - \frac{\overline{\rho}_{N_2}\overline{R}T}{P}\right). \tag{4.372}$$

The temperature dependency of the reaction is unchanged from the previous reaction:

$$k(T) = aT^\beta \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right), \tag{4.373}$$

$$= \left(7.0 \times 10^{18} \frac{m^3 K^{1.6}}{kmole\ s}\right) T^{-1.6} \exp\left(\frac{-941550 \frac{kJ}{kmole}}{8.314 \frac{kJ}{kmole\ K}T}\right), \tag{4.374}$$

$$= \frac{7.0 \times 10^{18}}{T^{1.6}} \exp\left(\frac{-1.1325 \times 10^5}{T}\right). \tag{4.375}$$

For this problem, $T = 6000\ K$, so

$$k(6000) = \frac{7.0 \times 10^{18}}{6000^{1.6}} \exp\left(\frac{-1.1325 \times 10^5}{6000}\right), \tag{4.376}$$

$$= 40130.2 \frac{m^3}{kmole\ s}. \tag{4.377}$$

The equilibrium constant K_c is also unchanged from the previous example. Recall

$$K_c = \left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^N \nu_i} \exp\left(\frac{-\Delta G^o}{\overline{R}T}\right). \tag{4.378}$$

For this system, since $\sum_{i=1}^N \nu_i = \Delta n = 1$, this reduces to

$$K_c = \left(\frac{P_o}{\overline{R}T}\right) \exp\left(\frac{-(2\overline{g}_N^o - \overline{g}_{N_2}^o)}{\overline{R}T}\right), \tag{4.379}$$

$$= \left(\frac{P_o}{\overline{R}T}\right) \exp\left(\frac{-(2\overline{g}_N^o - \overline{g}_{N_2}^o)}{\overline{R}T}\right), \tag{4.380}$$

$$= \left(\frac{P_o}{\overline{R}T}\right) \exp\left(\frac{-(2(\overline{h}_N^o - Ts_{T,N}^o) - (\overline{h}_{N_2}^o - Ts_{T,N_2}^o))}{\overline{R}T}\right), \tag{4.381}$$

$$= \left(\frac{100}{(8.314)(6000)}\right) \exp\left(\frac{-(2(597270 - (6000)216.926) - (205848 - (6000)292.984))}{(8.314)(6000)}\right), \tag{4.382}$$

$$= 0.000112112 \frac{kmole}{m^3}. \tag{4.383}$$

The differential equation for N_2 evolution is then given by

$$\frac{d\overline{\rho}_{N_2}}{dt} = \left(40130.2 \frac{m^3}{kmole}\right) \overline{\rho}_{N_2}^2 \left(1 - \frac{1}{0.000112112 \frac{kmole}{m^3}} \frac{\left(\left(2.00465 \times 10^{-3} \frac{kmole}{m^3}\right) - \overline{\rho}_{N_2}\right)^2}{\overline{\rho}_{N_2}}\right)$$

$$\times \left(-1 - \frac{\overline{\rho}_{N_2}\left(8.314 \frac{kJ}{kmole\ K}\right)(6000\ K)}{100\ kPa}\right),$$

$$\tag{4.384}$$

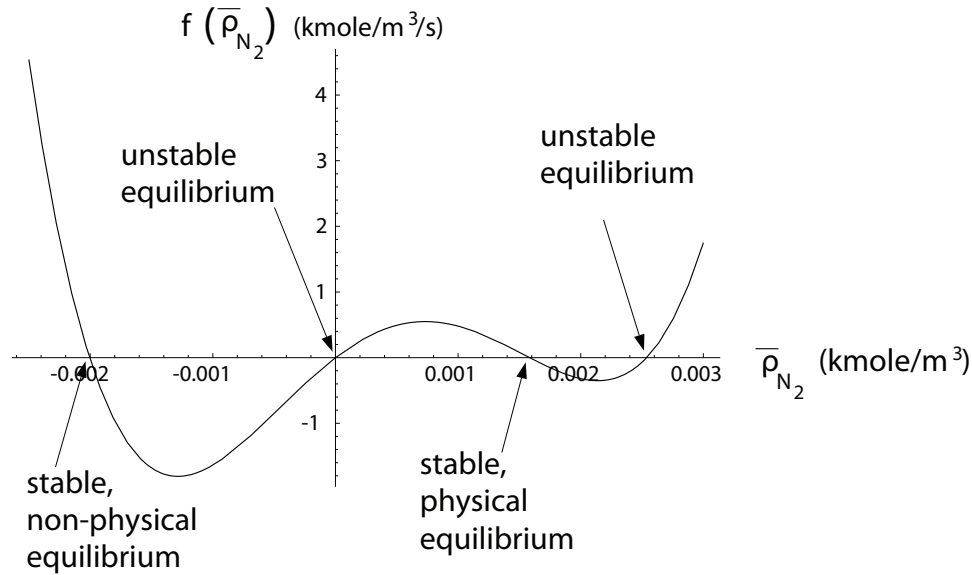$$\equiv f(\overline{\rho}_{N_2}). \tag{4.385}$$

Figure 4.4: Forcing function, $f(\overline{\rho}_{N_2})$, which drives changes of $\overline{\rho}_{N_2}$ as a function of $\overline{\rho}_{N_2}$ in isothermal, isobaric problem.

The system is at equilibrium when $f(\overline{\rho}_{N_2}) = 0$. This is an algebraic function of $\overline{\rho}_{N_2}$ only, and can be plotted. Figure 4.4 gives a plot of $f(\overline{\rho}_{N_2})$ and shows that it has four potential equilibrium points. It is seen there are four roots. Solving for the equilibria requires solving

$$
0 = \left(40130.2 \ \frac{m^3}{kmole}\right) \overline{\rho}_{N_2}^2 \left(1 - \frac{1}{0.000112112 \ \frac{kmole}{m^3}} \frac{\left(\left(2.00465 \times 10^{-3} \ \frac{kmole}{m^3}\right) - \overline{\rho}_{N_2}\right)^2}{\overline{\rho}_{N_2}}\right)
$$
$$
\times \left(-1 - \frac{\overline{\rho}_{N_2} \left(8.314 \ \frac{kJ}{kmole \ K}\right) (6000 \ K)}{100 \ kPa}\right). \tag{4.386}
$$

The four roots are

$$
\overline{\rho}_{N_2} = \underbrace{-0.002005 \ \frac{kmole}{m^3}}_{stable,non-physical}, \qquad \underbrace{0 \ \frac{kmole}{m^3}}_{unstable}, \qquad \underbrace{0.001583 \ \frac{kmole}{m^3}}_{stable,physical}, \qquad \underbrace{0.00254 \ \frac{kmole}{m^3}}_{unstable}. \tag{4.387}
$$

By inspection of the topology of Fig. 4.2, the only stable, physical root is $0.001583 \ kmole/m^3$. Small perturbations from this equilibrium induce the forcing function to supply dynamics which restore the system to its original equilibrium state. Small perturbations from the unstable equilibria induce non-restoring dynamics. For this root, one can then determine that the stable equilibrium value of $\overline{\rho}_N = 0.000421 \ kmole/m^3$.

A numerical solution via an explicit technique such as a Runge-Kutta integration is found for Eq. (4.386). The solution for $\overline{\rho}_{N_2}$, along with $\overline{\rho}_N$ is plotted in Fig. 4.5. Linearization of Eq. (4.386) about the equilibrium state gives rise to the locally linearly valid

$$
\frac{d}{dt}\left(\overline{\rho}_{N_2} - 0.001583\right) = -967.073(\overline{\rho}_{N_2} - 0.001583) + \dots \tag{4.388}
$$

This has local solution

$$
\overline{\rho}_{N_2} = 0.001583 + C \exp\left(-967.073t\right). \tag{4.389}
$$

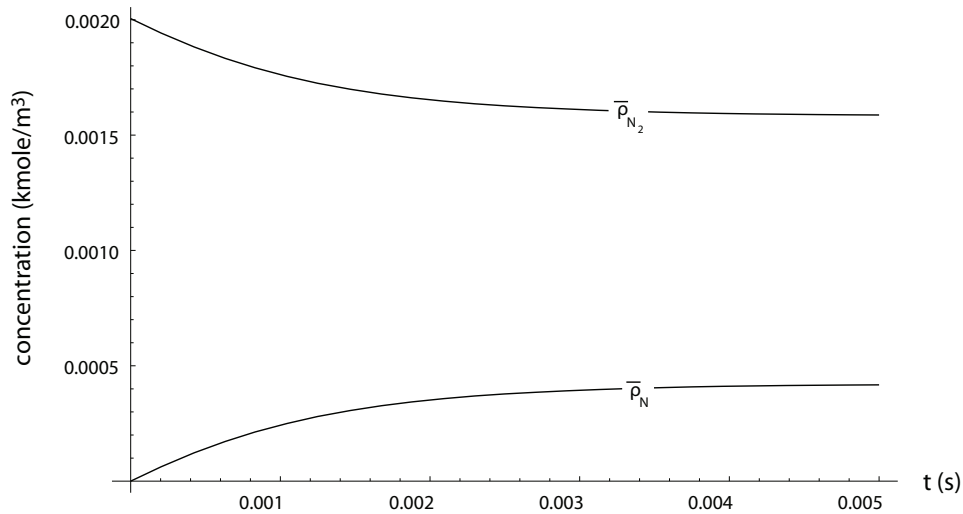Figure 4.5: $\overline{\rho}_{N_2}(t)$ and $\overline{\rho}_N(t)$ in isobaric, isothermal nitrogen dissociation problem.

Again, C is an irrelevant integration constant. The time scale of relaxation τ is the time when the argument of the exponential is -1, which is

$$\tau = \frac{1}{967.073 \ s^{-1}} = 1.03 \times 10^{-3} \ s. \tag{4.390}$$

Note that the time constant for the isobaric combustion is about a factor 1.25 greater than for isochoric combustion under the otherwise identical conditions.

The equilibrium values agree exactly with those found in the earlier example. Again, the kinetics provide the details of *how much time it takes* to achieve equilibrium.

4.6 Some conservation and evolution equations

Here, a few useful global conservation and evolution equations are presented for some key properties. Only some cases are considered, and one could develop more relations for other scenarios.

4.6.1 Total mass conservation: isochoric reaction

One can easily show that the isochoric reaction rate model, Eq. (4.279), satisfies the principle of mixture mass conservation. Begin with Eq. (4.279) in a compact form, using the definition of the reaction rate r, Eq. (4.281), and perform the following operations:

$$\frac{d\overline{\rho}_i}{dt} \quad = \quad \nu_i r, \tag{4.391}$$

$$\frac{d}{dt}\left(\frac{\rho Y_i}{M_i}\right) = \nu_i r, \tag{4.392}$$

$$\frac{d}{dt}\left(\rho Y_i\right) = \nu_i M_i r, \tag{4.393}$$

$$\frac{d}{dt}\left(\rho Y_i\right) = \nu_i \underbrace{\sum_{l=1}^{L} \mathcal{M}_l \phi_{li}}_{=M_i} r, \tag{4.394}$$

$$\frac{d}{dt}\left(\rho Y_i\right) = \sum_{l=1}^{L} \mathcal{M}_l \phi_{li} \nu_i r, \tag{4.395}$$

$$\sum_{i=1}^{N} \frac{d}{dt}\left(\rho Y_i\right) = \sum_{i=1}^{N}\sum_{l=1}^{L} \mathcal{M}_l \phi_{li} \nu_i r, \tag{4.396}$$

$$\frac{d}{dt}\left(\rho \underbrace{\sum_{i=1}^{N} Y_i}_{=1}\right) = \sum_{l=1}^{L}\sum_{i=1}^{N} \mathcal{M}_l \phi_{li} \nu_i r, \tag{4.397}$$

$$\frac{d\rho}{dt} = r \sum_{l=1}^{L} \mathcal{M}_l \underbrace{\sum_{i=1}^{N} \phi_{li} \nu_i}_{=0}, \tag{4.398}$$

$$\frac{d\rho}{dt} = 0. \tag{4.399}$$

Note the term $\sum_{i=1}^{N} \phi_{li} \nu_i = 0$ because of stoichiometry, Eq. (4.24).

4.6.2 Element mass conservation: isochoric reaction

Through a similar series of operations, one can show that the mass of each element, $l = 1, \ldots, L$, in conserved in this reaction, which is chemical, not nuclear. Once again, begin with Eq. (4.281) and perform a set of operations,

$$\frac{d\overline{\rho}_i}{dt} = \nu_i r, \tag{4.400}$$

$$\phi_{li}\frac{d\overline{\rho}_i}{dt} = \phi_{li}\nu_i r, \qquad l = 1, \ldots, L, \tag{4.401}$$

$$\frac{d}{dt}\left(\phi_{li}\overline{\rho}_i\right) = r\phi_{li}\nu_i, \qquad l = 1, \ldots, L, \tag{4.402}$$

$$\sum_{i=1}^{N}\frac{d}{dt}\left(\phi_{li}\overline{\rho}_i\right) = \sum_{i=1}^{N} r\phi_{li}\nu_i, \qquad l = 1, \ldots, L, \tag{4.403}$$

$$\frac{d}{dt}\left(\sum_{i=1}^{N}\phi_{li}\overline{\rho}_i\right) = r\underbrace{\sum_{i=1}^{N}\phi_{li}\nu_i}_{=0}, \qquad l = 1,\ldots,L, \tag{4.404}$$

$$\frac{d}{dt}\left(\sum_{i=1}^{N}\phi_{li}\overline{\rho}_i\right) = 0, \qquad l = 1,\ldots,L. \tag{4.405}$$

The term $\sum_{i=1}^{N}\phi_{li}\overline{\rho}_i$ represents the number of moles of element l per unit volume, by the following analysis

$$\sum_{i=1}^{N}\phi_{li}\overline{\rho}_i = \sum_{i=1}^{N}\frac{moles\ element\ l}{moles\ species\ i}\frac{moles\ species\ i}{volume} = \frac{moles\ element\ l}{volume} \equiv \overline{\rho}_l{}^e. \tag{4.406}$$

Here, the *elemental mole density*, $\overline{\rho}_l{}^e$, for element l has been defined. So, the element concentration for each element remains constant in a constant volume reaction process:

$$\frac{d\overline{\rho}_l{}^e}{dt} = 0, \qquad l = 1,\ldots,L. \tag{4.407}$$

One can also multiply by the elemental mass, $\mathcal{M}_l$ to get the *elemental mass density*, ρ_l^e:

$$\rho_l^e \equiv \mathcal{M}_l\overline{\rho}_l{}^e, \qquad l = 1,\ldots,L. \tag{4.408}$$

Since $\mathcal{M}_l$ is a constant, one can incorporate this definition into Eq. (4.407) to get

$$\frac{d\rho_l^e}{dt} = 0, \qquad l = 1,\ldots,L. \tag{4.409}$$

The element mass density remains constant in the constant volume reaction. One could also simply say since the elements' density is constant, and the mixture is simply a sum of the elements, that the mixture density is conserved as well.

4.6.3 Energy conservation: adiabatic, isochoric reaction

Consider a simple application of the first law of thermodynamics to reaction kinetics: that of a closed, adiabatic, isochoric combustion process in a mixture of ideal gases. One may be interested in the rate of temperature change. First, because the system is closed, there can be no mass change, and because the system is isochoric, the total volume is a non-zero constant; hence,

$$\frac{dm}{dt} = 0, \tag{4.410}$$

$$\frac{d}{dt}(\rho V) = 0, \tag{4.411}$$

$$V\frac{d\rho}{dt} = 0, \tag{4.412}$$

$$\frac{d\rho}{dt} = 0. \tag{4.413}$$

For such a process, the first law of thermodynamics is

$$\frac{dE}{dt} = \dot{Q} - \dot{W}. \tag{4.414}$$

But there is no heat transfer or work in the adiabatic isochoric process, so one gets

$$\frac{dE}{dt} = 0, \tag{4.415}$$

$$\frac{d}{dt}(me) = 0, \tag{4.416}$$

$$m\frac{de}{dt} + e\underbrace{\frac{dm}{dt}}_{=0} = 0, \tag{4.417}$$

$$\frac{de}{dt} = 0. \tag{4.418}$$

Thus, for the mixture of ideal gases, $e(T, \overline{\rho}_1, \ldots, \overline{\rho}_N) = e_o$. One can see how reaction rates affect temperature changes by expanding the derivative in Eq. (4.418)

$$\frac{d}{dt}\left(\sum_{i=1}^{N} Y_i e_i\right) = 0, \tag{4.419}$$

$$\sum_{i=1}^{N} \frac{d}{dt}(Y_i e_i) = 0, \tag{4.420}$$

$$\sum_{i=1}^{N}\left(Y_i \frac{de_i}{dt} + e_i \frac{dY_i}{dt}\right) = 0, \tag{4.421}$$

$$\sum_{i=1}^{N}\left(Y_i \underbrace{\frac{de_i}{dT}}_{c_{vi}} \frac{dT}{dt} + e_i \frac{dY_i}{dt}\right) = 0, \tag{4.422}$$

$$\sum_{i=1}^{N}\left(Y_i c_{vi} \frac{dT}{dt} + e_i \frac{dY_i}{dt}\right) = 0, \tag{4.423}$$

$$\frac{dT}{dt}\underbrace{\sum_{i=1}^{N} Y_i c_{vi}}_{=c_v} = -\sum_{i=1}^{N} e_i \frac{dY_i}{dt}, \tag{4.424}$$

$$c_v \frac{dT}{dt} = -\sum_{i=1}^{N} e_i \frac{d}{dt}\left(\frac{M_i \overline{\rho}_i}{\rho}\right), \tag{4.425}$$

$$\rho c_v \frac{dT}{dt} = -\sum_{i=1}^{N} e_i M_i \frac{d\overline{\rho}_i}{dt}, \tag{4.426}$$

$$\rho c_v \frac{dT}{dt} = -\sum_{i=1}^{N} e_i M_i \nu_i r, \tag{4.427}$$

$$\frac{dT}{dt} = -\frac{r \sum_{i=1}^{N} \nu_i \overline{e}_i}{\rho c_v}. \tag{4.428}$$

If one defines the net energy change of the reaction as

$$\Delta E \equiv \sum_{i=1}^{N} \nu_i \overline{e}_i, \tag{4.429}$$

one then gets

$$\frac{dT}{dt} = -\frac{r \Delta E}{\rho c_v}. \tag{4.430}$$

The rate of temperature change is dependent on the absolute energies, not the energy differences. If the reaction is going forward, so $r > 0$, and that is a direction in which the net molar energy change is negative, then the temperature will rise.

4.6.4 Energy conservation: adiabatic, isobaric reaction

Solving for the reaction dynamics in an adiabatic isobaric system requires some non-obvious manipulations. First, the first law of thermodynamics says $dE = \delta Q - \delta W$. Since the process is adiabatic, one has $\delta Q = 0$, so $dE + P dV = 0$. Since it is isobaric, one gets $d(E + PV) = 0$, or $dH = 0$. So, the total enthalpy is constant. Then

$$\frac{d}{dt} H = 0, \tag{4.431}$$

$$\frac{d}{dt} (mh) = 0, \tag{4.432}$$

$$\frac{dh}{dt} = 0, \tag{4.433}$$

$$\frac{d}{dt} \left(\sum_{i=1}^{N} Y_i h_i \right) = 0, \tag{4.434}$$

$$\sum_{i=1}^{N} \frac{d}{dt} (Y_i h_i) = 0, \tag{4.435}$$

$$\sum_{i=1}^{N} Y_i \frac{dh_i}{dt} + h_i \frac{dY_i}{dt} = 0, \tag{4.436}$$

$$\sum_{i=1}^{N} Y_i \underbrace{\frac{dh_i}{dT}}_{c_{Pi}} \frac{dT}{dt} + h_i \frac{dY_i}{dt} = 0, \tag{4.437}$$

$$\sum_{i=1}^{N} Y_i c_{Pi} \frac{dT}{dt} + \sum_{i=1}^{N} h_i \frac{dY_i}{dt} = 0, \tag{4.438}$$

$$\frac{dT}{dt} \underbrace{\sum_{i=1}^{N} Y_i c_{Pi}}_{=c_P} + \sum_{i=1}^{N} h_i \frac{dY_i}{dt} = 0, \tag{4.439}$$

$$c_P \frac{dT}{dt} + \sum_{i=1}^{N} h_i \frac{d}{dt} \left(\frac{\overline{\rho}_i M_i}{\rho} \right) = 0, \tag{4.440}$$

$$c_P \frac{dT}{dt} + \sum_{i=1}^{N} h_i M_i \frac{d}{dt} \left(\frac{\overline{\rho}_i}{\rho} \right) = 0. \tag{4.441}$$

Now, use Eq (4.340) to eliminate the term in Eq. (4.441) involving molar concentration derivatives to get

$$c_P \frac{dT}{dt} + \sum_{i=1}^{N} \overline{h}_i \frac{\nu_i r}{\rho} = 0, \tag{4.442}$$

$$\frac{dT}{dt} = -\frac{r \sum_{i=1}^{N} \overline{h}_i \nu_i}{\rho c_P}. \tag{4.443}$$

So, the temperature derivative is known as an algebraic function. If one defines the net enthalpy change as

$$\Delta H \equiv \sum_{i=1}^{N} \overline{h}_i \nu_i, \tag{4.444}$$

one gets that Eq. (4.443) transforms to

$$\frac{dT}{dt} = -\frac{r \Delta H}{\rho c_P}. \tag{4.445}$$

or

$$\rho c_P \frac{dT}{dt} = -r \Delta H. \tag{4.446}$$

Equation (4.446) is in a form which can easily be compared to a form to be derived later when we add variable pressure and diffusion effects.

Now, differentiate the isobaric ideal gas law to get the density derivative.

$$P = \sum_{i=1}^{N} \overline{\rho}_i \overline{R} T, \tag{4.447}$$

$$0 = \sum_{i=1}^{N} \overline{\rho}_i \overline{R} \frac{dT}{dt} + \sum_{i=1}^{N} \overline{R} T \frac{d\overline{\rho}_i}{dt}, \tag{4.448}$$

$$0 \; = \; \frac{dT}{dt}\sum_{i=1}^{N}\overline{\rho}_i + \sum_{i=1}^{N}T\left(\nu_i r + \frac{\overline{\rho}_i}{\rho}\frac{d\rho}{dt}\right), \tag{4.449}$$

$$0 \; = \; \frac{1}{T}\frac{dT}{dt}\sum_{i=1}^{N}\overline{\rho}_i + r\sum_{i=1}^{N}\nu_i + \frac{1}{\rho}\frac{d\rho}{dt}\sum_{i=1}^{N}\overline{\rho}_i, \tag{4.450}$$

$$\frac{d\rho}{dt} \; = \; \frac{-\frac{1}{T}\frac{dT}{dt}\sum_{i=1}^{N}\overline{\rho}_i - r\sum_{i=1}^{N}\nu_i}{\sum_{i=1}^{N}\frac{\overline{\rho}_i}{\rho}}. \tag{4.451}$$

One takes dT/dt from Eq. (4.443) to get

$$\frac{d\rho}{dt} \; = \; \frac{\frac{1}{T}\frac{r\sum_{i=1}^{N}\overline{h}_i\nu_i}{\rho c_P}\sum_{i=1}^{N}\overline{\rho}_i - r\sum_{i=1}^{N}\nu_i}{\sum_{i=1}^{N}\frac{\overline{\rho}_i}{\rho}}. \tag{4.452}$$

Now, recall from Eqs. (2.212) and (2.218) that $\overline{\rho} = \rho/M$ and $\overline{c}_P = c_P M$, so $\overline{\rho}\,\overline{c}_P = \rho c_P$. Then Equation (4.452) can be reduced slightly:

$$\frac{d\rho}{dt} \; = \; r\rho\frac{\frac{\sum_{i=1}^{N}\overline{h}_i\nu_i}{\overline{c}_P T}\overbrace{\sum_{i=1}^{N}\frac{\overline{\rho}_i}{\overline{\rho}}}^{=1} - \sum_{i=1}^{N}\nu_i}{\sum_{i=1}^{N}\overline{\rho}_i}, \tag{4.453}$$

$$= \; r\rho\frac{\sum_{i=1}^{N}\frac{\overline{h}_i\nu_i}{\overline{c}_P T} - \sum_{i=1}^{N}\nu_i}{\sum_{i=1}^{N}\overline{\rho}_i}, \tag{4.454}$$

$$= \; r\rho\frac{\sum_{i=1}^{N}\nu_i\left(\frac{\overline{h}_i}{\overline{c}_P T} - 1\right)}{\frac{P}{\overline{R}T}}, \tag{4.455}$$

$$= \; r\frac{\rho\overline{R}T}{P}\sum_{i=1}^{N}\nu_i\left(\frac{\overline{h}_i}{\overline{c}_P T} - 1\right), \tag{4.456}$$

$$= \; rM\sum_{i=1}^{N}\nu_i\left(\frac{\overline{h}_i}{\overline{c}_P T} - 1\right), \tag{4.457}$$

where M is the mean molecular mass. Note for exothermic reaction $\sum_{i=1}^{N}\nu_i\overline{h}_i < 0$, so exothermic reaction induces a density decrease as the increased temperature at constant pressure causes the volume to increase.

Then, using Eq. (4.457) to eliminate the density derivative in Eq. (4.339), and changing the dummy index from i to k, one gets an explicit expression for concentration evolution:

$$\frac{d\overline{\rho}_i}{dt} \; = \; \nu_i r + \frac{\overline{\rho}_i}{\rho}rM\sum_{k=1}^{N}\nu_k\left(\frac{\overline{h}_k}{\overline{c}_P T} - 1\right), \tag{4.458}$$

$$= r\left(\nu_i + \underbrace{\frac{\overline{\rho}_i}{\rho}}_{=y_i} M \sum_{k=1}^{N} \nu_k \left(\frac{\overline{h}_k}{\overline{c}_P T} - 1\right)\right), \tag{4.459}$$

$$= r\left(\nu_i + y_i \sum_{k=1}^{N} \nu_k \left(\frac{\overline{h}_k}{\overline{c}_P T} - 1\right)\right). \tag{4.460}$$

Defining the change of enthalpy of the reaction as $\Delta H \equiv \sum_{k=1}^{N} \nu_k \overline{h}_k$, and the change of number of the reaction as $\Delta \mathsf{n} \equiv \sum_{k=1}^{N} \nu_k$, one can also say

$$\frac{d\overline{\rho}_i}{dt} = r\left(\nu_i + y_i \left(\frac{\Delta H}{\overline{c}_P T} - \Delta\mathsf{n}\right)\right). \tag{4.461}$$

Exothermic reaction, $\Delta H < 0$, and net number increases, $\Delta \mathsf{n} > 0$, both tend to decrease the molar concentrations of the species in the isobaric reaction.

Lastly, the evolution of the adiabatic, isobaric system, can be described by the simultaneous, coupled ordinary differential equations: Eqs. (4.443, 4.452, 4.460). These require numerical solution in general. Note also that one could also employ a more fundamental treatment as a differential algebraic system involving $H = H_1$, $P = P_1 = \overline{R}T \sum_{i=1}^{N} \overline{\rho}_i$ and Eq. (4.339).

4.6.5 Non-adiabatic isochoric combustion

Consider briefly combustion in a fixed finite volume in which there is simple convective heat transfer with the surroundings. In general, the first law of thermodynamics is

$$\frac{dE}{dt} = \dot{Q} - \dot{W}. \tag{4.462}$$

Because the system is isochoric $\dot{W} = 0$. And using standard relations from simple convective heat transfer, one can say that

$$\frac{dE}{dt} = -\mathsf{h}A(T - T_\infty). \tag{4.463}$$

Here, h is the convective heat transfer coefficient and A is the surface area associated with the volume V, and T_∞ is the temperature of the surrounding medium. One can, much as before, write E in detail and get an equation for the evolution of T.

4.6.6 Entropy evolution: Clausius-Duhem relation

Now, consider whether the kinetics law that has been posed actually satisfies the second law of thermodynamics. Consider again Eq. (3.350). There is an algebraic relation on the right

side. If it can be shown that this algebraic relation is positive semi-definite, then the second law is satisfied, and the algebraic relation is known as a Clausius[12]-Duhem[13] relation.

Now, take Eq. (3.350) and perform some straightforward operations on it:

$$dS|_{E,V} = \underbrace{-\frac{1}{T}\sum_{i=1}^{N}\overline{\mu}_i dn_i}_{\text{irreversibility}} \geq 0, \tag{4.464}$$

$$\left.\frac{dS}{dt}\right|_{E,V} = -\frac{V}{T}\sum_{i=1}^{N}\overline{\mu}_i \frac{dn_i}{dt}\frac{1}{V} \geq 0, \tag{4.465}$$

$$= -\frac{V}{T}\sum_{i=1}^{N}\overline{\mu}_i \frac{d\overline{\rho}_i}{dt} \geq 0, \tag{4.466}$$

$$= -\frac{V}{T}\sum_{i=1}^{N}\overline{\mu}_i\nu_i \underbrace{\underbrace{aT^{\beta}\exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R}T}\right)}_{\equiv k(T)}\underbrace{\left(\prod_{k=1}^{N}\overline{\rho}_k^{\nu'_k}\right)}_{\text{forward reaction}}\left(1-\underbrace{\frac{1}{K_c}\prod_{k=1}^{N}\overline{\rho}_k^{\nu_k}}_{\text{reverse reaction}}\right)}_{\equiv r} \geq 0, \tag{4.467}$$

$$= -\frac{V}{T}\sum_{i=1}^{N}\overline{\mu}_i\nu_i k(T)\left(\prod_{k=1}^{N}\overline{\rho}_k^{\nu'_k}\right)\left(1-\frac{1}{K_c}\prod_{k=1}^{N}\overline{\rho}_k^{\nu_k}\right) \geq 0, \tag{4.468}$$

$$= -\frac{V}{T}k(T)\left(\prod_{k=1}^{N}\overline{\rho}_k^{\nu'_k}\right)\left(1-\frac{1}{K_c}\prod_{k=1}^{N}\overline{\rho}_k^{\nu_k}\right)\underbrace{\left(\sum_{i=1}^{N}\overline{\mu}_i\nu_i\right)}_{=-\overline{\alpha}} \geq 0. \tag{4.469}$$

Change the dummy index from k back to i.

$$\left.\frac{dS}{dt}\right|_{E,V} = \frac{V}{T}k(T)\left(\prod_{i=1}^{N}\overline{\rho}_i^{\nu'_i}\right)\left(1-\frac{1}{K_c}\prod_{i=1}^{N}\overline{\rho}_i^{\nu_i}\right)\overline{\alpha} \geq 0, \tag{4.470}$$

$$= \frac{V}{T}r\overline{\alpha}, \tag{4.471}$$

$$= \frac{\overline{\alpha}}{T}\frac{d\zeta}{dt}. \tag{4.472}$$

Consider now the affinity $\overline{\alpha}$ term in Eq. (4.469) and expand it so that it has a more useful form:

$$\overline{\alpha} = -\sum_{i=1}^{N}\overline{\mu}_i\nu_i = -\sum_{i=1}^{N}\overline{g}_i\nu_i, \tag{4.473}$$

---

[12]Rudolf Julius Emanuel Clausius, 1822-1888, German physicist.
[13]Pierre Maurice Marie Duhem, 1861-1916, French physicist.

$$= -\sum_{i=1}^{N} \left(\overline{g}_{T,i}^o + \overline{R}T \ln \left(\frac{P_i}{P_o} \right) \right) \nu_i, \tag{4.474}$$

$$= \underbrace{-\sum_{i=1}^{N} \overline{g}_{T,i}^o \nu_i}_{=\Delta G^o} - \overline{R}T \sum_{i=1}^{N} \ln \left(\frac{P_i}{P_o} \right)^{\nu_i}, \tag{4.475}$$

$$= \overline{R}T \left(\underbrace{\frac{-\Delta G^o}{\overline{R}T}}_{=\ln K_P} - \sum_{i=1}^{N} \ln \left(\frac{P_i}{P_o} \right)^{\nu_i} \right), \tag{4.476}$$

$$= \overline{R}T \left(\ln K_P - \ln \prod_{i=1}^{N} \left(\frac{P_i}{P_o} \right)^{\nu_i} \right), \tag{4.477}$$

$$= -\overline{R}T \left(\ln \frac{1}{K_P} + \ln \prod_{i=1}^{N} \left(\frac{P_i}{P_o} \right)^{\nu_i} \right), \tag{4.478}$$

$$= -\overline{R}T \ln \left(\frac{1}{K_P} \prod_{i=1}^{N} \left(\frac{P_i}{P_o} \right)^{\nu_i} \right), \tag{4.479}$$

$$= -\overline{R}T \ln \left(\frac{\left(\frac{P_o}{\overline{R}T} \right)^{\sum_{i=1}^{N} \nu_i}}{K_c} \prod_{i=1}^{N} \left(\frac{\overline{\rho}_i \overline{R}T}{P_o} \right)^{\nu_i} \right), \tag{4.480}$$

$$= -\overline{R}T \ln \left(\frac{1}{K_c} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i} \right). \tag{4.481}$$

Equation (4.481) is the common definition of affinity. Sometimes, it is written equivalently as

$$\overline{\alpha} = \overline{R}T \ln \left(\frac{K_c}{\prod_{i=1}^{N} \overline{\rho}_i^{\nu_i}} \right). \tag{4.482}$$

Another form can be found by employing the definition of K_c from Eq. (4.270) to get

$$\overline{\alpha} = -\overline{R}T \ln \left(\left(\frac{P_o}{\overline{R}T} \right)^{-\sum_{i=1}^{N} \nu_i} \exp \left(\frac{\Delta G^o}{\overline{R}T} \right) \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i} \right), \tag{4.483}$$

$$= -\overline{R}T \left(\frac{\Delta G^o}{\overline{R}T} + \ln \left(\left(\frac{P_o}{\overline{R}T} \right)^{-\sum_{i=1}^{N} \nu_i} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i} \right) \right), \tag{4.484}$$

$$= -\Delta G^o - \overline{R}T \ln \left(\left(\frac{P_o}{\overline{R}T} \right)^{-\sum_{i=1}^{N} \nu_i} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i} \right). \tag{4.485}$$

To see clearly that the entropy production rate is positive semi-definite, substitute Eq. (4.481) into Eq. (4.469) to get

$$
\left. \frac{dS}{dt} \right|_{E,V} = \frac{V}{T} k(T) \left(\prod_{i=1}^{N} \overline{\rho}_i^{\nu_i'} \right) \left(1 - \frac{1}{K_c} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i} \right) \left(-\overline{R}T \ln \left(\frac{1}{K_c} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i} \right) \right) \geq 0,
$$
(4.486)

$$
= -\overline{R}V k(T) \left(\prod_{i=1}^{N} \overline{\rho}_i^{\nu_i'} \right) \left(1 - \frac{1}{K_c} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i} \right) \ln \left(\frac{1}{K_c} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i} \right) \geq 0.
$$
(4.487)

Define forward and reverse reaction coefficients, $\mathcal{R}'$, and $\mathcal{R}''$, respectively, as

$$
\mathcal{R}' \equiv k(T) \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i'},
$$
(4.488)

$$
\mathcal{R}'' \equiv \frac{k(T)}{K_c} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i''}.
$$
(4.489)

Both $\mathcal{R}'$ and $\mathcal{R}''$ have units of $mole/cm^3/s$. It is easy to see that

$$
r = \mathcal{R}' - \mathcal{R}''.
$$
(4.490)

Note that since $k(T) > 0$, $K_c > 0$, and $\overline{\rho}_i \geq 0$, that both $\mathcal{R}' \geq 0$ and $\mathcal{R}'' \geq 0$. Since $\nu_i = \nu_i'' - \nu_i'$, one finds that

$$
\frac{1}{K_c} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i} = \frac{1}{K_c} \frac{k(T)}{k(T)} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_i'' - \nu_i'} = \frac{\mathcal{R}''}{\mathcal{R}'}.
$$
(4.491)

Then, Eq. (4.487) reduces to

$$
\left. \frac{dS}{dt} \right|_{E,V} = -\overline{R}V \mathcal{R}' \left(1 - \frac{\mathcal{R}''}{\mathcal{R}'} \right) \ln \left(\frac{\mathcal{R}''}{\mathcal{R}'} \right) \geq 0,
$$
(4.492)

$$
= \overline{R}V \left(\mathcal{R}' - \mathcal{R}'' \right) \ln \left(\frac{\mathcal{R}'}{\mathcal{R}''} \right) \geq 0.
$$
(4.493)

Obviously, if the forward rate is greater than the reverse rate $\mathcal{R}' - \mathcal{R}'' > 0$, $\ln(\mathcal{R}'/\mathcal{R}'') > 0$, and the entropy production is positive. If the forward rate is less than the reverse rate, $\mathcal{R}' - \mathcal{R}'' < 0$, $\ln(\mathcal{R}'/\mathcal{R}'') < 0$, and the entropy production is still positive. The production rate is zero when $\mathcal{R}' = \mathcal{R}''$.

Note that the affinity $\overline{\alpha}$ can be written as

$$
\overline{\alpha} = \overline{R}T \ln \left(\frac{\mathcal{R}'}{\mathcal{R}''} \right).
$$
(4.494)

And so when the forward reaction rate exceeds the reverse, the affinity is positive. It is zero at equilibrium, when the forward reaction rate equals the reverse.

4.7 Simple one-step kinetics

A common model in theoretical combustion is that of so-called simple one-step kinetics. Such a model, in which the molecular mass does not change, is quantitatively appropriate only for isomerization reactions. However, as a pedagogical tool as well as a qualitative model for real chemistry, it can be valuable.

Consider the reversible reaction

$$A \rightleftharpoons B. \tag{4.495}$$

where chemical species A and B have identical molecular masses $M_A = M_B = M$. Consider further the case in which at the initial state, n_o moles of A only are present. Also take the reaction to be isochoric and isothermal. These assumptions can easily be relaxed for more general cases. Specializing then Eq. (4.240) for this case, one has

$$n_A = \underbrace{\nu_A}_{=-1} \zeta + \underbrace{n_{Ao}}_{=n_o}, \tag{4.496}$$

$$n_B = \underbrace{\nu_B}_{=1} \zeta + \underbrace{n_{Bo}}_{=0}. \tag{4.497}$$

Thus

$$n_A = -\zeta + n_o, \tag{4.498}$$

$$n_B = \zeta. \tag{4.499}$$

Now, n_o is constant throughout the reaction. Scale by this and define the dimensionless reaction progress as $\lambda \equiv \zeta/n_o$ to get

$$\underbrace{\frac{n_A}{n_o}}_{=y_A} = -\lambda + 1, \tag{4.500}$$

$$\underbrace{\frac{n_B}{n_o}}_{=y_B} = \lambda. \tag{4.501}$$

In terms of the mole fractions then, one has

$$y_A = 1 - \lambda, \tag{4.502}$$

$$y_B = \lambda. \tag{4.503}$$

The reaction kinetics for each species reduce to

$$\frac{d\overline{\rho}_A}{dt} = -r, \qquad \overline{\rho}_A(0) = \frac{n_o}{V} \equiv \overline{\rho}_o, \tag{4.504}$$

$$\frac{d\overline{\rho}_B}{dt} = r, \qquad \overline{\rho}_B(0) = 0. \tag{4.505}$$

Addition of Eqs. (4.504) and (4.505) gives

$$\frac{d}{dt}\left(\overline{\rho}_A + \overline{\rho}_B\right) = 0, \tag{4.506}$$

$$\overline{\rho}_A + \overline{\rho}_B = \overline{\rho}_o, \tag{4.507}$$

$$\underbrace{\frac{\overline{\rho}_A}{\overline{\rho}_o}}_{=y_A} + \underbrace{\frac{\overline{\rho}_B}{\overline{\rho}_o}}_{=y_B} = 1. \tag{4.508}$$

In terms of the mole fractions y_i, one then has

$$y_A + y_B = 1. \tag{4.509}$$

The reaction rate r is then

$$r = k\overline{\rho}_A\left(1 - \frac{1}{K_c}\frac{\overline{\rho}_B}{\overline{\rho}_A}\right), \tag{4.510}$$

$$= k\overline{\rho}_o\frac{\overline{\rho}_A}{\overline{\rho}_o}\left(1 - \frac{1}{K_c}\frac{\overline{\rho}_B/\overline{\rho}_o}{\overline{\rho}_A/\overline{\rho}_o}\right), \tag{4.511}$$

$$= k\overline{\rho}_o y_A\left(1 - \frac{1}{K_c}\frac{y_B}{y_A}\right), \tag{4.512}$$

$$= k\overline{\rho}_o(1-\lambda)\left(1 - \frac{1}{K_c}\frac{\lambda}{1-\lambda}\right). \tag{4.513}$$

Now, $r = (1/V)d\zeta/dt = (1/V)d(n_o\lambda)/dt = (n_o/V)d(\lambda)/dt = \overline{\rho}_o d\lambda/dt$. So, the reaction dynamics can be described by a single ordinary differential equation in a single unknown:

$$\overline{\rho}_o\frac{d\lambda}{dt} = k\overline{\rho}_o(1-\lambda)\left(1 - \frac{1}{K_c}\frac{\lambda}{1-\lambda}\right), \tag{4.514}$$

$$\frac{d\lambda}{dt} = k(1-\lambda)\left(1 - \frac{1}{K_c}\frac{\lambda}{1-\lambda}\right). \tag{4.515}$$

Equation (4.515) is in equilibrium when

$$\lambda = \frac{1}{1 + \frac{1}{K_c}} \sim 1 - \frac{1}{K_c} + \dots \tag{4.516}$$

As $K_c \to \infty$, the equilibrium value of $\lambda \to 1$. In this limit, the reaction is irreversible. That is, the species B is preferred over A. Equation (4.515) has exact solution

$$\lambda = \frac{1 - \exp\left(-k\left(1 + \frac{1}{K_c}\right)t\right)}{1 + \frac{1}{K_c}}. \tag{4.517}$$

For $k > 0$, $K_c > 0$, the equilibrium is stable. The time constant of relaxation τ is

$$\tau = \frac{1}{k\left(1 + \frac{1}{K_c}\right)}. \tag{4.518}$$

For the isothermal, isochoric system, one should consider the second law in terms of the Helmholtz free energy. Combine then Eq. (3.356), $dA|_{T,V} \leq 0$, with Eq. (3.239), $dA = -SdT - PdV + \sum_{i=1}^{N} \overline{\mu}_i dn_i$ and taking time derivatives, one finds

$$dA|_{T,V} = \left(-SdT - PdV + \sum_{i=1}^{N} \overline{\mu}_i dn_i\right)\Bigg|_{T,V} \leq 0, \tag{4.519}$$

$$\frac{dA}{dt}\Bigg|_{T,V} = \sum_{i=1}^{N} \overline{\mu}_i \frac{dn_i}{dt} \leq 0, \tag{4.520}$$

$$-\frac{1}{T}\frac{dA}{dt} = -\frac{V}{T}\sum_{i=1}^{N} \overline{\mu}_i \frac{d\overline{\rho}_i}{dt} \geq 0. \tag{4.521}$$

This is exactly the same form as Eq. (4.487), which can be directly substituted into Eq. (4.521) to give

$$-\frac{1}{T}\frac{dA}{dt}\Bigg|_{T,V} = -\overline{R}Vk(T)\left(\prod_{i=1}^{N} \overline{\rho}_i^{\,\nu_i'}\right)\left(1 - \frac{1}{K_c}\prod_{i=1}^{N} \overline{\rho}_i^{\,\nu_i}\right)\ln\left(\frac{1}{K_c}\prod_{i=1}^{N} \overline{\rho}_i^{\,\nu_i}\right) \geq 0, \tag{4.522}$$

$$\frac{dA}{dt}\Bigg|_{T,V} = \overline{R}VTk(T)\left(\prod_{i=1}^{N} \overline{\rho}_i^{\,\nu_i'}\right)\left(1 - \frac{1}{K_c}\prod_{i=1}^{N} \overline{\rho}_i^{\,\nu_i}\right)\ln\left(\frac{1}{K_c}\prod_{i=1}^{N} \overline{\rho}_i^{\,\nu_i}\right) \leq 0. \tag{4.523}$$

For the assumptions of this section, Eq. (4.523) reduces to

$$\frac{dA}{dt}\Bigg|_{T,V} = \overline{R}Tk\overline{\rho}_o V(1 - \lambda)\left(1 - \frac{1}{K_c}\frac{\lambda}{1-\lambda}\right)\ln\left(\frac{1}{K_c}\frac{\lambda}{1-\lambda}\right) \leq 0, \tag{4.524}$$

$$= kn_o\overline{R}T(1 - \lambda)\left(1 - \frac{1}{K_c}\frac{\lambda}{1-\lambda}\right)\ln\left(\frac{1}{K_c}\frac{\lambda}{1-\lambda}\right) \leq 0. \tag{4.525}$$

Since the present analysis is nothing more than a special case of the previous section, Eq. (4.525) certainly holds. One questions however the behavior in the irreversible limit, $1/K_c \to 0$. Evaluating this limit, one finds

$$\lim_{1/K_c \to 0} \frac{dA}{dt}\Bigg|_{T,V} = kn_o\overline{R}T\left(\underbrace{(1 - \lambda)}_{>0}\underbrace{\ln\left(\frac{1}{K_c}\right)}_{\to -\infty} + (1 - \lambda)\ln\lambda - (1 - \lambda)\ln(1 - \lambda) + \ldots\right) \leq 0. \tag{4.526}$$

Now, performing the distinguished limit as $\lambda \to 1$; that is the reaction goes to completion, one notes that all terms are driven to zero for small $1/K_c$. Recall that $1-\lambda$ goes to zero faster than $\ln(1 - \lambda)$ goes to $-\infty$. Note that the entropy inequality is ill-defined for a formally irreversible reaction with $1/K_c = 0$.

Chapter 5

Thermochemistry of multiple reactions

This chapter will extend notions associated with the thermodynamics of a single chemical reactions to systems in which many reactions occur simultaneously. Some background is in some standard sources.[1][2][3]

5.1 Summary of multiple reaction extensions

Consider now the reaction of N species, composed of L elements, in J reactions. This section will focus on the most common case in which $J \geq (N - L)$, which is usually the case in large chemical kinetic systems in use in engineering models. While much of the analysis will only require $J > 0$, certain results will depend on $J \geq (N - L)$. It is not difficult to study the complementary case where $0 < J < (N - L)$.

The molecular mass of species i is still given by Eq. (4.1):

$$M_i = \sum_{l=1}^{L} \mathcal{M}_l \phi_{li}, \qquad i = 1, \ldots, N. \tag{5.1}$$

However, each reaction has a stoichiometric coefficient. The jth reaction can be summarized in the following ways:

$$\sum_{i=1}^{N} \chi_i \nu'_{ij} \;\rightleftharpoons\; \sum_{i=1}^{N} \chi_i \nu''_{ij}, \qquad j = 1, \ldots, J, \tag{5.2}$$

$$\sum_{i=1}^{N} \chi_i \nu_{ij} \;=\; 0, \qquad j = 1, \ldots, J. \tag{5.3}$$

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[1]Turns, S. R., 2011, *An Introduction to Combustion*, Third Edition, McGraw-Hill, Boston. Chapters 4-6.

[2]Kuo, K. K., 2005, *Principles of Combustion*, Second Edition, John Wiley, New York. Chapters 1 and 2.

[3]Kondepudi, D., and Prigogine, I., 1998, *Modern Thermodynamics: From Heat Engines to Dissipative Structures*, John Wiley, New York. Chapters 16 and 19.

Stoichiometry for the jth reaction and l^{th} element is given by the extension of Eq. (4.24):

$$\sum_{i=1}^{N} \phi_{li} \nu_{ij} = 0, \qquad l = 1, \ldots, L, \;\; j = 1, \ldots, J. \tag{5.4}$$

The net change in Gibbs free energy and equilibrium constants of the jth reaction are defined by extensions of Eqs. (4.268), (4.267), (4.270):

$$\Delta G_j^o \equiv \sum_{i=1}^{N} \overline{g}_{T,i}^o \nu_{ij}, \qquad j = 1, \ldots, J, \tag{5.5}$$

$$K_{P,j} \equiv \exp\left(\frac{-\Delta G_j^o}{\overline{R}T}\right), \qquad j = 1, \ldots, J, \tag{5.6}$$

$$K_{c,j} \equiv \left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^{N} \nu_{ij}} \exp\left(\frac{-\Delta G_j^o}{\overline{R}T}\right), \qquad j = 1, \ldots, J. \tag{5.7}$$

The equilibrium of the jth reaction is given by the extension of Eq. (4.253):

$$\sum_{i=1}^{N} \overline{\mu}_i \nu_{ij} = 0, \qquad j = 1, \ldots, J, \tag{5.8}$$

or the extension of Eq. (4.255):

$$\sum_{i=1}^{N} \overline{g}_i \nu_{ij} = 0, \qquad j = 1, \ldots, J. \tag{5.9}$$

The multi-reaction extension of Eq. (3.472) for affinity is

$$\overline{\alpha}_j = -\sum_{i=1}^{N} \overline{\mu}_i \nu_{ij}, \qquad j = 1, \ldots, J. \tag{5.10}$$

The multi-reaction extension of the affinity definition of Eq. (4.494) is

$$\overline{\alpha}_j = \overline{R}T \ln\left(\frac{\mathcal{R}_j'}{\mathcal{R}_j''}\right), \qquad j = 1, \ldots, J. \tag{5.11}$$

In terms of the chemical affinity of each reaction, the equilibrium condition is simply the extension of Eq. (4.254):

$$\overline{\alpha}_j = 0, \qquad j = 1, \ldots, J. \tag{5.12}$$

At equilibrium, then the equilibrium constraints can be shown to reduce to the extension of Eq. (4.266):

$$K_{P,j} = \prod_{i=1}^{N} \left(\frac{P_i}{P_o}\right)^{\nu_{ij}}, \qquad j = 1, \ldots, J, \tag{5.13}$$

or the extension of Eq. (4.274):

$$K_{c,j} \;=\; \prod_{i=1}^{N} \overline{\rho}_i^{\,\nu_{ij}}, \qquad j = 1, \ldots, J. \tag{5.14}$$

For isochoric reaction, the evolution of species concentration i due to the combined effect of J reactions is given by the extension of Eq. (4.279):

$$\frac{d\overline{\rho}_i}{dt} = \sum_{j=1}^{J} \nu_{ij} \underbrace{\overbrace{a_j T^{\beta_j} \exp\left(\frac{-\overline{\mathcal{E}}_j}{\overline{R}T}\right)}^{\equiv k_j(T)} \underbrace{\left(\prod_{k=1}^{N} \overline{\rho}_k^{\,\nu'_{kj}}\right)}_{\text{forward reaction}} \left(1 - \underbrace{\frac{1}{K_{c,j}} \prod_{k=1}^{N} \overline{\rho}_k^{\,\nu_{kj}}}_{\text{reverse reaction}}\right)}_{\equiv r_j = (1/V) d\zeta_j/dt}, \qquad i = 1, \ldots, N. \tag{5.15}$$

where the overbrace is labeled $\equiv \dot{\omega}_i$.

The extension to isobaric reactions, not given here, is straightforward, and follows the same analysis as for a single reaction. Again, three intermediate variables which are in common usage have been defined. First, one takes the reaction rate of the jth reaction to be the extension of Eq. (4.280):

$$r_j \;\equiv\; \underbrace{a_j T^{\beta_j} \exp\left(\frac{-\overline{\mathcal{E}}_j}{\overline{R}T}\right)}_{\equiv k_j(T)} \underbrace{\left(\prod_{k=1}^{N} \overline{\rho}_k^{\,\nu'_{kj}}\right)}_{\text{forward reaction}} \left(1 - \underbrace{\frac{1}{K_{c,j}} \prod_{k=1}^{N} \overline{\rho}_k^{\,\nu_{kj}}}_{\text{reverse reaction}}\right), \quad j = 1, \ldots, J, \tag{5.16}$$

or the extension of Eq. (4.281):

$$r_j \;=\; \underbrace{a_j T^{\beta_j} \exp\left(\frac{-\overline{\mathcal{E}}_j}{\overline{R}T}\right)}_{\equiv k_j(T),\ \text{Arrhenius rate}} \underbrace{\left(\underbrace{\prod_{k=1}^{N} \overline{\rho}_k^{\,\nu'_{kj}}}_{\text{forward reaction}} - \underbrace{\frac{1}{K_{c,j}} \prod_{k=1}^{N} \overline{\rho}_k^{\,\nu''_{kj}}}_{\text{reverse reaction}}\right)}_{\text{law of mass action}}, \qquad j = 1, \ldots, J, \tag{5.17}$$

$$\;=\; \frac{1}{V} \frac{d\zeta_j}{dt}. \tag{5.18}$$

Here, ζ_j is the reaction progress variable for the jth reaction.

Each reaction has a temperature-dependent rate function $k_j(T)$, which is and extension of Eq. (4.282):

$$k_j(T) \equiv a_j T^{\beta_j} \exp\left(\frac{-\overline{\mathcal{E}}_j}{\overline{R}T}\right), \qquad j = 1, \ldots, J. \tag{5.19}$$

The evolution rate of each species is given by $\dot{\omega}_i$, defined now as an extension of Eq. (4.284): now as

$$\dot{\omega}_i \equiv \sum_{j=1}^{J} \nu_{ij} r_j, \qquad i = 1, \ldots, N. \tag{5.20}$$

So, we can summarize the isochoric Eq. (5.15) as

$$\frac{d\overline{\rho}_i}{dt} = \dot{\omega}_i. \tag{5.21}$$

It will be useful to cast this in terms of mass fraction. Using the definition Eq. (2.43), Eq. (5.21) can be rewritten as

$$\frac{d}{dt}\left(\frac{\rho Y_i}{M_i}\right) = \dot{\omega}_i. \tag{5.22}$$

Because M_i is a constant, Eq. (5.22) can be recast as

$$\frac{d}{dt}(\rho Y_i) = M_i \dot{\omega}_i. \tag{5.23}$$

The multi-reaction extension of Eq. (4.239) for mole change in terms of progress variables is

$$dn_i = \sum_{j=1}^{J} \nu_{ij} d\zeta_j, \qquad i = 1, \ldots, N. \tag{5.24}$$

One also has Eq. (4.243):

$$dG|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i dn_i, \tag{5.25}$$

$$= \sum_{i=1}^{N} \overline{\mu}_i \sum_{k=1}^{J} \nu_{ik} d\zeta_k, \tag{5.26}$$

$$\frac{\partial G}{\partial \zeta_j}\bigg|_{\zeta_p} = \sum_{i=1}^{N} \overline{\mu}_i \sum_{k=1}^{J} \nu_{ik} \frac{\partial \zeta_k}{\partial \zeta_j}, \tag{5.27}$$

$$= \sum_{i=1}^{N} \overline{\mu}_i \sum_{j=1}^{J} \nu_{ik} \delta_{kj}, \tag{5.28}$$

$$= \sum_{i=1}^{N} \overline{\mu}_i \nu_{ij}, \tag{5.29}$$

$$= -\overline{\alpha}_j, \qquad j = 1, \ldots, J. \tag{5.30}$$

For a set of adiabatic, isochoric reactions, one can show the extension of Eq. (4.430) is

$$\frac{dT}{dt} = -\frac{\sum_{j=1}^{J} r_j \Delta E_j}{\rho c_v}, \tag{5.31}$$

where the energy change for a reaction ΔE_j is defined as the extension of Eq. (4.429):

$$\Delta E_j = \sum_{i=1}^{N} \overline{e}_i \nu_{ij}, \qquad j = 1, \dots, J. \tag{5.32}$$

Similarly for a set of adiabatic, isobaric reactions, one can show the extension of Eq. (4.445) to be

$$\frac{dT}{dt} = -\frac{\sum_{j=1}^{J} r_j \Delta H_j}{\rho c_P}, \tag{5.33}$$

where the enthalpy change for a reaction ΔH_j is defined as the extension of Eq. (4.444):

$$\Delta H_j = \sum_{i=1}^{N} \overline{h}_i \nu_{ij}, \qquad j = 1, \dots, J. \tag{5.34}$$

Moreover, the density and species concentration derivatives for an adiabatic, isobaric set can be shown to be the extensions of Eqs. (4.457) and (4.461):

$$\frac{d\rho}{dt} = M \sum_{j=1}^{J} r_j \sum_{i=1}^{N} \nu_{ij} \left(\frac{\overline{h}_i}{c_P T} - 1 \right), \tag{5.35}$$

$$\frac{d\overline{\rho}_i}{dt} = \sum_{j=1}^{J} r_j \left(\nu_{ij} + y_i \left(\frac{\Delta H_j}{\overline{c}_P T} - \Delta \mathsf{n}_j \right) \right), \tag{5.36}$$

where

$$\Delta \mathsf{n}_j = \sum_{k=1}^{N} \nu_{kj}. \tag{5.37}$$

In a similar fashion to that shown for a single reaction, one can further sum over all reactions and prove that mixture mass is conserved, element mass and number are conserved.

Example 5.1

Show that element mass and number are conserved for the multi-reaction formulation.

Start with Eq. (5.15) and expand as follows:

$$\frac{d\overline{\rho}_i}{dt} = \sum_{j=1}^{J} \nu_{ij} r_j, \tag{5.38}$$

$$\phi_{li} \frac{d\overline{\rho}_i}{dt} = \phi_{li} \sum_{j=1}^{J} \nu_{ij} r_j, \tag{5.39}$$

$$\frac{d}{dt}\left(\phi_{li}\overline{\rho}_i\right) = \sum_{j=1}^{J} \phi_{li}\nu_{ij} r_j, \tag{5.40}$$

$$\sum_{i=1}^{N} \frac{d}{dt}\left(\phi_{li}\overline{\rho}_i\right) = \sum_{i=1}^{N}\sum_{j=1}^{J} \phi_{li}\nu_{ij} r_j, \tag{5.41}$$

$$\frac{d}{dt}\underbrace{\left(\sum_{i=1}^{N} \phi_{li}\overline{\rho}_i\right)}_{=\overline{\rho}_l{}^e} = \sum_{j=1}^{J}\sum_{i=1}^{N} \phi_{li}\nu_{ij} r_j, \tag{5.42}$$

$$\frac{d\overline{\rho}_l{}^e}{dt} = \sum_{j=1}^{J} r_j \underbrace{\sum_{i=1}^{N} \phi_{li}\nu_{ij}}_{=0}, \tag{5.43}$$

$$\frac{d\overline{\rho}_l{}^e}{dt} = 0, \qquad l = 1, \ldots, L, \tag{5.44}$$

$$\frac{d}{dt}\left(\mathcal{M}_l\overline{\rho}_l{}^e\right) = 0, \qquad l = 1, \ldots, L, \tag{5.45}$$

$$\frac{d\rho_l{}^e}{dt} = 0, \qquad l = 1, \ldots, L. \tag{5.46}$$

It is also straightforward to show that the mixture density is conserved for the multi-reaction, multi-component mixture:

$$\frac{d\rho}{dt} = 0. \tag{5.47}$$

The proof of the Clausius-Duhem relationship for the second law is an extension of the single reaction result. Start with Eq. (4.464) and operate much as for a single reaction model.

$$dS|_{E,V} = \underbrace{-\frac{1}{T}\sum_{i=1}^{N} \overline{\mu}_i dn_i}_{\text{irreversibility}} \geq 0, \tag{5.48}$$

$$\left.\frac{dS}{dt}\right|_{E,V} = -\frac{V}{T}\sum_{i=1}^{N} \overline{\mu}_i \frac{dn_i}{dt}\frac{1}{V} \geq 0, \tag{5.49}$$

$$= -\frac{V}{T}\sum_{i=1}^{N} \overline{\mu}_i \frac{d\overline{\rho}_i}{dt} \geq 0, \tag{5.50}$$

$$= -\frac{V}{T} \sum_{i=1}^{N} \overline{\mu}_i \sum_{j=1}^{J} \nu_{ij} r_j \geq 0, \tag{5.51}$$

$$= -\frac{V}{T} \sum_{i=1}^{N} \sum_{j=1}^{J} \overline{\mu}_i \nu_{ij} r_j \geq 0, \tag{5.52}$$

$$= -\frac{V}{T} \sum_{j=1}^{J} r_j \sum_{i=1}^{N} \overline{\mu}_i \nu_{ij} \geq 0, \tag{5.53}$$

$$= -\frac{V}{T} \sum_{j=1}^{J} k_j \prod_{i=1}^{N} \overline{\rho}_i^{\nu'_{ij}} \left(1 - \frac{1}{K_{c,j}} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_{ij}}\right) \sum_{i=1}^{N} \overline{\mu}_i \nu_{ij} \geq 0, \tag{5.54}$$

$$= -\frac{V}{T} \sum_{j=1}^{J} k_j \prod_{i=1}^{N} \overline{\rho}_i^{\nu'_{ij}} \left(1 - \frac{1}{K_{c,j}} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_{ij}}\right) \left(\overline{R}T \ln\left(\frac{1}{K_{c,j}} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_{ij}}\right)\right) \geq 0, \tag{5.55}$$

$$= -\overline{R}V \sum_{j=1}^{J} k_j \prod_{i=1}^{N} \overline{\rho}_i^{\nu'_{ij}} \left(1 - \frac{1}{K_{c,j}} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_{ij}}\right) \ln\left(\frac{1}{K_{c,j}} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_{ij}}\right) \geq 0, \tag{5.56}$$

Note that Eq. (5.53) can also be written in terms of the affinities (see Eq. (5.10)) and reaction progress variables (see Eq. (5.18)) as

$$\left.\frac{dS}{dt}\right|_{E,V} = \frac{1}{T} \sum_{j=1}^{J} \overline{\alpha}_j \frac{d\zeta_j}{dt} \geq 0. \tag{5.57}$$

Similar to the argument for a single reaction, if one defines

$$\mathcal{R}'_j = k_j \prod_{i=1}^{N} \overline{\rho}_i^{\nu'_{ij}}, \tag{5.58}$$

$$\mathcal{R}''_j = \frac{k_j}{K_{c,j}} \prod_{i=1}^{N} \overline{\rho}_i^{\nu''_{ij}}, \tag{5.59}$$

then it is easy to show that

$$r_j = \mathcal{R}'_j - \mathcal{R}''_j, \tag{5.60}$$

and we get the equivalent of Eq. (4.493):

$$\left.\frac{dS}{dt}\right|_{E,V} = \overline{R}V \sum_{j=1}^{J} \left(\mathcal{R}'_j - \mathcal{R}''_j\right) \ln\left(\frac{\mathcal{R}'_j}{\mathcal{R}''_j}\right) \geq 0. \tag{5.61}$$

Since $k_j(T) > 0$, $\overline{R} > 0$, and $V \geq 0$, and each term in the summation combines to be positive semi-definite, one sees that the Clausius-Duhem inequality is guaranteed to be satisfied for multi-component reactions.

Now, let us cast this analysis with some of the language and notation similar to that of Prigogine's[4] monograph.[5] We will use a "P" to denote equations found in Prigogine's text. First, note that Eq. (5.53) can also be written in terms of the affinities (see Eq. (5.10)) as

$$\left. \frac{dS}{dt} \right|_{E,V} = V\mathbf{r}^T \cdot \left(\frac{\overline{\boldsymbol{\alpha}}}{T} \right). \tag{5.62}$$

We can take Prigogine's so-called "generalized force" to be $\mathbf{x}$ with

$$\mathbf{x} = \frac{\overline{\boldsymbol{\alpha}}}{T}. \tag{5.63}$$

We can then take the so-called "generalized flux" $\mathbf{j}$ to be

$$\mathbf{j} = V\mathbf{r}. \tag{5.64}$$

Therefore, Eq. (5.62) can be recast as

$$\left. \frac{dS}{dt} \right|_{E,V} = \mathbf{j}^T \cdot \mathbf{x}. \tag{5.65}$$

Equations (5.63-5.65) can be compared with Eqs. (P4.2). Note, we know that at equilibrium both $\mathbf{j} = \mathbf{0}$ and $\mathbf{x} = \mathbf{0}$ from earlier analysis: When all $\overline{\alpha}_j$ are zero, $\mathbf{x} = \mathbf{0}$, and by Eq. (5.11), we must have $\mathcal{R}'_j = \mathcal{R}''_j$, and thus since by Eq. (5.60), $r_j = \mathcal{R}'_j - \mathcal{R}''_j$, $r_j = 0$. When all r_j are zero, $\mathbf{j} = \mathbf{0}$. Moreover, Eq. (5.20) shows all $\dot{\omega}_i$ are zero; thus, Eq. (5.21) is in equilibrium. This proof did not rely on any linearization near equilibrium.

5.2   Equilibrium conditions

For multicomponent mixtures undergoing multiple reactions, determining the equilibrium condition is more difficult. There are two primary approaches, both of which are essentially equivalent. The most straightforward method requires formal minimization of the Gibbs free energy of the mixture. It can be shown that this actually finds the equilibrium associated with *all possible reactions.*

5.2.1   Minimization of G via Lagrange multipliers

Recall Eq. (3.357), $dG|_{T,P} \leq 0$. Recall also Eq. (3.359), $G = \sum_{i=1}^{N} \overline{g}_i n_i$. Since $\overline{\mu}_i = \overline{g}_i = \partial G/\partial n_i|_{P,T,n_j}$, one also has $G = \sum_{i=1}^{N} \overline{\mu}_i n_i$. From Eq. (3.360), $dG|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i dn_i$. Now, one must also demand for a system coming to equilibrium that the element numbers are conserved. This can be achieved by requiring

$$\sum_{i=1}^{N} \phi_{li}(n_{io} - n_i) = 0, \qquad l = 1, \dots, L. \tag{5.66}$$

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[4]Ilya Prigogine, 1917-2003, Russian-Belgian chemist.
[5]Prigogine, I., 1967, *Introduction to Thermodynamics of Irreversible Processes*, Interscience, New York.

Here, recall n_{io} is the initial number of moles of species i in the mixture, and ϕ_{li} is the number of moles of element l in species i.

One can now use the method of constrained optimization given by the method of Lagrange multipliers to extremize G subject to the constraints of element conservation. The extremum will be a minimum; this will not be proved, but it will be demonstrated. Define a set of L Lagrange[6] multipliers λ_l. Next define an augmented Gibbs free energy function G^*, which is simply G plus the product of the Lagrange multipliers and the constraints:

$$G^* = G + \sum_{l=1}^{L} \lambda_l \sum_{i=1}^{N} \phi_{li}(n_{io} - n_i). \tag{5.67}$$

Now, when the constraints are satisfied, one has $G^* = G$, so assuming the constraints can be satisfied, extremizing G is equivalent to extremizing G^*. To extremize G^*, take its differential with respect to n_i, with P, T and n_j constant and set it to zero for each species:

$$\left.\frac{\partial G^*}{\partial n_i}\right|_{T,P,n_j} = \underbrace{\left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_j}}_{=\overline{\mu}_i} - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0. \qquad i = 1,\ldots,N. \tag{5.68}$$

With the definition of the partial molar property $\overline{\mu}_i$, one then gets

$$\overline{\mu}_i - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1,\ldots,N. \tag{5.69}$$

Next, for an ideal gas, one can expand the chemical potential so as to get

$$\underbrace{\overline{\mu}_{T,i}^o + \overline{R}T\ln\left(\frac{P_i}{P_o}\right)}_{=\overline{\mu}_i} - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1,\ldots,N, \tag{5.70}$$

$$\overline{\mu}_{T,i}^o + \overline{R}T\ln\left(\underbrace{\left(\frac{n_i P}{\sum_{k=1}^{N} n_k}\right)\frac{1}{P_o}}_{=P_i}\right) - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1,\ldots,N. \tag{5.71}$$

Recalling that $\sum_{k=1}^{N} n_k = n$, in summary then, one has $N + L$ equations

$$\overline{\mu}_{T,i}^o + \overline{R}T\ln\left(\frac{n_i}{n}\frac{P}{P_o}\right) - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1,\ldots,N, \tag{5.72}$$

$$\sum_{i=1}^{N} \phi_{li}(n_{io} - n_i) = 0, \qquad l = 1,\ldots,L. \tag{5.73}$$

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[6]Joseph-Louis Lagrange, 1736-1813, Italian-French mathematician.

in $N + L$ unknowns: $n_i, i = 1, \ldots, N, \; \lambda_l, l = 1, \ldots, L$.

Example 5.2

Consider a previous example problem, p. 134, in which

$$N_2 + N_2 \rightleftharpoons 2N + N_2. \tag{5.74}$$

Take the reaction to be isothermal and isobaric with $T = 6000 \; K$ and $P = 100 \; kPa$. Initially one has 1 $kmole$ of N_2 and 0 $kmole$ of N. Use the extremization of Gibbs free energy to find the equilibrium composition.

First, find the chemical potentials at the reference pressure of each of the possible constituents.

$$\overline{\mu}^o_{T,i} = \overline{g}^o_i = \overline{h}^o_i - T\overline{s}^o_i = \overline{h}^o_{298,i} + \Delta\overline{h}^o_i - T\overline{s}^o_i. \tag{5.75}$$

For each species, one then finds

$$\overline{\mu}^o_{N_2} = 0 + 205848 - (6000)(292.984) = -1552056 \; \frac{kJ}{kmole}, \tag{5.76}$$

$$\overline{\mu}^o_{N} = 472680 + 124590 - (6000)(216.926) = -704286 \; \frac{kJ}{kmole}. \tag{5.77}$$

To each of these one must add

$$\overline{R}T \ln\left(\frac{n_i P}{n P_o}\right)$$

to get the full chemical potential. Now, $P = P_o = 100 \; kPa$ for this problem, so one only must consider $\overline{R}T = 8.314(6000) = 49884 \; kJ/kmole$. So, the chemical potentials are

$$\overline{\mu}_{N_2} = -1552056 + 49884 \ln\left(\frac{n_{N_2}}{n_N + n_{N_2}}\right), \tag{5.78}$$

$$\overline{\mu}_{N} = -704286 + 49884 \ln\left(\frac{n_N}{n_N + n_{N_2}}\right). \tag{5.79}$$

Then, one adds on the Lagrange multiplier and then considers element conservation to get the following coupled set of nonlinear algebraic equations:

$$-1552056 + 49884 \ln\left(\frac{n_{N_2}}{n_N + n_{N_2}}\right) - 2\lambda_N = 0, \tag{5.80}$$

$$-704286 + 49884 \ln\left(\frac{n_N}{n_N + n_{N_2}}\right) - \lambda_N = 0, \tag{5.81}$$

$$n_N + 2n_{N_2} = 2. \tag{5.82}$$

These non-linear equations are solved numerically to get

$$n_{N_2} = 0.88214 \; kmole, \tag{5.83}$$

$$n_N = 0.2357 \; kmole, \tag{5.84}$$

$$\lambda_N = -781934 \; \frac{kJ}{kmole}. \tag{5.85}$$

These agree with results found in the earlier example problem of p. 134.

Example 5.3

Consider a mixture of 2 $kmole$ of H_2 and 1 $kmole$ of O_2 at $T = 3000\ K$ and $P = 100\ kPa$. Assuming an isobaric and isothermal equilibration process with the products consisting of H_2, O_2, H_2O, OH, H, and O, find the equilibrium concentrations. Consider the same mixture at $T = 298\ K$ and $T = 1000\ K$.

The first task is to find the chemical potentials of each species at the reference pressure and $T = 3000\ K$. Here, one can use the standard tables along with the general equation

$$\overline{\mu}^o_{T,i} = \overline{g}^o_i = \overline{h}^o_i - T\overline{s}^o_i = \overline{h}^o_{298,i} + \Delta\overline{h}^o_i - T\overline{s}^o_i. \tag{5.86}$$

For each species, one then finds

$$\overline{\mu}^o_{H_2} = 0 + 88724 - 3000(202.989) = -520242\ \frac{kJ}{kmole}, \tag{5.87}$$

$$\overline{\mu}^o_{O_2} = 0 + 98013 - 3000(284.466) = -755385\ \frac{kJ}{kmole}, \tag{5.88}$$

$$\overline{\mu}^o_{H_2O} = -241826 + 126548 - 3000(286.504) = -974790\ \frac{kJ}{kmole}, \tag{5.89}$$

$$\overline{\mu}^o_{OH} = 38987 + 89585 - 3000(256.825) = -641903\ \frac{kJ}{kmole}, \tag{5.90}$$

$$\overline{\mu}^o_H = 217999 + 56161 - 3000(162.707) = -213961\ \frac{kJ}{kmole}, \tag{5.91}$$

$$\overline{\mu}^o_O = 249170 + 56574 - 3000(209.705) = -323371\ \frac{kJ}{kmole}. \tag{5.92}$$

To each of these one must add

$$\overline{R}T\ln\left(\frac{n_i P}{n P_o}\right)$$

to get the full chemical potential. Now, $P = P_o = 100\ kPa$ for this problem, so one must only consider $\overline{R}T = 8.314(3000) = 24942\ kJ/kmole$. So, the chemical potentials are

$$\overline{\mu}_{H_2} = -520243 + 24942\ln\left(\frac{n_{H_2}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right), \tag{5.93}$$

$$\overline{\mu}_{O_2} = -755385 + 24942\ln\left(\frac{n_{O_2}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right), \tag{5.94}$$

$$\overline{\mu}_{H_2O} = -974790 + 24942\ln\left(\frac{n_{H_2O}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right), \tag{5.95}$$

$$\overline{\mu}_{OH} = -641903 + 24942\ln\left(\frac{n_{OH}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right), \tag{5.96}$$

$$\overline{\mu}_H = -213961 + 24942\ln\left(\frac{n_H}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right), \tag{5.97}$$

$$\overline{\mu}_O = -323371 + 24942\ln\left(\frac{n_O}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right). \tag{5.98}$$

Then, one adds on the Lagrange multipliers and then considers element conservation to get the following coupled set of nonlinear equations:

$$-520243 + 24942 \ln \left(\frac{n_{H_2}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O} \right) - 2\lambda_H \quad = \quad 0, \qquad (5.99)$$

$$-755385 + 24942 \ln \left(\frac{n_{O_2}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O} \right) - 2\lambda_O \quad = \quad 0, \qquad (5.100)$$

$$-974790 + 24942 \ln \left(\frac{n_{H_2O}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O} \right) - 2\lambda_H - \lambda_O \quad = \quad 0, \qquad (5.101)$$

$$-641903 + 24942 \ln \left(\frac{n_{OH}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O} \right) - \lambda_H - \lambda_O \quad = \quad 0, \qquad (5.102)$$

$$-213961 + 24942 \ln \left(\frac{n_H}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O} \right) - \lambda_H \quad = \quad 0, \qquad (5.103)$$

$$-323371 + 24942 \ln \left(\frac{n_O}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O} \right) - \lambda_O \quad = \quad 0, \qquad (5.104)$$

$$2n_{H_2} + 2n_{H_2O} + n_{OH} + n_H \quad = \quad 4, \qquad (5.105)$$

$$2n_{O_2} + n_{H_2O} + n_{OH} + n_O \quad = \quad 2. \qquad (5.106)$$

These non-linear algebraic equations can be solved numerically via a Newton-Raphson technique. The equations are sensitive to the initial guess, and one can use ones intuition to help guide the selection. For example, one might expect to have n_{H_2O} somewhere near 2 $kmole$. Application of the Newton-Raphson iteration yields

$$n_{H_2} \quad = \quad 3.19 \times 10^{-1} \ kmole, \qquad (5.107)$$

$$n_{O_2} \quad = \quad 1.10 \times 10^{-1} \ kmole, \qquad (5.108)$$

$$n_{H_2O} \quad = \quad 1.50 \times 10^{0} \ kmole, \qquad (5.109)$$

$$n_{OH} \quad = \quad 2.20 \times 10^{-1} \ kmole, \qquad (5.110)$$

$$n_H \quad = \quad 1.36 \times 10^{-1} \ kmole, \qquad (5.111)$$

$$n_O \quad = \quad 5.74 \times 10^{-2} \ kmole, \qquad (5.112)$$

$$\lambda_H \quad = \quad -2.85 \times 10^{5} \ \frac{kJ}{kmole}, \qquad (5.113)$$

$$\lambda_O \quad = \quad -4.16 \times 10^{5} \ \frac{kJ}{kmole}. \qquad (5.114)$$

At this relatively high value of temperature, all species considered have a relatively major presence. That is, there are no truly minor species.

Unless a good guess is provided, it may be difficult to find a solution for this set of non-linear equations. Straightforward algebra allows the equations to be recast in a form which sometimes converges more rapidly:

$$\frac{n_{H_2}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O} \quad = \quad \exp \left(\frac{520243}{24942} \right) \left(\exp \left(\frac{\lambda_H}{24942} \right) \right)^2, \qquad (5.115)$$

$$\frac{n_{O_2}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O} \quad = \quad \exp \left(\frac{755385}{24942} \right) \left(\exp \left(\frac{\lambda_O}{24942} \right) \right)^2, \qquad (5.116)$$

$$\frac{n_{H_2O}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O} \quad = \quad \exp \left(\frac{974790}{24942} \right) \exp \left(\frac{\lambda_O}{24942} \right) \left(\exp \left(\frac{\lambda_H}{24942} \right) \right)^2, \ (5.117)$$

$$\frac{n_{OH}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O} \quad = \quad \exp \left(\frac{641903}{24942} \right) \exp \left(\frac{\lambda_O}{24942} \right) \exp \left(\frac{\lambda_H}{24942} \right), \qquad (5.118)$$
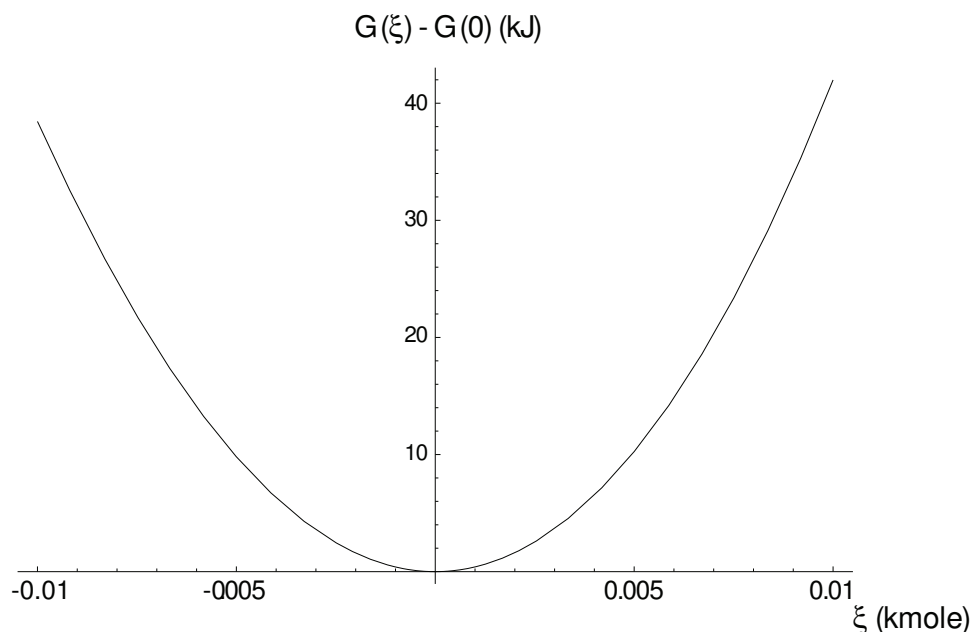
Figure 5.1: Gibbs free energy variation as mixture composition is varied maintaining element conservation for mixture of H_2, O_2, H_2O, OH, H, and O at $T = 3000\ K$, $P = 100\ kPa$.

$$\frac{n_H}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O} = \exp\left(\frac{213961}{24942}\right) \exp\left(\frac{\lambda_H}{24942}\right), \tag{5.119}$$

$$\frac{n_O}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O} = \exp\left(\frac{323371}{24942}\right) \exp\left(\frac{\lambda_O}{24942}\right), \tag{5.120}$$

$$2n_{H_2} + 2n_{H_2O} + n_{OH} + n_H = 4, \tag{5.121}$$

$$2n_{O_2} + n_{H_2O} + n_{OH} + n_O = 2. \tag{5.122}$$

Then, solve these considering n_i, $\exp(\lambda_O/24942)$, and $\exp(\lambda_H/24942)$ as unknowns. The same result is recovered, but a broader range of initial guesses converge to the correct solution.

One can verify that this choice extremizes G by direct computation; moreover, this will show that the extremum is actually a minimum. In so doing, one must exercise care to see that element conservation is retained. As an example, perturb the equilibrium solution for n_{H_2} and n_H such that

$$n_{H_2} = 3.19 \times 10^{-1} + \xi, \tag{5.123}$$

$$n_H = 1.36 \times 10^{-1} - 2\xi. \tag{5.124}$$

Leave all other species mole numbers the same. In this way, when $\xi = 0$, one has the original equilibrium solution. For $\xi \neq 0$, the solution moves off the equilibrium value in such a way that elements are conserved. Then, one has $G = \sum_{i=1}^{N} \overline{\mu}_i n_i = G(\xi)$.

The difference $G(\xi) - G(0)$ is plotted in Fig. 5.1. When $\xi = 0$, there is no deviation from the value predicted by the Newton-Raphson iteration. Clearly when $\xi = 0$, $G(\xi) - G(0)$, takes on a minimum value, and so then does $G(\xi)$. So, the procedure works.

At the lower temperature, $T = 298\ K$, application of the same procedure yields very different results:

$$n_{H_2} = 4.88 \times 10^{-27}\ kmole, \tag{5.125}$$

$$n_{O_2} = 2.44 \times 10^{-27} \ kmole, \tag{5.126}$$

$$n_{H_2O} = 2.00 \times 10^0 \ kmole, \tag{5.127}$$

$$n_{OH} = 2.22 \times 10^{-29} \ kmole, \tag{5.128}$$

$$n_H = 2.29 \times 10^{-49} \ kmole, \tag{5.129}$$

$$n_O = 1.67 \times 10^{-54} \ kmole, \tag{5.130}$$

$$\lambda_H = -9.54 \times 10^4 \ \frac{kJ}{kmole}, \tag{5.131}$$

$$\lambda_O = -1.07 \times 10^5 \ \frac{kJ}{kmole}. \tag{5.132}$$

At the intermediate temperature, $T = 1000 \ K$, application of the same procedure shows the minor species become slightly more prominent:

$$n_{H_2} = 4.99 \times 10^{-7} \ kmole, \tag{5.133}$$

$$n_{O_2} = 2.44 \times 10^{-7} \ kmole, \tag{5.134}$$

$$n_{H_2O} = 2.00 \times 10^0 \ kmole, \tag{5.135}$$

$$n_{OH} = 2.09 \times 10^{-8} \ kmole, \tag{5.136}$$

$$n_H = 2.26 \times 10^{-12} \ kmole, \tag{5.137}$$

$$n_O = 1.10 \times 10^{-13} \ kmole, \tag{5.138}$$

$$\lambda_H = -1.36 \times 10^5 \ \frac{kJ}{kmole}, \tag{5.139}$$

$$\lambda_O = -1.77 \times 10^5 \ \frac{kJ}{kmole}. \tag{5.140}$$

5.2.2   Equilibration of all reactions

In another equivalent method, if one commences with a multi-reaction model, one can require each reaction to be in equilibrium. This leads to a set of algebraic equations for $r_j = 0$, which from Eq. (5.17) leads to

$$K_{c,j} = \left(\frac{P_o}{\overline{R}T} \right)^{\sum_{i=1}^N \nu_{ij}} \exp \left(\frac{-\Delta G_j^o}{\overline{R}T} \right) = \prod_{k=1}^N \overline{\rho}_k^{\ \nu_{kj}}, \qquad j = 1, \ldots, J. \tag{5.141}$$

With some effort it can be shown that not all of the J equations are linearly independent. Moreover, they do not possess a unique solution. However, for closed systems, only one of the solutions is physical, as will be shown in the following section. The others typically involve non-physical, negative concentrations.

Nevertheless, Eqs. (5.141) are entirely consistent with the predictions of the $N + L$ equations which arise from extremization of Gibbs free energy while enforcing element number

constraints. This can be shown by beginning with Eq. (5.71), rewritten in terms of molar concentrations, and performing the following sequence of operations:

$$\overline{\mu}_{T,i}^o + \overline{R}T \ln \left(\frac{n_i/V}{\sum_{k=1}^{N} n_k/V} \frac{P}{P_o} \right) - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1, \dots, N, \quad (5.142)$$

$$\overline{\mu}_{T,i}^o + \overline{R}T \ln \left(\frac{\overline{\rho}_i}{\sum_{k=1}^{N} \overline{\rho}_k} \frac{P}{P_o} \right) - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1, \dots, N, \quad (5.143)$$

$$\overline{\mu}_{T,i}^o + \overline{R}T \ln \left(\frac{\overline{\rho}_i}{\overline{\rho}} \frac{P}{P_o} \right) - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1, \dots, N, \quad (5.144)$$

$$\overline{\mu}_{T,i}^o + \overline{R}T \ln \left(\overline{\rho}_i \frac{\overline{R}T}{P_o} \right) - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1, \dots, N, \quad (5.145)$$

$$\nu_{ij}\overline{\mu}_{T,i}^o + \nu_{ij}\overline{R}T \ln \left(\overline{\rho}_i \frac{\overline{R}T}{P_o} \right) - \nu_{ij} \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1, \dots, N,$$
$$j = 1, \dots, J, \qquad (5.146)$$

$$\underbrace{\sum_{i=1}^{N} \nu_{ij}\overline{\mu}_{T,i}^o}_{=\Delta G_j^o} + \sum_{i=1}^{N} \nu_{ij}\overline{R}T \ln \left(\overline{\rho}_i \frac{\overline{R}T}{P_o} \right) - \sum_{i=1}^{N} \nu_{ij} \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad j = 1, \dots, J, \quad (5.147)$$

$$\Delta G_j^o + \overline{R}T \sum_{i=1}^{N} \nu_{ij} \ln \left(\overline{\rho}_i \frac{\overline{R}T}{P_o} \right) - \sum_{l=1}^{L} \lambda_l \underbrace{\sum_{i=1}^{N} \phi_{li} \nu_{ij}}_{=0} = 0, \qquad j = 1, \dots, J, \quad (5.148)$$

$$\Delta G_j^o + \overline{R}T \sum_{i=1}^{N} \nu_{ij} \ln \left(\overline{\rho}_i \frac{\overline{R}T}{P_o} \right) = 0, \qquad j = 1, \dots, J. \quad (5.149)$$

Here, the stoichiometry for each reaction has been employed to remove the Lagrange multipliers. Continue to find

$$\sum_{i=1}^{N} \ln \left(\overline{\rho}_i \frac{\overline{R}T}{P_o} \right)^{\nu_{ij}} = -\frac{\Delta G_j^o}{\overline{R}T}, \qquad j = 1, \dots, J, \quad (5.150)$$

$$\exp \left(\sum_{i=1}^{N} \ln \left(\overline{\rho}_i \frac{\overline{R}T}{P_o} \right)^{\nu_{ij}} \right) = \exp \left(-\frac{\Delta G_j^o}{\overline{R}T} \right), \qquad j = 1, \dots, J, \quad (5.151)$$

$$\prod_{i=1}^{N} \left(\overline{\rho}_i \frac{\overline{R}T}{P_o} \right)^{\nu_{ij}} = \exp \left(-\frac{\Delta G_j^o}{\overline{R}T} \right), \qquad j = 1, \dots, J, \quad (5.152)$$

$$\left(\frac{\overline{R}T}{P_o} \right)^{\sum_{i=1}^{N} \nu_{ij}} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_{ij}} = \exp \left(-\frac{\Delta G_j^o}{\overline{R}T} \right), \qquad j = 1, \dots, J, \quad (5.153)$$

$$\prod_{i=1}^{N} \overline{\rho}_i^{\ \nu_{ij}} = \underbrace{\left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^{N} \nu_{ij}} \exp\left(-\frac{\Delta G_j^o}{\overline{R}T}\right)}_{=K_{c,j}}, \qquad j = 1, \ldots, J, \tag{5.154}$$

$$\prod_{i=1}^{N} \overline{\rho}_i^{\ \nu_{ij}} = K_{c,j}, \qquad j = 1, \ldots, J. \tag{5.155}$$

Thus, extremization of Gibbs free energy is consistent with equilibrating each of the J reactions.

5.2.3   Zel'dovich's uniqueness proof

Here, a proof is given for the global uniqueness of the equilibrium point in the physically accessible region of composition space following a procedure given in a little known paper by the great Russian physicist Zel'dovich.[7] The proof follows the basic outline of Zel'dovich, but the notation will be consistent with the present development. Some simplifications were available to Zel'dovich but not employed by him. For further background see Powers and Paolucci.[8]

5.2.3.1   Isothermal, isochoric case

Consider a mixture of ideal gases in a closed fixed volume V at fixed temperature T. For such a system, the canonical equilibration relation is given by Eq. (3.356), $dA|_{T,V} \leq 0$. So, A must be always decreasing until it reaches a minimum. Consider then A. First, combining Eqs. (3.235) and (3.236), one finds

$$A = -PV + G. \tag{5.156}$$

Now, from Eq. (3.359) one can eliminate G to get

$$A = -PV + \sum_{i=1}^{N} n_i \overline{\mu}_i. \tag{5.157}$$

From the ideal gas law, $PV = n\overline{R}T$, and again with $n = \sum_{i=1}^{N} n_i$, one gets

$$A = -n\overline{R}T + \sum_{i=1}^{N} n_i \overline{\mu}_i, \tag{5.158}$$

$$= -\sum_{i=1}^{N} n_i \overline{R}T + \sum_{i=1}^{N} n_i \left(\overline{\mu}_{T,i}^o + \overline{R}T \ln\left(\frac{P_i}{P_o}\right)\right), \tag{5.159}$$

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[7]Zel'dovich, Ya. B., 1938, "A Proof of the Uniqueness of the Solution of the Equations for the Law of Mass Action," *Zhurnal Fizicheskoi Khimii*, 11: 685-687.

[8]Powers, J. M., and Paolucci, S., 2008, "Uniqueness of Chemical Equilibria in Ideal Mixtures of Ideal Gases," *American Journal of Physics*, 76(9): 848-855.

$$= \overline{R}T \sum_{i=1}^{N} n_i \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} - 1 + \ln\left(\frac{n_i P}{n P_o}\right) \right), \tag{5.160}$$

$$= \overline{R}T \sum_{i=1}^{N} n_i \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} - 1 + \ln\left(n_i \frac{\overline{R}T}{P_o V}\right) \right). \tag{5.161}$$

For convenience, define, for this isothermal isochoric problem n^o, the total number of moles at the reference pressure, which for this isothermal isochoric problem, is a constant:

$$n^o \equiv \frac{P_o V}{\overline{R}T}. \tag{5.162}$$

So

$$A = \overline{R}T \sum_{i=1}^{N} n_i \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} - 1 + \ln\left(\frac{n_i}{n^o}\right) \right). \tag{5.163}$$

Now, recall that the atomic element conservation, Eq. (5.66), demands that

$$\sum_{i=1}^{N} \phi_{li}(n_{io} - n_i) = 0, \qquad l = 1, \dots, L. \tag{5.164}$$

As defined earlier, ϕ_{li} is the number of atoms of element l in species i; note that $\phi_{li} \geq 0$. It is described by a $L \times N$ non-square matrix, typically of full rank, L. Defining the initial number of moles of element l, $\varepsilon_l = \sum_{i=1}^{N} \phi_{li} n_{io}$, one can rewrite Eq. (5.164) as

$$\sum_{i=1}^{N} \phi_{li} n_i = \varepsilon_l, \qquad l = 1, \dots, L. \tag{5.165}$$

Equation (5.165) is generally under-constrained, and one can find solutions of the form

$$\begin{pmatrix} n_1 \\ n_2 \\ \vdots \\ n_N \end{pmatrix} = \begin{pmatrix} n_{1o} \\ n_{2o} \\ \vdots \\ n_{No} \end{pmatrix} + \begin{pmatrix} \mathcal{D}_{11} \\ \mathcal{D}_{21} \\ \vdots \\ \mathcal{D}_{N\ 1} \end{pmatrix} \xi_1 + \begin{pmatrix} \mathcal{D}_{12} \\ \mathcal{D}_{22} \\ \vdots \\ \mathcal{D}_{N\ 2} \end{pmatrix} \xi_2 + \dots + \begin{pmatrix} \mathcal{D}_{1\ N-L} \\ \mathcal{D}_{2\ N-L} \\ \vdots \\ \mathcal{D}_{N\ N-L} \end{pmatrix} \xi_{N-L}. \tag{5.166}$$

Here, $\mathcal{D}_{ik}$ represents a dimensionless component of a matrix of dimension $N \times (N-L)$. Here, in contrast to earlier analysis, ξ_i is interpreted as having the dimensions of *mole*. Each of the $N-L$ column vectors of the matrix whose components are $\mathcal{D}_{ik}$ has length N and lies in the right null space of the matrix whose components are ϕ_{li}. That is,

$$\sum_{i=1}^{N} \phi_{li} \mathcal{D}_{ik} = 0, \qquad k = 1, \dots, N - L, \quad l = 1, \dots, L. \tag{5.167}$$

There is an exception to this rule when the left null space of ν_{ij} is of higher dimension than the right null space of ϕ_{li}. In such a case, there are quantities conserved in addition to the

elements as a consequence of the form of the reaction law. The most common exception occurs when each of the reactions also conserves the number of molecules. In such a case, there will be $N - L - 1$ free variables, rather than $N - L$. One can robustly form $\mathcal{D}_{ij}$ from the set of independent column space vectors of ν_{ij}. These vectors are included in the right null space of ϕ_{li} since $\sum_{i=1}^{N} \phi_{li}\nu_{ij} = 0$.

One can have $\mathcal{D}_{ik} \in (-\infty, \infty)$. Each of these is a function of ϕ_{li}. In matrix form, one can say

$$
\begin{pmatrix} n_1 \\ n_2 \\ \vdots \\ n_N \end{pmatrix} = \begin{pmatrix} n_{1o} \\ n_{2o} \\ \vdots \\ n_{No} \end{pmatrix} + \begin{pmatrix} \mathcal{D}_{11} & \mathcal{D}_{12} & \dots & \mathcal{D}_{1\ N-L} \\ \mathcal{D}_{21} & \mathcal{D}_{22} & \dots & \mathcal{D}_{2\ N-L} \\ \vdots & \vdots & \vdots & \vdots \\ \mathcal{D}_{N1} & \mathcal{D}_{N2} & \dots & \mathcal{D}_{N\ N-L} \end{pmatrix} \begin{pmatrix} \xi_1 \\ \xi_2 \\ \vdots \\ \xi_{N-L} \end{pmatrix}. \tag{5.168}
$$

In index form, this becomes

$$
n_i = n_{io} + \sum_{k=1}^{N-L} \mathcal{D}_{ik}\xi_k, \qquad i = 1, \dots, N. \tag{5.169}
$$

It is also easy to show that the $N - L$ column space vectors in $\mathcal{D}_{ik}$ are linear combinations of $N - L$ column space vectors that span the column space of the rank-deficient $N \times J$ components of ν_{ij}. The N values of n_i are uniquely determined once $N - L$ values of ξ_k are specified. That is, a set of independent ξ_k, $k = 1, \dots, N - L$, is sufficient to describe the system. This insures the initial element concentrations are always maintained. One can also develop a J-reaction generalization of the single reaction Eq. (4.99). Let Ξ_{kj}, $k = 1, \dots, N - L$, $j = 1, \dots, J$, be the extension of ξ_k. Then, the appropriate generalization of Eq. (4.99) is

$$
\nu_{ij} = \sum_{k=1}^{N-L} \mathcal{D}_{ik}\Xi_{kj}. \tag{5.170}
$$

In Gibbs notation, one would say

$$
\boldsymbol{\nu} = \mathbf{D} \cdot \boldsymbol{\Xi}. \tag{5.171}
$$

One can find the matrix $\boldsymbol{\Xi}$ by the following operations

$$
\begin{aligned}
\mathbf{D} \cdot \boldsymbol{\Xi} &= \boldsymbol{\nu}, \tag{5.172} \\
\mathbf{D}^T \cdot \mathbf{D} \cdot \boldsymbol{\Xi} &= \mathbf{D}^T \cdot \boldsymbol{\nu}, \tag{5.173} \\
\boldsymbol{\Xi} &= \left(\mathbf{D}^T \cdot \mathbf{D}\right)^{-1} \cdot \mathbf{D}^T \cdot \boldsymbol{\nu}. \tag{5.174}
\end{aligned}
$$

This calculation has only marginal utility.

Returning to the primary exercise, note that one can form the partial derivative of Eq. (5.169):

$$
\left. \frac{\partial n_i}{\partial \xi_p} \right|_{\xi_j} = \sum_{k=1}^{N-L} \mathcal{D}_{ik} \left. \frac{\partial \xi_k}{\partial \xi_p} \right|_{\xi_j}, \qquad i = 1, \dots, N; \ p = 1, \dots, N - L, \tag{5.175}
$$

$$= \sum_{k=1}^{N-L} \mathcal{D}_{ik}\delta_{kp}, \qquad i=1,\dots,N; \; p=1,\dots,N-L, \qquad (5.176)$$

$$= \mathcal{D}_{ip}, \qquad i=1,\dots,N; \; p=1,\dots,N-L. \qquad (5.177)$$

Here, δ_{kp} is the Kronecker delta function.

Next, return to consideration of Eq. (5.161). It is sought to minimize A while holding T and V constant. The only available variables are n_i, $i=1,\dots,N$. These are not fully independent, but they are known in terms of the independent ξ_p, $p=1,\dots,N-L$. So, one can find an extremum of A by differentiating it with respect to each of the ξ_p and setting each derivative to zero:

$$\left.\frac{\partial A}{\partial \xi_p}\right|_{\xi_j,T,V} = \overline{R}T \sum_{i=1}^{N}\left(\left.\frac{\partial n_i}{\partial \xi_p}\right|_{\xi_j}\left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T}-1\right) + \left.\frac{\partial n_i}{\partial \xi_p}\right|_{\xi_j}\ln\left(\frac{n_i}{n^o}\right) + n_i\frac{\partial}{\partial \xi_p}\ln\left(\frac{n_i}{n^o}\right)\right) = 0,$$
$$p=1,\dots,N-L, \quad (5.178)$$

$$= \overline{R}T \sum_{i=1}^{N}\left(\left.\frac{\partial n_i}{\partial \xi_p}\right|_{\xi_j}\left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T}-1\right) + \left.\frac{\partial n_i}{\partial \xi_p}\right|_{\xi_j}\ln\left(\frac{n_i}{n^o}\right) + n_i\sum_{q=1}^{N}\frac{\partial n_q}{\partial \xi_p}\frac{\partial}{\partial n_q}\ln\left(\frac{n_i}{n^o}\right)\right) = 0,$$
$$p=1,\dots,N-L, \quad (5.179)$$

$$= \overline{R}T \sum_{i=1}^{N}\left(\mathcal{D}_{ip}\left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T}-1\right) + \mathcal{D}_{ip}\ln\left(\frac{n_i}{n^o}\right) + n_i\sum_{q=1}^{N}\mathcal{D}_{qp}\frac{1}{n_i}\delta_{iq}\right) = 0,$$
$$p=1,\dots,N-L, \quad (5.180)$$

$$= \overline{R}T \sum_{i=1}^{N}\left(\mathcal{D}_{ip}\left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T}-1\right) + \mathcal{D}_{ip}\ln\left(\frac{n_i}{n^o}\right) + \mathcal{D}_{ip}\right) = 0,$$
$$p=1,\dots,N-L, \quad (5.181)$$

$$= \overline{R}T \sum_{i=1}^{N}\mathcal{D}_{ip}\left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} + \ln\left(\frac{n_i}{n^o}\right)\right) = 0, \quad p=1,\dots,N-L. \quad (5.182)$$

Following Zel'dovich, one then rearranges Eq. (5.182) to define the equations for equilibrium:

$$\sum_{i=1}^{N}\mathcal{D}_{ip}\ln\left(\frac{n_i}{n^o}\right) = -\sum_{i=1}^{N}\frac{\mathcal{D}_{ip}\overline{\mu}_{T,i}^o}{\overline{R}T}, \qquad p=1,\dots,N-L, \quad (5.183)$$

$$\sum_{i=1}^{N}\ln\left(\frac{n_i}{n^o}\right)^{\mathcal{D}_{ip}} = -\sum_{i=1}^{N}\frac{\mathcal{D}_{ip}\overline{\mu}_{T,i}^o}{\overline{R}T}, \qquad p=1,\dots,N-L, \quad (5.184)$$

$$\ln\prod_{i=1}^{N}\left(\frac{n_i}{n^o}\right)^{\mathcal{D}_{ip}} = -\sum_{i=1}^{N}\frac{\mathcal{D}_{ip}\overline{\mu}_{T,i}^o}{\overline{R}T}, \qquad p=1,\dots,N-L, \quad (5.185)$$

$$\ln\prod_{i=1}^{N}\left(\left(n_{io} + \sum_{k=1}^{N-L}\mathcal{D}_{ik}\xi_k\right)\frac{1}{n^o}\right)^{\mathcal{D}_{ip}} = -\sum_{i=1}^{N}\frac{\mathcal{D}_{ip}\overline{\mu}_{T,i}^o}{\overline{R}T}, \qquad p=1,\dots,N-L. \quad (5.186)$$

Equation (5.186) forms $N - L$ equations in the $N - L$ unknown values of ξ_p and can be solved by Newton iteration. Note that as of yet, no proof exists that this is a unique solution. Nor is it certain whether or not A is maximized or minimized at such a solution point.

One also notices that the method of Zel'dovich is consistent with a more rudimentary form. Rearrange Eq. (5.182) to get

$$\left. \frac{\partial A}{\partial \xi_p} \right|_{\xi_j, T, V} = \sum_{i=1}^{N} \mathcal{D}_{ip} \left(\overline{\mu}_{T,i}^{o} + \overline{R}T \ln \left(\frac{n_i}{n^o} \right) \right) = 0, \quad p = 1, \dots, N - L, \qquad (5.187)$$

$$= \sum_{i=1}^{N} \mathcal{D}_{ip} \left(\overline{\mu}_{T,i}^{o} + \overline{R}T \ln \left(\frac{n_i P}{n P_o} \right) \right), \qquad (5.188)$$

$$= \sum_{i=1}^{N} \mathcal{D}_{ip} \left(\overline{\mu}_{T,i}^{o} + \overline{R}T \ln \left(\frac{P_i}{P_o} \right) \right), \qquad (5.189)$$

$$= \sum_{i=1}^{N} \overline{\mu}_i \mathcal{D}_{ip}. \qquad (5.190)$$

Now, Eq. (5.190) is easily found via another method. Recall Eq. (3.239), and then operate on it in an isochoric, isothermal limit, taking derivative with respect to ξ_p, $p = 1, \dots, N - L$:

$$dA = -S dT - P dV + \sum_{i=1}^{N} \overline{\mu}_i dn_i, \qquad (5.191)$$

$$dA|_{T,V} = \sum_{i=1}^{N} \overline{\mu}_i dn_i, \qquad (5.192)$$

$$\left. \frac{\partial A}{\partial \xi_p} \right|_{\xi_j, T, V} = \sum_{i=1}^{N} \overline{\mu}_i \frac{\partial n_i}{\partial \xi_p}, \qquad (5.193)$$

$$= \sum_{i=1}^{N} \overline{\mu}_i \mathcal{D}_{ip}. \qquad (5.194)$$

One can determine whether such a solution, if it exists, is a maxima or minima by examining the second derivative, given by differentiating Eq. (5.182). We find the Hessian[9], **H**, to be

$$\mathbf{H} = \frac{\partial^2 A}{\partial \xi_j \partial \xi_p} = \overline{R}T \sum_{i=1}^{N} \mathcal{D}_{ip} \frac{\partial}{\partial \xi_j} \ln \left(\frac{n_i}{n^o} \right), \qquad (5.195)$$

$$= \overline{R}T \sum_{i=1}^{N} \mathcal{D}_{ip} \left(\frac{\partial}{\partial \xi_j} \ln n_i - \frac{\partial}{\partial \xi_j} \ln n^o \right), \qquad (5.196)$$

---

[9]after Ludwig Otto Hesse, 1811-1874, German mathematician.

$$= \overline{R}T \sum_{i=1}^{N} \mathcal{D}_{ip} \frac{1}{n_i} \frac{\partial n_i}{\partial \xi_j}, \tag{5.197}$$

$$= \overline{R}T \sum_{i=1}^{N} \frac{\mathcal{D}_{ip}\mathcal{D}_{ij}}{n_i}. \tag{5.198}$$

Here, $j = 1, \ldots, N - L$. Scaling each of the rows of $\mathcal{D}_{ip}$ by a constant does not affect the rank. So, we can say that the $N \times (N - L)$ matrix whose entries are $\mathcal{D}_{ip}/\sqrt{n_i}$ has rank $N - L$, and consequently the Hessian $\mathbf{H}$, of dimension $(N - L) \times (N - L)$, has full rank $N - L$, and is symmetric. It is easy to show by means of singular value decomposition, or other methods, that the eigenvalues of a full rank symmetric square matrix are all real and non-zero.

Now, consider whether $\partial^2 A / \partial \xi_j \partial \xi_p$ is positive definite. By definition, it is positive definite if for an arbitrary vector z_i of length $N - L$ with non-zero norm that the term Υ_{TV}, defined below, be always positive:

$$\Upsilon_{TV} = \sum_{j=1}^{N-L} \sum_{p=1}^{N-L} \frac{\partial^2 A}{\partial \xi_j \partial \xi_p} z_j z_p > 0. \tag{5.199}$$

Substitute Eq. (5.198) into Eq. (5.199) to find

$$\Upsilon_{TV} = \sum_{j=1}^{N-L} \sum_{p=1}^{N-L} \overline{R}T \sum_{i=1}^{N} \frac{\mathcal{D}_{ip}\mathcal{D}_{ij}}{n_i} z_j z_p, \tag{5.200}$$

$$= \overline{R}T \sum_{i=1}^{N} \frac{1}{n_i} \sum_{j=1}^{N-L} \sum_{p=1}^{N-L} \mathcal{D}_{ip}\mathcal{D}_{ij} z_j z_p, \tag{5.201}$$

$$= \overline{R}T \sum_{i=1}^{N} \frac{1}{n_i} \sum_{j=1}^{N-L} \mathcal{D}_{ij} z_j \sum_{p=1}^{N-L} \mathcal{D}_{ip} z_p, \tag{5.202}$$

$$= \overline{R}T \sum_{i=1}^{N} \frac{1}{n_i} \left(\sum_{j=1}^{N-L} \mathcal{D}_{ij} z_j \right) \left(\sum_{p=1}^{N-L} \mathcal{D}_{ip} z_p \right). \tag{5.203}$$

Define now

$$y_i \equiv \sum_{j=1}^{N-L} \mathcal{D}_{ij} z_j, \qquad i = 1, \ldots, N. \tag{5.204}$$

This yields

$$\Upsilon_{TV} = \overline{R}T \sum_{i=1}^{N} \frac{y_i^2}{n_i}. \tag{5.205}$$

Now, to restrict the domain to physically accessible space, one is only concerned with $n_i \geq 0$, $T > 0$, so for arbitrary y_i, one finds $\Upsilon_{TV} > 0$, so one concludes that the second mixed partial of A is positive definite *globally*.

We next consider the behavior of A near a generic point in the physical space $\hat{\boldsymbol{\xi}}$ where $A = \hat{A}$. If we let $d\boldsymbol{\xi}$ represent $\boldsymbol{\xi} - \hat{\boldsymbol{\xi}}$, we can represent the Helmholtz free energy by the Taylor series

$$A(\boldsymbol{\xi}) = \hat{A} + d\boldsymbol{\xi}^T \cdot \nabla A + \frac{1}{2}d\boldsymbol{\xi}^T \cdot \mathbf{H} \cdot d\boldsymbol{\xi} + \dots, \tag{5.206}$$

where ∇A and $\mathbf{H}$ are evaluated at $\hat{\boldsymbol{\xi}}$. Now, if $\hat{\boldsymbol{\xi}} = \boldsymbol{\xi}^{\mathrm{eq}}$, where eq denotes an equilibrium point, $\nabla A = 0$, $\hat{A} = A^{\mathrm{eq}}$, and

$$A(\boldsymbol{\xi}) - A^{\mathrm{eq}} = \frac{1}{2}d\boldsymbol{\xi}^T \cdot \mathbf{H} \cdot d\boldsymbol{\xi} + \dots. \tag{5.207}$$

Because $\mathbf{H}$ is positive definite in the entire physical domain, any isolated critical point will be a minimum. Note that if more than one isolated minimum point of A were to exist in the domain interior, a maximum would also have to exist in the interior, but maxima are not allowed by the global positive definite nature of $\mathbf{H}$. Subsequently, any extremum which exists away from the boundary of the physical region must be a minimum, and the minimum is global.

Global positive definiteness of $\mathbf{H}$ alone does not rule out the possibility of non-isolated multiple equilibria, as seen by the following analysis. Because it is symmetric, $\mathbf{H}$ can be orthogonally decomposed into $\mathbf{H} = \mathbf{Q}^T \cdot \boldsymbol{\Lambda} \cdot \mathbf{Q}$, where $\mathbf{Q}$ is an orthogonal matrix whose columns are the normalized eigenvectors of $\mathbf{H}$. Note that $\mathbf{Q}^T = \mathbf{Q}^{-1}$. Also $\boldsymbol{\Lambda}$ is a diagonal matrix with real eigenvalues on its diagonal. We can effect a volume-preserving rotation of axes by taking the transformation $d\mathbf{w} = \mathbf{Q} \cdot d\boldsymbol{\xi}$; thus, $d\boldsymbol{\xi} = \mathbf{Q}^T \cdot d\mathbf{w}$. Hence,

$$A - A^{\mathrm{eq}} = \frac{1}{2}(\mathbf{Q}^T \cdot d\mathbf{w})^T \cdot \mathbf{H} \cdot \mathbf{Q}^T \cdot d\mathbf{w} = \frac{1}{2}d\mathbf{w}^T \cdot \mathbf{Q} \cdot \mathbf{Q}^T \cdot \boldsymbol{\Lambda} \cdot \mathbf{Q} \cdot \mathbf{Q}^T \cdot d\mathbf{w} = \frac{1}{2}d\mathbf{w}^T \cdot \boldsymbol{\Lambda} \cdot d\mathbf{w}. \tag{5.208}$$

The application of these transformations gives in the neighborhood of equilibrium the quadratic form

$$A - A^{\mathrm{eq}} = \frac{1}{2}\sum_{p=1}^{N-L} \lambda_p (dw_p)^2. \tag{5.209}$$

For A to be a unique minimum, $\lambda_p > 0$. If one or more of the $\lambda_p = 0$, then the minimum could be realized on a line or higher dimensional plane, depending on how many zeros are present. The full rank of $\mathbf{H}$ guarantees that $\lambda_p > 0$. For our problem the unique global minimum which exists in the interior will exist at a unique point.

Lastly, one must check the boundary of the physical region to see if it can form an extremum. Near a physical boundary given by $n_q = 0$, one finds that A behaves as

$$\lim_{n_q \to 0} A \quad \sim \quad \overline{R}T\sum_{i=1}^{N} n_i \left(\frac{\overline{\mu}_{T,i}}{\overline{R}T} - 1 + \ln\left(\frac{n_i}{n^o}\right)\right) \to \text{finite}. \tag{5.210}$$

The behavior of A itself is finite because $\lim_{n_q \to 0} n_q \ln n_q = 0$, and the remaining terms in the summation are non-zero and finite.

The analysis of the behavior of the derivative of A on a boundary of $n_q = 0$ is more complex. We require that $n_q \geq 0$ for all N species. The hyperplanes given by $n_q = 0$ define a closed physical boundary in reduced composition space. We require that changes in n_q which originate from the surface $n_q = 0$ be positive. For such curves we thus require that near $n_q = 0$, perturbations $d\xi_k$ be such that

$$dn_q = \sum_{k=1}^{N-L} \mathcal{D}_{qk} d\xi_k > 0. \tag{5.211}$$

We next examine changes in A in the vicinity of boundaries given by $n_q = 0$. We will restrict our attention to changes which give rise to $dn_q > 0$. We employ Eq. (5.187) and find that

$$dA = \sum_{p=1}^{N-L} d\xi_p \left. \frac{\partial A}{\partial \xi_p} \right|_{T,V,\xi_{j \neq p}} = \sum_{i=1}^{N} \left(\overline{\mu}_i^o + \overline{R}T \ln \left(\frac{n_i}{n^o} \right) \right) \sum_{p=1}^{N-L} \mathcal{D}_{ip} d\xi_p. \tag{5.212}$$

On the boundary given by $n_q = 0$, the dominant term in the sum is for $i = q$, and so on this boundary

$$\lim_{n_q \to 0} dA = \overline{R}T \ln \left(\frac{n_q}{n^o} \right) \underbrace{\sum_{p=1}^{N-L} \mathcal{D}_{qp} d\xi_p}_{>0} \to -\infty. \tag{5.213}$$

The term identified by the brace is positive because of Eq. (5.211). Because $\overline{R}$ and $T > 0$, we see that as n_q moves away from zero into the physical region, changes in A are large and negative. So, the physical boundary can be a local maximum, but never a local minimum in A. Hence, the only admissible equilibrium is the unique minimum of A found from Eq. (5.186); this equilibrium is found at a unique point in reduced composition space.

5.2.3.2 Isothermal, isobaric case

Next, consider the related case in which T and P are constant. For such a system, the canonical equilibration relation is given by Eq. (3.357) holds that $dG|_{T,P} \leq 0$. So, G must be decreasing until it reaches a minimum. So, consider G, which from Eq. (3.359) is

$$G = \sum_{i=1}^{N} n_i \overline{\mu}_i, \tag{5.214}$$

$$= \sum_{i=1}^{N} n_i \left(\overline{\mu}_{T,i}^o + \overline{R}T \ln \left(\frac{P_i}{P_o} \right) \right), \tag{5.215}$$

$$= \sum_{i=1}^{N} n_i \left(\overline{\mu}_{T,i}^o + \overline{R}T \ln \left(\frac{n_i P}{n P_o} \right) \right), \tag{5.216}$$

$$= \overline{R}T \sum_{i=1}^{N} \left(n_i \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} + \ln\left(\frac{P}{P_o}\right) \right) + n_i \ln\left(\frac{n_i}{\sum_{k=1}^{N} n_k} \right) \right). \tag{5.217}$$

Next, differentiate with respect to each of the independent variables ξ_p for $p = 1, \ldots, N - L$:

$$\frac{\partial G}{\partial \xi_p} = \overline{R}T \sum_{i=1}^{N} \left(\frac{\partial n_i}{\partial \xi_p} \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} + \ln\left(\frac{P}{P_o}\right) \right) + \frac{\partial}{\partial \xi_p} \left(n_i \ln\left(\frac{n_i}{\sum_{k=1}^{N} n_k} \right) \right) \right), \tag{5.218}$$

$$= \overline{R}T \sum_{i=1}^{N} \left(\frac{\partial n_i}{\partial \xi_p} \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} + \ln\left(\frac{P}{P_o}\right) \right) \right.$$
$$\left. + \sum_{q=1}^{N} \frac{\partial n_q}{\partial \xi_p} \frac{\partial}{\partial n_q} \left(n_i \ln\left(\frac{n_i}{\sum_{k=1}^{N} n_k} \right) \right) \right), \tag{5.219}$$

$$= \overline{R}T \sum_{i=1}^{N} \left(\mathcal{D}_{ip} \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} + \ln\left(\frac{P}{P_o}\right) \right) \right.$$
$$\left. + \sum_{q=1}^{N} \mathcal{D}_{qp} \left(-\frac{n_i}{\sum_{k=1}^{N} n_k} + \delta_{iq} \left(1 + \ln\left(\frac{n_i}{\sum_{k=1}^{N} n_k} \right) \right) \right) \right), \tag{5.220}$$

$$= \overline{R}T \sum_{i=1}^{N} \left(\mathcal{D}_{ip} \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} + \ln\left(\frac{P}{P_o}\right) + 1 + \ln\left(\frac{n_i}{n}\right) \right) - \frac{n_i}{n} \sum_{q=1}^{N} \mathcal{D}_{qp} \right), \tag{5.221}$$

$$= \overline{R}T \sum_{i=1}^{N} \left(\mathcal{D}_{ip} \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} + \ln\left(\frac{P}{P_o}\right) + 1 + \ln\left(\frac{n_i}{n}\right) \right) \right)$$
$$- \overline{R}T \sum_{i=1}^{N} \frac{n_i}{n} \sum_{q=1}^{N} \mathcal{D}_{qp}, \tag{5.222}$$

$$= \overline{R}T \sum_{i=1}^{N} \left(\mathcal{D}_{ip} \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} + \ln\left(\frac{P}{P_o}\right) + 1 + \ln\left(\frac{n_i}{n}\right) \right) \right)$$
$$- \overline{R}T \sum_{q=1}^{N} \mathcal{D}_{qp} \sum_{i=1}^{N} \frac{n_i}{n}, \tag{5.223}$$

$$= \overline{R}T \sum_{i=1}^{N} \left(\mathcal{D}_{ip} \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} + \ln\left(\frac{P}{P_o}\right) + 1 + \ln\left(\frac{n_i}{n}\right) \right) \right) - \overline{R}T \sum_{q=1}^{N} \mathcal{D}_{qp}, \tag{5.224}$$

$$= \overline{R}T \sum_{i=1}^{N} \left(\mathcal{D}_{ip} \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} + \ln\left(\frac{P}{P_o}\right) + 1 + \ln\left(\frac{n_i}{n}\right) \right) \right) - \overline{R}T \sum_{i=1}^{N} \mathcal{D}_{ip}, \tag{5.225}$$

$$= \overline{R}T \sum_{i=1}^{N} \left(\mathcal{D}_{ip} \left(\frac{\overline{\mu}_{T,i}^o}{\overline{R}T} + \ln\left(\frac{P}{P_o}\right) + \ln\left(\frac{n_i}{n}\right) \right) \right), \tag{5.226}$$

$$= \sum_{i=1}^{N} \mathcal{D}_{ip} \left(\overline{\mu}_{T,i}^{o} + \overline{R}T \ln \left(\frac{n_i P}{n P_o} \right) \right), \tag{5.227}$$

$$= \sum_{i=1}^{N} \mathcal{D}_{ip} \left(\overline{\mu}_{T,i}^{o} + \overline{R}T \ln \left(\frac{n_i P}{n P_o} \right) \right), \tag{5.228}$$

$$= \sum_{i=1}^{N} \overline{\mu}_i \mathcal{D}_{ip}, \qquad p = 1, \ldots, N - L. \tag{5.229}$$

Note this simple result is entirely consistent with a result that could have been deduced by commencing with the alternative Eq. (3.361), $dG|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i dn_i$. Had this simplification been taken, one could readily deduce that

$$\left. \frac{\partial G}{\partial \xi_p} \right|_{\xi_j} = \sum_{i=1}^{N} \overline{\mu}_i \frac{\partial n_i}{\partial \xi_p}, \qquad p = 1, \ldots N - L, \tag{5.230}$$

$$= \sum_{i=1}^{N} \overline{\mu}_i \mathcal{D}_{ip}, \qquad p = 1, \ldots N - L. \tag{5.231}$$

Now, to equilibrate, one sets the derivatives to zero to get

$$\sum_{i=1}^{N} \mathcal{D}_{ip} \left(\overline{\mu}_{T,i}^{o} + \overline{R}T \ln \left(\frac{n_i P}{n P_o} \right) \right) = 0, \quad p = 1, \ldots, N - L, \tag{5.232}$$

$$\sum_{i=1}^{N} \ln \left(\frac{n_i P}{n P_o} \right)^{\mathcal{D}_{ip}} = -\sum_{i=1}^{N} \mathcal{D}_{ip} \frac{\overline{\mu}_{T,i}^{o}}{\overline{R}T}, \tag{5.233}$$

$$\ln \prod_{i=1}^{N} \left(\frac{n_i P}{n P_o} \right)^{\mathcal{D}_{ip}} = -\sum_{i=1}^{N} \mathcal{D}_{ip} \frac{\overline{\mu}_{T,i}^{o}}{\overline{R}T}, \tag{5.234}$$

$$\ln \prod_{i=1}^{N} \left(\frac{\left(n_{io} + \sum_{k=1}^{N-L} \mathcal{D}_{ik} \xi_k \right) P}{\left(\sum_{q=1}^{N} \left(n_{qo} + \sum_{k=1}^{N-L} \mathcal{D}_{qk} \xi_k \right) \right) P_o} \right)^{\mathcal{D}_{ip}} = -\sum_{i=1}^{N} \mathcal{D}_{ip} \frac{\overline{\mu}_{T,i}^{o}}{\overline{R}T},$$
$$p = 1, \ldots, N - L. \tag{5.235}$$

These $N - L$ non-linear algebraic equations can be solved for the $N - L$ unknown values of ξ_p via an iterative technique. One can extend the earlier analysis to show that the equilibrium is unique in the physically accessible region of composition space.

We can repeat our previous analysis to show that this equilibrium is unique in the physically accessible region of composition space. By differentiating Eq. (5.231) it is seen that

$$\frac{\partial^2 G}{\partial \xi_j \partial \xi_p} = \overline{R}T \sum_{i=1}^{N} \mathcal{D}_{ip} \frac{\partial}{\partial \xi_j} \ln \left(\frac{n_i}{n} \right), \tag{5.236}$$

$$= \overline{R}T \left(\sum_{i=1}^{N} \mathcal{D}_{ip} \frac{\partial}{\partial \xi_j} \ln n_i - \sum_{i=1}^{N} \mathcal{D}_{ip} \frac{\partial}{\partial \xi_j} \ln n \right), \tag{5.237}$$

$$= \overline{R}T \left(\sum_{i=1}^{N} \mathcal{D}_{ip} \frac{1}{n_i} \frac{\partial n_i}{\partial \xi_j} - \sum_{i=1}^{N} \mathcal{D}_{ip} \frac{1}{n} \frac{\partial n}{\partial \xi_j} \right), \tag{5.238}$$

$$= \overline{R}T \left(\sum_{i=1}^{N} \mathcal{D}_{ip} \frac{1}{n_i} \frac{\partial n_i}{\partial \xi_j} - \sum_{i=1}^{N} \mathcal{D}_{ip} \frac{1}{n} \frac{\partial}{\partial \xi_j} \left(\sum_{q=1}^{N} n_q \right) \right), \tag{5.239}$$

$$= \overline{R}T \left(\sum_{i=1}^{N} \mathcal{D}_{ip} \frac{1}{n_i} \frac{\partial n_i}{\partial \xi_j} - \sum_{i=1}^{N} \left(\sum_{q=1}^{N} \mathcal{D}_{ip} \frac{1}{n} \frac{\partial n_q}{\partial \xi_j} \right) \right), \tag{5.240}$$

$$= \overline{R}T \left(\sum_{i=1}^{N} \frac{\mathcal{D}_{ip} \mathcal{D}_{ij}}{n_i} - \frac{1}{n} \sum_{i=1}^{N} \sum_{q=1}^{N} \mathcal{D}_{ip} \mathcal{D}_{qj} \right). \tag{5.241}$$

Next consider the sum

$$\Upsilon_{TP} = \sum_{j=1}^{N-L} \sum_{p=1}^{N-L} \frac{\partial^2 G}{\partial \xi_j \partial \xi_p} z_j z_p = \overline{R}T \sum_{j=1}^{N-L} \sum_{p=1}^{N-L} \left(\sum_{i=1}^{N} \frac{\mathcal{D}_{ip} \mathcal{D}_{ij}}{n_i} - \frac{1}{n} \sum_{i=1}^{N} \sum_{q=1}^{N} \mathcal{D}_{ip} \mathcal{D}_{qj} \right) z_j z_p. \tag{5.242}$$

We use Eq. (5.204) and following a long series of calculations, reduce Eq. (5.242), to the positive definite form

$$\Upsilon_{TP} = \frac{\overline{R}T}{n} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left(\sqrt{\frac{n_j}{n_i}} y_i - \sqrt{\frac{n_i}{n_j}} y_j \right)^2 > 0. \tag{5.243}$$

It is easily verified by direct expansion that Eqs. (5.242) and (5.243) are equivalent.

On the boundary $n_i = 0$, and as for the isothermal-isochoric case, it can be shown that $dG \rightarrow -\infty$ for changes with $dn_i > 0$. Thus, the boundary has no local minimum, and we can conclude that G is minimized in the interior and the minimum is unique.

5.2.3.3   Adiabatic, isochoric case

One can extend Zel'dovich's proof to other sets of conditions. For example, consider a case which is isochoric and isoenergetic. This corresponds to a chemical reaction in an fixed volume which is thermally insulated. In this case, one operates on Eq. (3.357):

$$\underbrace{dE}_{=0} = -P \underbrace{dV}_{=0} + TdS + \sum_{i=1}^{N} \overline{\mu}_i dn_i, \tag{5.244}$$

$$0 = TdS + \sum_{i=1}^{N} \overline{\mu}_i dn_i, \tag{5.245}$$

$$dS \;=\; -\frac{1}{T}\sum_{i=1}^{N}\overline{\mu}_i \, dn_i, \tag{5.246}$$

$$=\; -\frac{1}{T}\sum_{i=1}^{N}\overline{\mu}_i\sum_{k=1}^{N-L}\mathcal{D}_{ik}\,d\xi_k, \tag{5.247}$$

$$=\; -\frac{1}{T}\sum_{i=1}^{N}\sum_{k=1}^{N-L}\overline{\mu}_i\mathcal{D}_{ik}\,d\xi_k, \tag{5.248}$$

$$\frac{\partial S}{\partial \xi_j}\;=\; -\frac{1}{T}\sum_{i=1}^{N}\sum_{k=1}^{N-L}\overline{\mu}_i\mathcal{D}_{ik}\frac{\partial \xi_k}{\partial \xi_j}, \tag{5.249}$$

$$=\; -\frac{1}{T}\sum_{i=1}^{N}\sum_{k=1}^{N-L}\overline{\mu}_i\mathcal{D}_{ik}\delta_{kj}, \tag{5.250}$$

$$=\; -\frac{1}{T}\sum_{i=1}^{N}\overline{\mu}_i\mathcal{D}_{ij}, \tag{5.251}$$

$$=\; -\frac{1}{T}\sum_{i=1}^{N}\left(\overline{\mu}_{T,i}^{o}+\overline{R}T\ln\left(\frac{P_i}{P_o}\right)\right)\mathcal{D}_{ij}, \tag{5.252}$$

$$=\; -\frac{1}{T}\sum_{i=1}^{N}\left(\overline{\mu}_{T,i}^{o}+\overline{R}T\ln\left(\frac{n_i P}{n P_o}\right)\right)\mathcal{D}_{ij}, \tag{5.253}$$

$$=\; -\frac{1}{T}\sum_{i=1}^{N}\left(\overline{\mu}_{T,i}^{o}+\overline{R}T\ln\left(\frac{n_i\overline{R}TT_o}{P_o V T_o}\right)\right)\mathcal{D}_{ij}, \tag{5.254}$$

$$=\; -\frac{1}{T}\sum_{i=1}^{N}\left(\overline{\mu}_{T,i}^{o}+\overline{R}T\ln\left(\frac{T}{T_o}\right)+\overline{R}T\ln\left(\frac{n_i\overline{R}T_o}{P_o V}\right)\right)\mathcal{D}_{ij}, \tag{5.255}$$

$$=\; -\sum_{i=1}^{N}\left(\underbrace{\frac{\overline{\mu}_{T,i}^{o}}{T}+\overline{R}\ln\left(\frac{T}{T_o}\right)}_{\equiv\psi_i(T)}+\overline{R}\ln\left(\frac{n_i\overline{R}T_o}{P_o V}\right)\right)\mathcal{D}_{ij}, \tag{5.256}$$

$$=\; -\sum_{i=1}^{N}\left(\psi_i(T)+\overline{R}\ln\left(\frac{n_i\overline{R}T_o}{P_o V}\right)\right)\mathcal{D}_{ij}, \tag{5.257}$$

$$\frac{\partial^2 S}{\partial \xi_k \partial \xi_j}\;=\; -\sum_{i=1}^{N}\left(\frac{\partial \psi_i(T)}{\partial T}\frac{\partial T}{\partial \xi_k}+\frac{\overline{R}}{n_i}\frac{\partial n_i}{\partial \xi_k}\right)\mathcal{D}_{ij}, \tag{5.258}$$

$$=\; -\sum_{i=1}^{N}\left(\frac{\partial \psi_i(T)}{\partial T}\frac{\partial T}{\partial \xi_k}+\frac{\overline{R}}{n_i}\mathcal{D}_{ik}\right)\mathcal{D}_{ij}. \tag{5.259}$$

Now, consider dT for the adiabatic system.

$$E = E_o \;=\; \sum_{q=1}^{N} n_q \overline{e}_q(T), \tag{5.260}$$

$$dE = 0 \;=\; \sum_{q=1}^{N} \left(n_q \underbrace{\frac{\partial \overline{e}_q}{\partial T}}_{=\overline{c}_{vq}} dT + \overline{e}_q dn_q \right), \tag{5.261}$$

$$0 \;=\; \sum_{q=1}^{N} \left(n_q \overline{c}_{vq} dT + \overline{e}_q dn_q \right), \tag{5.262}$$

$$dT \;=\; -\frac{\sum_{q=1}^{N} \overline{e}_q dn_q}{\sum_{q=1}^{N} n_q \overline{c}_{vq}}, \tag{5.263}$$

$$\;=\; -\frac{1}{n\overline{c}_v} \sum_{q=1}^{N} \overline{e}_q \sum_{p=1}^{N-L} \mathcal{D}_{qp} d\xi_p, \tag{5.264}$$

$$\;=\; -\frac{1}{n\overline{c}_v} \sum_{q=1}^{N} \sum_{p=1}^{N-L} \overline{e}_q \mathcal{D}_{qp} d\xi_p, \tag{5.265}$$

$$\frac{\partial T}{\partial \xi_k} \;=\; -\frac{1}{n\overline{c}_v} \sum_{q=1}^{N} \sum_{p=1}^{N-L} \overline{e}_q \mathcal{D}_{qp} \frac{\partial \xi_p}{\partial \xi_k}, \tag{5.266}$$

$$\;=\; -\frac{1}{n\overline{c}_v} \sum_{q=1}^{N} \sum_{p=1}^{N-L} \overline{e}_q \mathcal{D}_{qp} \delta_{pk}, \tag{5.267}$$

$$\;=\; -\frac{1}{n\overline{c}_v} \sum_{q=1}^{N} \overline{e}_q \mathcal{D}_{qk}. \tag{5.268}$$

Now, return to Eq. (5.259), using Eq. (5.268) to expand:

$$\frac{\partial^2 S}{\partial \xi_k \partial \xi_j} \;=\; \sum_{i=1}^{N} \left(\frac{\partial \psi_i(T)}{\partial T} \frac{1}{n\overline{c}_v} \sum_{q=1}^{N} \overline{e}_q \mathcal{D}_{qk} - \frac{\overline{R}}{n_i} \mathcal{D}_{ik} \right) \mathcal{D}_{ij}, \tag{5.269}$$

$$\;=\; \sum_{i=1}^{N} \frac{\partial \psi_i(T)}{\partial T} \frac{1}{n\overline{c}_v} \sum_{q=1}^{N} \overline{e}_q \mathcal{D}_{qk} \mathcal{D}_{ij} - \sum_{i=1}^{N} \frac{\overline{R}}{n_i} \mathcal{D}_{ik} \mathcal{D}_{ij}, \tag{5.270}$$

$$\;=\; \frac{1}{n\overline{c}_v} \sum_{i=1}^{N} \sum_{q=1}^{N} \frac{\partial \psi_i(T)}{\partial T} \overline{e}_q \mathcal{D}_{qk} \mathcal{D}_{ij} - \overline{R} \sum_{i=1}^{N} \frac{\mathcal{D}_{ik} \mathcal{D}_{ij}}{n_i}. \tag{5.271}$$

Now, consider the temperature derivative of $\psi_i(T)$, where $\psi_i(T)$ is defined in Eq. (5.256):

$$\psi_i \;\equiv\; \frac{\overline{\mu}_{T,i}^o}{T} + \overline{R} \ln \left(\frac{T}{T_o} \right), \tag{5.272}$$

$$\frac{d\psi_i}{dT} = -\frac{\overline{\mu}^o_{T,i}}{T^2} + \frac{1}{T}\frac{d\overline{\mu}^o_{T,i}}{dT} + \frac{\overline{R}}{T}. \tag{5.273}$$

Now

$$\overline{\mu}^o_{T,i} = \overline{h}^o_{T,i} - T\overline{s}^o_{T,i}, \tag{5.274}$$

$$= \underbrace{\overline{h}^o_{T_o,i} + \int_{T_o}^{T}\overline{c}_{Pi}(\hat{T})d\hat{T}}_{=\overline{h}^o_{T,i}} - T\underbrace{\left(\overline{s}^o_{T_o,i} + \int_{T_o}^{T}\frac{\overline{c}_{Pi}(\hat{T})}{\hat{T}}d\hat{T}\right)}_{=\overline{s}^o_{T,i}}, \tag{5.275}$$

$$\frac{d\overline{\mu}^o_{T,i}}{dT} = \overline{c}_{Pi} - \overline{s}^o_{T_o,i} - \int_{T_o}^{T}\frac{\overline{c}_{Pi}(\hat{T})}{\hat{T}}d\hat{T} - \overline{c}_{Pi}, \tag{5.276}$$

$$= -\overline{s}^o_{T_o,i} - \int_{T_o}^{T}\frac{\overline{c}_{Pi}(\hat{T})}{\hat{T}}d\hat{T}, \tag{5.277}$$

$$= -\overline{s}^o_{T,i}. \tag{5.278}$$

Note that Eq. 5.278 is a special case of the Gibbs equation given by Eq. 3.252. With this, one finds that Eq. 5.273 reduces to

$$\frac{d\psi_i}{dT} = -\frac{\overline{\mu}^o_{T,i}}{T^2} - \frac{\overline{s}^o_{T,i}}{T} + \frac{\overline{R}}{T}, \tag{5.279}$$

$$= -\frac{1}{T^2}\left(\overline{\mu}^o_{T,i} + T\overline{s}^o_{T,i} - \overline{R}T\right), \tag{5.280}$$

$$= -\frac{1}{T^2}\left(\overline{g}^o_{T,i} + T\overline{s}^o_{T,i} - \overline{R}T\right), \tag{5.281}$$

$$= -\frac{1}{T^2}\left(\underbrace{\overline{h}^o_{T,i} - T\overline{s}^o_{T,i}}_{=\overline{g}^o_{T,i}} + T\overline{s}^o_{T,i} - \overline{R}T\right), \tag{5.282}$$

$$= -\frac{1}{T^2}\left(\overline{h}^o_{T,i} - \overline{R}T\right), \tag{5.283}$$

$$= -\frac{1}{T^2}\left(\overline{e}_i + P_i\overline{v}_i - \overline{R}T\right), \tag{5.284}$$

$$= -\frac{1}{T^2}\left(\overline{e}_i + \overline{R}T - \overline{R}T\right), \tag{5.285}$$

$$= -\frac{1}{T^2}\overline{e}_i. \tag{5.286}$$

So, substituting Eq. (5.286) into Eq. (5.271), one gets

$$\frac{\partial^2 S}{\partial\xi_k\partial\xi_j} = -\frac{1}{n\overline{c}_v T^2}\sum_{i=1}^{N}\sum_{q=1}^{N}\overline{e}_i\overline{e}_q\mathcal{D}_{qk}\mathcal{D}_{ij} - \overline{R}\sum_{i=1}^{N}\frac{\mathcal{D}_{ik}\mathcal{D}_{ij}}{n_i}. \tag{5.287}$$

Next, as before, consider the sum

$$
\begin{aligned}
\sum_{k=1}^{N-L}\sum_{j=1}^{N-L}\frac{\partial^2 S}{\partial\xi_k\partial\xi_j}z_k z_j &= -\frac{1}{n\overline{c}_v T^2}\sum_{k=1}^{N-L}\sum_{j=1}^{N-L}\sum_{i=1}^{N}\sum_{q=1}^{N}\overline{e}_i\overline{e}_q\mathcal{D}_{qk}\mathcal{D}_{ij}z_k z_j \\
&\quad -\overline{R}\sum_{k=1}^{N-L}\sum_{j=1}^{N-L}\sum_{i=1}^{N}\frac{\mathcal{D}_{ik}\mathcal{D}_{ij}}{n_i}z_k z_j, &(5.288)\\[4pt]
&= -\frac{1}{n\overline{c}_v T^2}\sum_{i=1}^{N}\sum_{q=1}^{N}\sum_{k=1}^{N-L}\sum_{j=1}^{N-L}\overline{e}_q\mathcal{D}_{qk}z_k\overline{e}_i\mathcal{D}_{ij}z_j \\
&\quad -\overline{R}\sum_{i=1}^{N}\sum_{k=1}^{N-L}\sum_{j=1}^{N-L}\frac{\mathcal{D}_{ik}z_k\mathcal{D}_{ij}z_j}{n_i}, &(5.289)\\[4pt]
&= -\frac{1}{n\overline{c}_v T^2}\sum_{i=1}^{N}\sum_{q=1}^{N}\left(\sum_{k=1}^{N-L}\overline{e}_q\mathcal{D}_{qk}z_k\right)\left(\sum_{j=1}^{N-L}\overline{e}_i\mathcal{D}_{ij}z_j\right) \\
&\quad -\overline{R}\sum_{i=1}^{N}\frac{1}{n_i}\left(\sum_{k=1}^{N-L}\mathcal{D}_{ik}z_k\right)\left(\sum_{j=1}^{N-L}\mathcal{D}_{ij}z_j\right), &(5.290)\\[4pt]
&= -\frac{1}{n\overline{c}_v T^2}\left(\sum_{i=1}^{N}\sum_{j=1}^{N-L}\overline{e}_i\mathcal{D}_{ij}z_j\right)\left(\sum_{q=1}^{N}\sum_{k=1}^{N-L}\overline{e}_q\mathcal{D}_{qk}z_k\right) \\
&\quad -\overline{R}\sum_{i=1}^{N}\frac{1}{n_i}\left(\sum_{k=1}^{N-L}\mathcal{D}_{ik}z_k\right)\left(\sum_{j=1}^{N-L}\mathcal{D}_{ij}z_j\right), &(5.291)\\[4pt]
&= -\frac{1}{n\overline{c}_v T^2}\left(\sum_{i=1}^{N}\sum_{j=1}^{N-L}\overline{e}_i\mathcal{D}_{ij}z_j\right)^2 -\overline{R}\sum_{i=1}^{N}\frac{1}{n_i}\left(\sum_{k=1}^{N-L}\mathcal{D}_{ik}z_k\right)^2 &(5.292)\\[4pt]
&= -\frac{1}{n\overline{c}_v T^2}\left(\sum_{i=1}^{N}\overline{e}_i y_i\right)^2 -\overline{R}\sum_{i=1}^{N}\frac{y_i^2}{n_i}. &(5.293)
\end{aligned}
$$

Since $\overline{c}_v > 0$, $T > 0$, $\overline{R} > 0$, $n_i > 0$, and the other terms are perfect squares, it is obvious that the second partial derivative of $S < 0$; consequently, critical points of S represent a maximum. Again near the boundary of the physical region, $S \sim -n_i \ln n_i$, so $\lim_{n_i \to 0} S \to 0$. From Eq. (5.268), there is no formal restriction on the slope at the boundary. However, if a critical point is to exist in the physical domain in which the second derivative is guaranteed negative, the slope at the boundary must be positive everywhere. This combines to guarantee that if a critical point exists in the physically accessible region of composition space, it is unique.

5.2.3.4 Adiabatic, isobaric case

A similar proof holds for the adiabatic-isobaric case. Here, the appropriate Legendre transformation is $H = E + PV$, where H is the enthalpy. We omit the details, which are similar to those of previous sections, and find a term which must be negative semi-definite, Υ_{HP}:

$$\Upsilon_{HP} = \sum_{k=1}^{N-L} \sum_{j=1}^{N-L} \frac{\partial^2 S}{\partial \xi_k \partial \xi_j} z_k z_j \tag{5.294}$$

$$= -\frac{1}{n\overline{c}_P T^2} \left(\sum_{i=1}^{N} \overline{h}_i y_i \right)^2 - \frac{\overline{R}}{n} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left(\sqrt{\frac{n_j}{n_i}} y_i - \sqrt{\frac{n_i}{n_j}} y_j \right)^2. \tag{5.295}$$

Because $\overline{c}_P > 0$ and $n_i \geq 0$, the term involving $\overline{h}_i y_i$ is a perfect square, and the term multiplying $\overline{R}$ is positive definite for the same reasons as discussed before. Hence, $\Upsilon_{HP} < 0$, and the Hessian matrix is negative definite.

5.3 Concise reaction rate law formulations

One can employ notions developed in the Zel'dovich uniqueness proof to obtain a more efficient representation of the reaction rate law for multiple reactions. There are two important cases: 1) $J \geq (N - L)$; this is most common for large chemical kinetic systems, and 2) $J < (N - L)$; this is common for simple chemistry models.

The species production rate is given by Eq. (5.15), which reduces to

$$\frac{d\overline{\rho}_i}{dt} = \frac{1}{V} \sum_{j=1}^{J} \nu_{ij} \frac{d\zeta_j}{dt}, \qquad i = 1, \ldots, N. \tag{5.296}$$

Now, differentiating Eq. (5.169), one obtains

$$dn_i = \sum_{k=1}^{N-L} \mathcal{D}_{ik} d\xi_k, \qquad i = 1, \ldots, N. \tag{5.297}$$

Comparing then Eq. (5.297) to Eq. (5.24), one sees that

$$\sum_{j=1}^{J} \nu_{ij} d\zeta_j = \sum_{k=1}^{N-L} \mathcal{D}_{ik} d\xi_k, \qquad i = 1, \ldots, N, \tag{5.298}$$

$$\frac{1}{V} \sum_{j=1}^{J} \nu_{ij} d\zeta_j = \frac{1}{V} \sum_{k=1}^{N-L} \mathcal{D}_{ik} d\xi_k, \qquad i = 1, \ldots, N, \tag{5.299}$$

$$\tag{5.300}$$

5.3.1   Reaction dominant: $J \geq (N - L)$

Consider first the most common case in which $J \geq (N - L)$. One can say the species production rate is given

$$\frac{d\overline{\rho}_i}{dt} = \frac{1}{V} \sum_{k=1}^{N-L} \mathcal{D}_{ik} \frac{d\xi_k}{dt} = \sum_{j=1}^{J} \nu_{ij} r_j, \qquad i = 1, \ldots, N. \tag{5.301}$$

One would like to invert and solve directly for $d\xi_k/dt$. However, $\mathcal{D}_{ik}$ is non-square and has no inverse. But since $\sum_{i=1}^{N} \phi_{li} \mathcal{D}_{ip} = 0$, and $\sum_{i=1}^{N} \phi_{li} \nu_{ij} = 0$, L of the equations N equations in Eq. (5.301) are redundant.

At this point, it is more convenient to go to a Gibbs vector notation, where there is an obvious correspondence between the bold vectors and the indicial counterparts:

$$\frac{d\overline{\boldsymbol{\rho}}}{dt} = \frac{1}{V} \mathbf{D} \cdot \frac{d\boldsymbol{\xi}}{dt} = \boldsymbol{\nu} \cdot \mathbf{r}, \tag{5.302}$$

$$\mathbf{D}^T \cdot \mathbf{D} \cdot \frac{d\boldsymbol{\xi}}{dt} = V \mathbf{D}^T \cdot \boldsymbol{\nu} \cdot \mathbf{r}, \tag{5.303}$$

$$\frac{d\boldsymbol{\xi}}{dt} = V (\mathbf{D}^T \cdot \mathbf{D})^{-1} \cdot \mathbf{D}^T \cdot \boldsymbol{\nu} \cdot \mathbf{r}. \tag{5.304}$$

Because of the L linear dependencies, there is no loss of information in this matrix projection. This system of $N - L$ equations is the smallest number of differential equations that can be solved for a general system in which $J > (N - L)$.

Lastly, one recovers the original system when forming

$$\mathbf{D} \cdot \frac{d\boldsymbol{\xi}}{dt} = V \underbrace{\mathbf{D} \cdot (\mathbf{D}^T \cdot \mathbf{D})^{-1} \cdot \mathbf{D}^T}_{=\mathbf{P}} \cdot \boldsymbol{\nu} \cdot \mathbf{r}. \tag{5.305}$$

Here, the $N \times N$ projection matrix $\mathbf{P}$ is symmetric, has norm of unity, has rank of $N - L$, has $N - L$ eigenvalues of value unity, and L eigenvalues of value zero. And, while application of a general projection matrix to $\boldsymbol{\nu} \cdot \mathbf{r}$ filters some of the information in $\boldsymbol{\nu} \cdot \mathbf{r}$, because the $N \times (N - L)$ matrix $\mathbf{D}$ spans the same column space as the $N \times J$ matrix $\boldsymbol{\nu}$, no information is lost in Eq. (5.305) relative to the original Eq. (5.302). Mathematically, one can say

$$\mathbf{P} \cdot \boldsymbol{\nu} = \boldsymbol{\nu}. \tag{5.306}$$

5.3.2   Species dominant: $J < (N - L)$

Next consider the case in which $J < (N-L)$. This often arises in models of simple chemistry, for example one- or two-step kinetics.

The fundamental reaction dynamics are most concisely governed by the J equations which form

$$\frac{1}{V} \frac{d\boldsymbol{\zeta}}{dt} = \mathbf{r}. \tag{5.307}$$

However, $\mathbf{r}$ is a function of the concentrations; one must therefore recover $\boldsymbol{\rho}$ as a function of reaction progress $\boldsymbol{\zeta}$. In vector form, Eq. (5.296) is written as

$$\frac{d\overline{\boldsymbol{\rho}}}{dt} = \frac{1}{V}\boldsymbol{\nu} \cdot \frac{d\boldsymbol{\zeta}}{dt}. \qquad (5.308)$$

Take as an initial condition that the reaction progress is zero at $t = 0$ and that there are an appropriate set of initial conditions on the species concentrations $\overline{\boldsymbol{\rho}}$:

$$\boldsymbol{\zeta} = \mathbf{0}, \qquad t = 0, \qquad (5.309)$$
$$\overline{\boldsymbol{\rho}} = \overline{\boldsymbol{\rho}}_o, \qquad t = 0. \qquad (5.310)$$

Then, since $\boldsymbol{\nu}$ is a constant, Eq. (5.308) is easily integrated. After applying the initial conditions, Eq. (5.310), one gets

$$\overline{\boldsymbol{\rho}} = \overline{\boldsymbol{\rho}}_o + \frac{1}{V}\boldsymbol{\nu} \cdot \boldsymbol{\zeta}. \qquad (5.311)$$

Last, if $J = (N - L)$, either approach yields the same number of equations, and is equally concise.

5.4 Irreversibility production

This section will consider the production of entropy due to irreversible chemical reactions. It is closely related to the Clausius-Duhem inequality discussed on p. 198. We will first consider the production of irreversibility in the context of what is known as Onsager[10] reciprocity. This notion relies on a linearization of the reaction rate laws in the neighborhood of equilibrium. Note that because the Clausius-Duhem relation, Eq. (5.61) is already known to hold for the full non-linear regime, that we find only that Onsager's analysis simply reinforces this notion in a simpler context. We then go on to give a more general analysis, and finish with an illustration based on 1) the Zel'dovich mechanism for the example problem of Sec. 1.1.2, and 2) an extended Zel'dovich mechanism including N_2 and O_2 dissociation. The original Zel'dovich mechanism induces a strictly diagonal Onsager matrix, and thus does not fully capture the essence of the analysis; the extended Zel'dovich mechanism induces a full Onsager matrix.

5.4.1 Onsager reciprocity

There is a powerful result from physical chemistry which speaks to how systems behave near equilibrium. The principle was developed by Onsager in the early twentieth century, and is known as the reciprocity principle. Where it holds, one can guarantee that on their approach to equilibrium, systems will approach the equilibrium in a non-oscillatory manner. It will be illustrated here.

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[10]Lars Onsager, 1903-1976, Norwegian-American physicist.

Note that Eq. (5.18) can be written as

$$\frac{1}{V}\frac{d\zeta_j}{dt} = r_j \;\; = \;\; \mathcal{R}'_j - \mathcal{R}''_j, \qquad j = 1, \ldots, J, \tag{5.312}$$

$$= \;\; \mathcal{R}'_j\left(1 - \frac{\mathcal{R}''_j}{\mathcal{R}'_j}\right), \qquad j = 1, \ldots, J. \tag{5.313}$$

Note further that the definition of affinity, Eq. (5.11), gives

$$\exp\left(\frac{-\overline{\alpha}_j}{\overline{R}T}\right) \;\; = \;\; \frac{\mathcal{R}''_j}{\mathcal{R}'_j}, \qquad j = 1, \ldots, J. \tag{5.314}$$

Therefore, one can say

$$\frac{1}{V}\frac{d\zeta_j}{dt} = r_j = \mathcal{R}'_j\left(1 - \exp\left(\frac{-\overline{\alpha}_j}{\overline{R}T}\right)\right), \qquad j = 1, \ldots, J. \tag{5.315}$$

Now, as each reaction comes to equilibrium, one finds that $\overline{\alpha}_j \to 0$, so a Taylor series expansion of r_j yields

$$\frac{1}{V}\frac{d\zeta_j}{dt} = r_j \;\; \sim \;\; \mathcal{R}'_j\left(1 - \left(1 - \frac{\overline{\alpha}_j}{\overline{R}T} + \ldots\right)\right), \qquad j = 1, \ldots, J, \tag{5.316}$$

$$\sim \;\; \mathcal{R}'_j\frac{\overline{\alpha}_j}{\overline{R}T}, \qquad j = 1, \ldots, J. \tag{5.317}$$

Note that $\mathcal{R}'_j > 0$, while $\overline{\alpha}_j$ can be positive or negative. Note also there is no summation on j. Take now the matrix $\mathbf{R}'$ to be the diagonal matrix with $\mathcal{R}_j$ populating its diagonal:

$$\mathbf{R}' \equiv \begin{pmatrix} \mathcal{R}'_1 & 0 & \ldots & 0 \\ 0 & \mathcal{R}'_2 & \ldots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \mathcal{R}'_J \end{pmatrix}. \tag{5.318}$$

Adopt the vector notation

$$\mathbf{r} = \frac{1}{\overline{R}T}\mathbf{R}' \cdot \overline{\boldsymbol{\alpha}}. \tag{5.319}$$

Now, the entropy production is given for multi-component systems by Eq. (5.57):

$$\left.\frac{dS}{dt}\right|_{E,V} \;\; = \;\; \frac{V}{T}\sum_{j=1}^{J}\overline{\alpha}_j r_j \geq 0. \tag{5.320}$$

Cast this entropy inequality into Gibbs notation:

$$\left.\frac{dS}{dt}\right|_{E,V} \;\; = \;\; \frac{V}{T}\overline{\boldsymbol{\alpha}}^T \cdot \mathbf{r} \geq 0. \tag{5.321}$$

Now, consider the definition of affinity, Eq. (5.10), in Gibbs notation:

$$\overline{\boldsymbol{\alpha}} = -\boldsymbol{\nu}^T \cdot \overline{\boldsymbol{\mu}}. \tag{5.322}$$

Now, $\boldsymbol{\nu}^T$ is of dimension $J \times N$ with rank typically $N - L$. Because $\boldsymbol{\nu}^T$ is typically not of full rank, one finds only $N - L$ of the components of $\overline{\boldsymbol{\alpha}}$ to be linearly independent. When one recalls that $\boldsymbol{\nu}^T$ maps vectors $\overline{\boldsymbol{\mu}}$ into the column space of $\boldsymbol{\nu}^T$, one recognizes that $\overline{\boldsymbol{\alpha}}$ can be represented as

$$\overline{\boldsymbol{\alpha}} = \mathbf{C} \cdot \hat{\overline{\boldsymbol{\alpha}}}. \tag{5.323}$$

Here, $\mathbf{C}$ is a $J \times (N - L)$-dimensional matrix of full rank, $N - L$, whose $N - L$ columns are populated by the linearly independent vectors which form the column space of $\boldsymbol{\nu}^T$, and $\hat{\overline{\boldsymbol{\alpha}}}$ is a column vector of dimension $(N - L) \times 1$. If $J \geq N - L$, one can explicitly solve for $\hat{\overline{\boldsymbol{\alpha}}}$, starting by operating on both sides of Eq. (5.323) by $\mathbf{C}^T$:

$$\mathbf{C}^T \cdot \overline{\boldsymbol{\alpha}} = \mathbf{C}^T \cdot \mathbf{C} \cdot \hat{\overline{\boldsymbol{\alpha}}}, \tag{5.324}$$

$$\mathbf{C}^T \cdot \mathbf{C} \cdot \hat{\overline{\boldsymbol{\alpha}}} = \mathbf{C}^T \cdot \overline{\boldsymbol{\alpha}}, \tag{5.325}$$

$$\hat{\overline{\boldsymbol{\alpha}}} = \left(\mathbf{C}^T \cdot \mathbf{C}\right)^{-1} \cdot \mathbf{C}^T \cdot \overline{\boldsymbol{\alpha}}, \tag{5.326}$$

$$= -\left(\mathbf{C}^T \cdot \mathbf{C}\right)^{-1} \cdot \mathbf{C}^T \cdot \boldsymbol{\nu}^T \cdot \overline{\boldsymbol{\mu}}, \tag{5.327}$$

$$\overline{\boldsymbol{\alpha}} = \mathbf{C} \cdot \hat{\overline{\boldsymbol{\alpha}}} = -\underbrace{\mathbf{C} \cdot \left(\mathbf{C}^T \cdot \mathbf{C}\right)^{-1} \cdot \mathbf{C}^T}_{\equiv \mathbf{B}} \cdot \boldsymbol{\nu}^T \cdot \overline{\boldsymbol{\mu}}. \tag{5.328}$$

Here, in the recomposition of $\overline{\boldsymbol{\alpha}}$, one can employ the $J \times J$ symmetric projection matrix $\mathbf{B}$, which has $N - L$ eigenvalues of unity and $J - (N - L)$ eigenvalues of zero. The matrix $\mathbf{B}$ has rank $N - L$, and is thus not full rank.

Substitute Eqs. (5.319, 5.323) into Eq. (5.321) to get

$$\left. \frac{dS}{dt} \right|_{E,V} = \frac{V}{T} \overbrace{\left(\mathbf{C} \cdot \hat{\overline{\boldsymbol{\alpha}}}\right)^T}^{=\overline{\boldsymbol{\alpha}}^T} \cdot \underbrace{\frac{1}{\overline{R}T} \mathbf{R}'}_{=\mathbf{r}} \cdot \overbrace{\mathbf{C} \cdot \hat{\overline{\boldsymbol{\alpha}}}}^{=\overline{\boldsymbol{\alpha}}} \geq 0, \tag{5.329}$$

$$= \frac{V}{\overline{R}} \left(\frac{\hat{\overline{\boldsymbol{\alpha}}}^T}{T}\right) \cdot \underbrace{\mathbf{C}^T \cdot \mathbf{R}' \cdot \mathbf{C}}_{\equiv \mathbf{L}} \cdot \left(\frac{\hat{\overline{\boldsymbol{\alpha}}}}{T}\right) \geq 0. \tag{5.330}$$
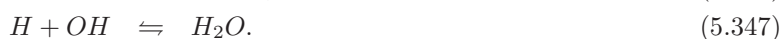
Since each of the entries of the diagonal $\mathbf{R}'$ are guaranteed positive semi-definite in the physical region of composition space, the entropy production rate near equilibrium is also positive semi-definite. The constant square matrix $\mathbf{L}$, of dimension $(N - L) \times (N - L)$, is given by

$$\mathbf{L} \equiv \mathbf{C}^T \cdot \mathbf{R}' \cdot \mathbf{C}. \tag{5.331}$$

The matrix $\mathbf{L}$ has rank $N - L$ and is thus full rank. Because $\mathbf{R}'$ is diagonal with positive semi-definite elements, $\mathbf{L}$ is symmetric positive semi-definite. Thus, its eigenvalues are guaranteed to be positive and real. Note that off-diagonal elements of $\mathbf{L}$ can be negative, but that

the matrix itself remains positive semi-definite. Onsager reciprocity simply demands that near equilibrium, the linearized version of the combination of the thermodynamic "forces" (here the affinity $\overline{\boldsymbol{\alpha}}$) and "fluxes" (here the reaction rate $\mathbf{r}$) be positive semi-definite. Upon linearization, one should always be able to find a positive semi-definite matrix associated with the dynamics of the approach to equilibrium. Here, that matrix is $\mathbf{L}$, and by choices made in its construction, it has the desired properties.

One can also formulate an alternative version of Onsager reciprocity using the projection matrix $\mathbf{B}$, which from Eq. (5.328), is

$$\mathbf{B} \equiv \mathbf{C} \cdot \left(\mathbf{C}^T \cdot \mathbf{C}\right)^{-1} \cdot \mathbf{C}^T. \tag{5.332}$$

With a series of straightforward substitutions, it can be shown that the entropy production rate given by Eq. (5.330) reduces to

$$\left.\frac{dS}{dt}\right|_{E,V} = \frac{V}{\overline{\overline{R}}} \left(\frac{\overline{\boldsymbol{\alpha}}^T}{T}\right) \cdot \underbrace{\mathbf{B}^T \cdot \mathbf{R}' \cdot \mathbf{B}}_{\equiv\mathsf{L}} \cdot \left(\frac{\overline{\boldsymbol{\alpha}}}{T}\right) \geq 0. \tag{5.333}$$

Here, an alternative symmetric positive semi-definite matrix L, of dimension $J \times J$ and rank $N - L$, has been defined as

$$\mathsf{L} \equiv \mathbf{B}^T \cdot \mathbf{R}' \cdot \mathbf{B}. \tag{5.334}$$

One can also express the entropy generation directly in terms of the chemical potential rather than the affinity by defining the $J \times N$ matrix $\mathbf{S}$ as

$$\begin{aligned}
\mathbf{S} &\equiv \mathbf{B} \cdot \boldsymbol{\nu}^T, \tag{5.335}\\
&= \mathbf{C} \cdot \left(\mathbf{C}^T \cdot \mathbf{C}\right)^{-1} \cdot \mathbf{C} \cdot \boldsymbol{\nu}^T. \tag{5.336}
\end{aligned}$$

The matrix $\mathbf{S}$ has rank $N - L$ and thus is not full rank. With a series of straightforward substitutions, it can be shown that the entropy production rate given by Eq. (5.333) reduces to

$$\left.\frac{dS}{dt}\right|_{E,V} = \frac{V}{\overline{\overline{R}}} \left(\frac{\overline{\boldsymbol{\mu}}^T}{T}\right) \cdot \underbrace{\mathbf{S}^T \cdot \mathbf{R}' \cdot \mathbf{S}}_{\equiv\mathcal{L}} \cdot \left(\frac{\overline{\boldsymbol{\mu}}}{T}\right) \geq 0. \tag{5.337}$$

Here, an alternative symmetric positive semi-definite matrix $\mathcal{L}$, of dimension $N \times N$ and rank $N - L$, has been defined as

$$\mathcal{L} \equiv \mathbf{S}^T \cdot \mathbf{R}' \cdot \mathbf{S}. \tag{5.338}$$

Example 5.4

Find the matrices associated with Onsager reciprocity for the reaction mechanism given by

$$\begin{aligned}
H_2 + O_2 &\rightleftharpoons 2OH, \tag{5.339}\\
H_2 + OH &\rightleftharpoons H + H_2O, \tag{5.340}\\
H + O_2 &\rightleftharpoons O + OH, \tag{5.341}\\
H_2 + O &\rightleftharpoons H + OH, \tag{5.342}
\end{aligned}$$

$$H + H \;\; \rightleftharpoons \;\; H_2, \tag{5.343}$$

$$2OH \;\; \rightleftharpoons \;\; O + H_2O, \tag{5.344}$$

$$H_2 \;\; \rightleftharpoons \;\; H + H, \tag{5.345}$$

$$O_2 \;\; \rightleftharpoons \;\; O + O, \tag{5.346}$$

$$H + OH \;\; \rightleftharpoons \;\; H_2O. \tag{5.347}$$

Here, there are $N = 6$ species (H, H_2, O, O_2, OH, H_2O), composed of $L = 2$ elements (H, O), reacting in $J = 9$ reactions. Here, $J \geq N - L$, so the analysis of this section can be performed.

Take species $i = 1$ as H, $i = 2$ as H_2,..., $i = N = 6$ as H_2O. Take element $l = 1$ as H and element $l = L = 2$ as O. The full rank stoichiometric matrix ϕ, of dimension $2 \times 6 = L \times N$ and rank $2 = L$, is

$$\phi = \begin{pmatrix} 1 & 2 & 0 & 0 & 1 & 2 \\ 0 & 0 & 1 & 2 & 1 & 1 \end{pmatrix}. \tag{5.348}$$

The rank-deficient matrix of stoichiometric coefficients ν, of dimension $6 \times 9 = N \times J$ and rank $4 = N - L$ is

$$\nu = \begin{pmatrix} 0 & 1 & -1 & 1 & -2 & 0 & 2 & 0 & -1 \\ -1 & -1 & 0 & -1 & 1 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 1 & 0 & 2 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & 0 & -1 & 0 \\ 2 & -1 & 1 & 1 & 0 & -2 & 0 & 0 & -1 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \end{pmatrix}. \tag{5.349}$$

Check for stoichiometric balance:

$$\phi \cdot \nu = \begin{pmatrix} 1 & 2 & 0 & 0 & 1 & 2 \\ 0 & 0 & 1 & 2 & 1 & 1 \end{pmatrix} \cdot \begin{pmatrix} 0 & 1 & -1 & 1 & -2 & 0 & 2 & 0 & -1 \\ -1 & -1 & 0 & -1 & 1 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 1 & 0 & 2 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & 0 & -1 & 0 \\ 2 & -1 & 1 & 1 & 0 & -2 & 0 & 0 & -1 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \end{pmatrix}, \tag{5.350}$$

$$= \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \tag{5.351}$$

So, the number and mass of every element is conserved in every reaction; every vector in the column space of ν is in the right null space of ϕ.

The detailed version of the reaction kinetics law is given by

$$\frac{d\overline{\rho}}{dt} = \nu \cdot \mathbf{r}, \tag{5.352}$$

$$= \begin{pmatrix} 0 & 1 & -1 & 1 & -2 & 0 & 2 & 0 & -1 \\ -1 & -1 & 0 & -1 & 1 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 1 & 0 & 2 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & 0 & -1 & 0 \\ 2 & -1 & 1 & 1 & 0 & -2 & 0 & 0 & -1 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \\ r_5 \\ r_6 \\ r_7 \\ r_8 \\ r_9 \end{pmatrix}, \tag{5.353}$$

$$= \begin{pmatrix} r_2 - r_3 + r_4 - 2r_5 + 2r_7 - r_9 \\ -r_1 - r_2 - r_4 + r_5 - r_7 \\ r_3 - r_4 + r_6 + 2r_8 \\ -r_1 - r_3 - r_8 \\ 2r_1 - r_2 + r_3 + r_4 - 2r_6 - r_9 \\ r_2 + r_6 + r_9 \end{pmatrix}. \tag{5.354}$$

The full rank matrix $\mathbf{D}$, of dimension $6 \times 4 = N \times (N - L)$ and rank $4 = N - L$, is composed of vectors in the right null space of $\boldsymbol{\phi}$. It is non-unique, as linear combinations of right null space vectors suffice. It is equivalently composed by casting the $N - L$ linearly independent vectors of the column space of $\boldsymbol{\nu}$ in its columns. Recall that some of the columns of $\boldsymbol{\nu}$ are linearly dependent. In the present example, the first $N - L = 4$ column vectors of $\boldsymbol{\nu}$ happen to be linearly dependent, and thus will not suffice. Other sets are not; the last $N - L = 4$ column vectors of $\boldsymbol{\nu}$ happen to be linearly independent and thus suffice for the present purposes. Take then

$$\mathbf{D} = \begin{pmatrix} 0 & 2 & 0 & -1 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 2 & 0 \\ 0 & 0 & -1 & 0 \\ -2 & 0 & 0 & -1 \\ 1 & 0 & 0 & 1 \end{pmatrix}. \tag{5.355}$$

It is easily verified by direct substitution that $\mathbf{D}$ is in the right null space of $\boldsymbol{\phi}$:

$$\boldsymbol{\phi} \cdot \mathbf{D} = \begin{pmatrix} 1 & 2 & 0 & 0 & 1 & 2 \\ 0 & 0 & 1 & 2 & 1 & 1 \end{pmatrix} \cdot \begin{pmatrix} 0 & 2 & 0 & -1 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 2 & 0 \\ 0 & 0 & -1 & 0 \\ -2 & 0 & 0 & -1 \\ 1 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{5.356}$$

Since $\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \mathbf{0}$ and $\boldsymbol{\phi} \cdot \mathbf{D} = \mathbf{0}$, one concludes that the column spaces of both $\boldsymbol{\nu}$ and $\mathbf{D}$ are one and the same.

The non-unique concise version of the reaction kinetics law is given by

$$\frac{d\boldsymbol{\xi}}{dt} = V(\mathbf{D}^T \cdot \mathbf{D})^{-1} \cdot \mathbf{D}^T \cdot \boldsymbol{\nu} \cdot \mathbf{r}, \tag{5.357}$$

$$= V \left(\left(\begin{pmatrix} 0 & 0 & 1 & 0 & -2 & 1 \\ 2 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} 0 & 2 & 0 & -1 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 2 & 0 \\ 0 & 0 & -1 & 0 \\ -2 & 0 & 0 & -1 \\ 1 & 0 & 0 & 1 \end{pmatrix} \right)^{-1} \cdot \begin{pmatrix} 0 & 0 & 1 & 0 & -2 & 1 \\ 2 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 & -1 & 1 \end{pmatrix} \right).$$

$$\begin{pmatrix} 0 & 1 & -1 & 1 & -2 & 0 & 2 & 0 & -1 \\ -1 & -1 & 0 & -1 & 1 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 1 & 0 & 2 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & 0 & -1 & 0 \\ 2 & -1 & 1 & 1 & 0 & -2 & 0 & 0 & -1 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \\ r_5 \\ r_6 \\ r_7 \\ r_8 \\ r_9 \end{pmatrix}, \tag{5.358}$$

$$= V \begin{pmatrix} -2r_1 - r_3 - r_4 + r_6 \\ r_1 + r_2 + r_4 - r_5 + r_7 \\ r_1 + r_3 + r_8 \\ 2r_1 + r_2 + r_3 + r_4 + r_9 \end{pmatrix}. \tag{5.359}$$

The rank-deficient projection matrix $\mathbf{P}$, of dimension $6 \times 6 = N \times N$ and rank $4 = N - L$, is

$$\mathbf{P} = \mathbf{D} \cdot (\mathbf{D}^T \cdot \mathbf{D})^{-1} \cdot \mathbf{D}^T, \tag{5.360}$$

$$
= \begin{pmatrix}
\frac{54}{61} & \frac{-14}{61} & \frac{3}{61} & \frac{6}{61} & \frac{-4}{61} & \frac{-11}{61} \\
\frac{-14}{61} & \frac{33}{61} & \frac{6}{61} & \frac{12}{61} & \frac{-8}{61} & \frac{-22}{61} \\
\frac{3}{61} & \frac{6}{61} & \frac{51}{61} & \frac{-20}{61} & \frac{-7}{61} & \frac{-4}{61} \\
\frac{6}{61} & \frac{12}{61} & \frac{-20}{61} & \frac{21}{61} & \frac{-14}{61} & \frac{-8}{61} \\
\frac{-4}{61} & \frac{-8}{61} & \frac{-7}{61} & \frac{-14}{61} & \frac{50}{61} & \frac{-15}{61} \\
\frac{-11}{61} & \frac{-22}{61} & \frac{-4}{61} & \frac{-8}{61} & \frac{-15}{61} & \frac{35}{61}
\end{pmatrix}.
\tag{5.361}
$$

The projection matrix $\mathbf{P}$ has $4 = N - L$ eigenvalues of unity and $2 = L$ eigenvalues of zero.

The affinity vector $\overline{\boldsymbol{\alpha}}$, of dimension $9 \times 1 = J \times 1$, is given by

$$
\overline{\boldsymbol{\alpha}} = -\boldsymbol{\nu}^T \cdot \overline{\boldsymbol{\mu}},
\tag{5.362}
$$

$$
= -\begin{pmatrix}
0 & 1 & -1 & 1 & -2 & 0 & 2 & 0 & -1 \\
-1 & -1 & 0 & -1 & 1 & 0 & -1 & 0 & 0 \\
0 & 0 & 1 & -1 & 0 & 1 & 0 & 2 & 0 \\
-1 & 0 & -1 & 0 & 0 & 0 & 0 & -1 & 0 \\
2 & -1 & 1 & 1 & 0 & -2 & 0 & 0 & -1 \\
0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 1
\end{pmatrix}^T
\cdot
\begin{pmatrix}
\overline{\mu}_1 \\ \overline{\mu}_2 \\ \overline{\mu}_3 \\ \overline{\mu}_4 \\ \overline{\mu}_5 \\ \overline{\mu}_6
\end{pmatrix},
\tag{5.363}
$$

$$
= -\begin{pmatrix}
0 & -1 & 0 & -1 & 2 & 0 \\
1 & -1 & 0 & 0 & -1 & 1 \\
-1 & 0 & 1 & -1 & 1 & 0 \\
1 & -1 & -1 & 0 & 1 & 0 \\
-2 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & -2 & 1 \\
2 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 2 & -1 & 0 & 0 \\
-1 & 0 & 0 & 0 & -1 & 1
\end{pmatrix}
\cdot
\begin{pmatrix}
\overline{\mu}_1 \\ \overline{\mu}_2 \\ \overline{\mu}_3 \\ \overline{\mu}_4 \\ \overline{\mu}_5 \\ \overline{\mu}_6
\end{pmatrix},
\tag{5.364}
$$

$$
= \begin{pmatrix}
\overline{\mu}_2 + \overline{\mu}_4 - 2\overline{\mu}_5 \\
-\overline{\mu}_1 + \overline{\mu}_2 + \overline{\mu}_5 - \overline{\mu}_6 \\
\overline{\mu}_1 - \overline{\mu}_3 + \overline{\mu}_4 - \overline{\mu}_5 \\
-\overline{\mu}_1 + \overline{\mu}_2 + \overline{\mu}_3 - \overline{\mu}_5 \\
2\overline{\mu}_1 - \overline{\mu}_2 \\
-\overline{\mu}_3 + 2\overline{\mu}_5 - \overline{\mu}_6 \\
-2\overline{\mu}_1 + \overline{\mu}_2 \\
-2\overline{\mu}_3 + \overline{\mu}_4 \\
\overline{\mu}_1 + \overline{\mu}_5 - \overline{\mu}_6
\end{pmatrix}.
\tag{5.365}
$$

The full rank matrix $\mathbf{C}$, of dimension $9 \times 4 = J \times (N - L)$ and rank $4 = N - L$, is composed of the set of $N - L = 4$ linearly independent column space vectors of $\boldsymbol{\nu}^T$; thus, they also comprise the $N - L = 4$ linearly independent row space vectors of $\boldsymbol{\nu}$. It does not matter which four are chosen, so long as they are linearly independent. In this case, the first four column vectors of $\boldsymbol{\nu}^T$ suffice:

$$
\mathbf{C} = \begin{pmatrix}
0 & -1 & 0 & -1 \\
1 & -1 & 0 & 0 \\
-1 & 0 & 1 & -1 \\
1 & -1 & -1 & 0 \\
-2 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
2 & -1 & 0 & 0 \\
0 & 0 & 2 & -1 \\
-1 & 0 & 0 & 0
\end{pmatrix}.
\tag{5.366}
$$

When $J > N - L$, not all of the components of $\overline{\boldsymbol{\alpha}}$ are linearly independent. In this case, one can

form the reduced affinity vector, $\hat{\overline{\boldsymbol{\alpha}}}$, of dimension $4 \times 1 = (N - L) \times 1$ via

$$\hat{\overline{\boldsymbol{\alpha}}} = (\mathbf{C}^T \cdot \mathbf{C})^{-1} \cdot \mathbf{C}^T \cdot \overline{\boldsymbol{\alpha}}, \tag{5.367}$$

$$= \left(\begin{pmatrix} 0 & 1 & -1 & 1 & -2 & 0 & 2 & 0 & -1 \\ -1 & -1 & 0 & -1 & 1 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 1 & 0 & 2 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & 0 & -1 & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 & -1 & 0 & -1 \\ 1 & -1 & 0 & 0 \\ -1 & 0 & 1 & -1 \\ 1 & -1 & -1 & 0 \\ -2 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 2 & -1 & 0 & 0 \\ 0 & 0 & 2 & -1 \\ -1 & 0 & 0 & 0 \end{pmatrix} \right)^{-1} .$$

$$\begin{pmatrix} 0 & 1 & -1 & 1 & -2 & 0 & 2 & 0 & -1 \\ -1 & -1 & 0 & -1 & 1 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 1 & 0 & 2 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & 0 & -1 & 0 \end{pmatrix} \cdot \begin{pmatrix} \overline{\mu}_2 + \overline{\mu}_4 - 2\overline{\mu}_5 \\ -\overline{\mu}_1 + \overline{\mu}_2 + \overline{\mu}_5 - \overline{\mu}_6 \\ \overline{\mu}_1 - \overline{\mu}_3 + \overline{\mu}_4 - \overline{\mu}_5 \\ -\overline{\mu}_1 + \overline{\mu}_2 + \overline{\mu}_3 - \overline{\mu}_5 \\ 2\overline{\mu}_1 - \overline{\mu}_2 \\ -\overline{\mu}_3 + 2\overline{\mu}_5 - \overline{\mu}_6 \\ -2\overline{\mu}_1 + \overline{\mu}_2 \\ -2\overline{\mu}_3 + \overline{\mu}_4 \\ \overline{\mu}_1 + \overline{\mu}_5 - \overline{\mu}_6 \end{pmatrix} , \tag{5.368}$$

$$= \begin{pmatrix} -\overline{\mu}_1 - \overline{\mu}_5 + \overline{\mu}_6 \\ -\overline{\mu}_2 - 2\overline{\mu}_5 + 2\overline{\mu}_6 \\ -\overline{\mu}_3 + 2\overline{\mu}_5 - \overline{\mu}_6 \\ -\overline{\mu}_4 + 4\overline{\mu}_5 - 2\overline{\mu}_6 \end{pmatrix} . \tag{5.369}$$

The rank-deficient projection matrix $\mathbf{B}$, of dimension $9 \times 9 = J \times J$ and rank $4 = N - L$, is found to be

$$\mathbf{B} = \mathbf{C} \cdot (\mathbf{C}^T \cdot \mathbf{C})^{-1} \cdot \mathbf{C}^T, \tag{5.370}$$

$$= \begin{pmatrix} \frac{57}{94} & \frac{9}{94} & \frac{31}{94} & \frac{26}{94} & \frac{-1}{94} & \frac{-17}{94} & \frac{1}{94} & \frac{6}{94} & \frac{8}{94} \\ \frac{9}{94} & \frac{41}{94} & \frac{-5}{94} & \frac{-5}{94} & \frac{-15}{94} & \frac{27}{94} & \frac{15}{94} & \frac{-4}{94} & \frac{26}{94} \\ \frac{31}{94} & \frac{-5}{94} & \frac{35}{94} & \frac{-4}{94} & \frac{11}{94} & \frac{-1}{94} & \frac{-11}{94} & \frac{28}{94} & \frac{6}{94} \\ \frac{26}{94} & \frac{14}{94} & \frac{-4}{94} & \frac{30}{94} & \frac{-12}{94} & \frac{16}{94} & \frac{12}{94} & \frac{-22}{94} & \frac{2}{94} \\ \frac{-1}{94} & \frac{-15}{94} & \frac{11}{94} & \frac{-12}{94} & \frac{33}{94} & \frac{-3}{94} & \frac{-33}{94} & \frac{-10}{94} & \frac{18}{94} \\ \frac{-17}{94} & \frac{27}{94} & \frac{-1}{94} & \frac{-16}{94} & \frac{-3}{94} & \frac{43}{94} & \frac{3}{94} & \frac{18}{94} & \frac{24}{94} \\ \frac{1}{94} & \frac{15}{94} & \frac{-11}{94} & \frac{12}{94} & \frac{-33}{94} & \frac{3}{94} & \frac{33}{94} & \frac{10}{94} & \frac{-18}{94} \\ \frac{6}{94} & \frac{-4}{94} & \frac{28}{94} & \frac{-22}{94} & \frac{-10}{94} & \frac{18}{94} & \frac{10}{94} & \frac{60}{94} & \frac{-14}{94} \\ \frac{8}{94} & \frac{26}{94} & \frac{6}{94} & \frac{2}{94} & \frac{18}{94} & \frac{24}{94} & \frac{-18}{94} & \frac{-14}{94} & \frac{44}{94} \end{pmatrix} . \tag{5.371}$$

The projection matrix $\mathbf{B}$ has a set of $9 = J$ eigenvalues, $4 = N - L$ of which are unity, and $5 = J - (N - L)$ of which are zero. One can recover $\overline{\boldsymbol{\alpha}}$ by the operation $\overline{\boldsymbol{\alpha}} = \mathbf{C} \cdot \hat{\overline{\boldsymbol{\alpha}}} = -\mathbf{B} \cdot \boldsymbol{\nu}^T \cdot \overline{\boldsymbol{\mu}}$.

The square full rank Onsager matrix $\mathbf{L}$, of dimension $4 \times 4 = (N - L) \times (N - L)$ and rank $4 = N - L$, is given by

$$\mathbf{L} = \mathbf{C}^T \cdot \mathbf{R} \cdot \mathbf{C}, \tag{5.372}$$

$$
= \begin{pmatrix} 0 & 1 & -1 & 1 & -2 & 0 & 2 & 0 & -1 \\ -1 & -1 & 0 & -1 & 1 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 1 & 0 & 2 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & 0 & -1 & 0 \end{pmatrix} \cdot \begin{pmatrix} \mathcal{R}_1' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathcal{R}_2' & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathcal{R}_3' & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathcal{R}_4' & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathcal{R}_5' & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathcal{R}_6' & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathcal{R}_7' & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathcal{R}_8' & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathcal{R}_9' \end{pmatrix}
$$

$$
\cdot \begin{pmatrix} 0 & -1 & 0 & -1 \\ 1 & -1 & 0 & 0 \\ -1 & 0 & 1 & -1 \\ 1 & -1 & -1 & 0 \\ -2 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 2 & -1 & 0 & 0 \\ 0 & 0 & 2 & -1 \\ -1 & 0 & 0 & 0 \end{pmatrix},
$$

$$
(5.373)
$$

$$
= \begin{pmatrix} \mathcal{R}_2' + \mathcal{R}_3' + \mathcal{R}_4' + 4\mathcal{R}_5' + 4\mathcal{R}_7' + \mathcal{R}_9' & -\mathcal{R}_2' - \mathcal{R}_4' - 2\mathcal{R}_5' - 2\mathcal{R}_7' & -\mathcal{R}_3' - \mathcal{R}_4' & \mathcal{R}_3' \\ -\mathcal{R}_2' - \mathcal{R}_4' - 2\mathcal{R}_5' - 2\mathcal{R}_7' & \mathcal{R}_1' + \mathcal{R}_2' + \mathcal{R}_4' + \mathcal{R}_5' + \mathcal{R}_7' & \mathcal{R}_4' & \mathcal{R}_1' \\ -\mathcal{R}_3' - \mathcal{R}_4' & \mathcal{R}_4' & \mathcal{R}_3' + \mathcal{R}_4' + \mathcal{R}_6' + 4\mathcal{R}_8' & -\mathcal{R}_3' - 2\mathcal{R}_8' \\ \mathcal{R}_3' & \mathcal{R}_1' & -\mathcal{R}_3' - 2\mathcal{R}_8' & \mathcal{R}_1' + \mathcal{R}_3' + \mathcal{R}_8' \end{pmatrix}.
$$

$$
(5.374)
$$

Obviously $\mathbf{L}$ is symmetric, and thus has all real eigenvalues. It is also positive semi-definite. With a similar effort, one can obtain the alternate rank-deficient square Onsager matrices L and $\mathcal{L}$. Recall that $\mathbf{L}$, L, and $\mathcal{L}$ each have rank $N - L$, while $\mathbf{L}$ has the smallest dimension, $(N - L) \times (N - L)$, and so forms the most efficient Onsager matrix.

5.4.2 General analysis

This section will be restricted to isothermal, isochoric reaction. It is known that Gibbs free energy and irreversibility production rates reach respective minima at equilibrium.

Consider the gradient of the irreversibility production rate in the space of species progress variables ξ_k. First, recall Eq. (5.231) for the gradient of Gibbs free energy with respect to the independent species progress variables, $\partial G / \partial \xi_k = \sum_{i=1}^{N} \overline{\mu}_i \mathcal{D}_{ik}$. Now, beginning from Eq. (4.464), define the differential irreversibility $d\mathcal{I}$ as

$$
d\mathcal{I} = -\frac{1}{T} \sum_{i=1}^{N} \overline{\mu}_i dn_i. \tag{5.375}
$$

In terms of an irreversibility production rate, one has

$$
\frac{d\mathcal{I}}{dt} = \dot{\mathcal{I}} = -\frac{1}{T} \sum_{i=1}^{N} \overline{\mu}_i \frac{dn_i}{dt}. \tag{5.376}
$$

Take now the time derivative of Eq. (5.169) to get

$$\frac{dn_i}{dt} = \sum_{k=1}^{N-L} \mathcal{D}_{ik} \frac{d\xi_k}{dt}. \tag{5.377}$$

Substitute from Eq. (5.377) into Eq. (5.376) to get

$$\dot{\mathcal{I}} = -\frac{1}{T} \sum_{i=1}^{N} \overline{\mu}_i \sum_{k=1}^{N-L} \mathcal{D}_{ik} \frac{d\xi_k}{dt}, \tag{5.378}$$

$$= -\frac{1}{T} \sum_{k=1}^{N-L} \frac{d\xi_k}{dt} \underbrace{\sum_{i=1}^{N} \overline{\mu}_i \mathcal{D}_{ik}}_{= \frac{\partial G}{\partial \xi_k}}, \tag{5.379}$$

$$= -\frac{1}{T} \sum_{k=1}^{N-L} \frac{d\xi_k}{dt} \frac{\partial G}{\partial \xi_k}. \tag{5.380}$$

Now, Eq. (5.304) gives an explicit algebraic formula for $d\xi_k/dt$. Define then the constitutive function $\hat{\omega}_k$:

$$\hat{\omega}_k(\xi_1, \ldots, \xi_{N-L}) \equiv \frac{d\xi_k}{dt} = V(\mathbf{D}^T \cdot \mathbf{D})^{-1} \cdot \mathbf{D}^T \cdot \boldsymbol{\nu} \cdot \mathbf{r}. \tag{5.381}$$

So, the irreversibility production rate is

$$\dot{\mathcal{I}} = -\frac{1}{T} \sum_{k=1}^{N-L} \hat{\omega}_k \frac{\partial G}{\partial \xi_k}. \tag{5.382}$$

The gradient of this field is given by

$$\frac{\partial \dot{\mathcal{I}}}{\partial \xi_p} = -\frac{1}{T} \sum_{k=1}^{N-L} \left(\frac{\partial \hat{\omega}_k}{\partial \xi_p} \frac{\partial G}{\partial \xi_k} + \hat{\omega}_k \frac{\partial^2 G}{\partial \xi_p \partial \xi_k} \right). \tag{5.383}$$

The Hessian of this field is given by

$$\frac{\partial^2 \dot{\mathcal{I}}}{\partial \xi_l \partial \xi_p} = -\frac{1}{T} \sum_{k=1}^{N-L} \left(\frac{\partial^2 \hat{\omega}_k}{\partial \xi_l \partial \xi_p} \frac{\partial G}{\partial \xi_k} + \frac{\partial \hat{\omega}_k}{\partial \xi_p} \frac{\partial^2 G}{\partial \xi_l \partial \xi_k} + \frac{\partial \hat{\omega}_k}{\partial \xi_l} \frac{\partial^2 G}{\partial \xi_p \partial \xi_k} + \hat{\omega}_k \frac{\partial^3 G}{\partial \xi_l \partial \xi_p \partial \xi_k} \right) \tag{5.384}$$

Now, at equilibrium, $\xi_k = \xi_k^e$, we have $\hat{\omega}_k = 0$ as well as $\partial G/\partial \xi_k = 0$. Thus

$$\left. \dot{\mathcal{I}} \right|_{\xi_k = \xi_k^e} = 0, \tag{5.385}$$

$$\left. \frac{\partial \dot{\mathcal{I}}}{\partial \xi_k} \right|_{\xi_k = \xi_k^e} = 0, \tag{5.386}$$

$$\left. \frac{\partial^2 \dot{\mathcal{I}}}{\partial \xi_l \partial \xi_p} \right|_{\xi_k = \xi_k^e} = -\frac{1}{T} \sum_{k=1}^{N-L} \left(\frac{\partial \hat{\omega}_k}{\partial \xi_p} \frac{\partial^2 G}{\partial \xi_l \partial \xi_k} + \frac{\partial \hat{\omega}_k}{\partial \xi_l} \frac{\partial^2 G}{\partial \xi_p \partial \xi_k} \right)_{\xi_k = \xi_k^e}. \tag{5.387}$$

It can be shown for arbitrary matrices that the first term in the right hand side of Eq. (5.387) is the transpose of the second; moreover, for arbitrary matrices, the two terms are in general asymmetric. But, their sum is a symmetric matrix, as must be since the Hessian of $\dot{\mathcal{I}}$ must be symmetric. But for arbitrary matrices, we find no guarantee that the Hessian of $\dot{\mathcal{I}}$ is positive semi-definite, as the eigenvalues can take any sign. However, it can be verified by direct expansion for actual physical systems that the two terms in the Hessian evaluated at equilibrium are identical. This must be attributable to extra hidden symmetries in the system. Moreover, for actual physical systems, the eigenvalues of the Hessian of $\dot{\mathcal{I}}$ are positive semi-definite. So, one can say

$$\left.\frac{\partial^2 \dot{\mathcal{I}}}{\partial \xi_l \partial \xi_p}\right|_{\xi_k = \xi_k^e} = -\frac{2}{T} \sum_{k=1}^{N-L} \left.\frac{\partial \hat{\dot{\omega}}_k}{\partial \xi_p}\right|_{\xi_k = \xi_k^e} \left.\frac{\partial^2 G}{\partial \xi_l \partial \xi_k}\right|_{\xi_k = \xi_k^e}. \tag{5.388}$$

Where does the hidden symmetry arise? The answer lies in the fact that the $\hat{\dot{\omega}}_k$ and G are not independent. Using notions from Onsager reciprocity, let us see why the Hessian of $\dot{\mathcal{I}}$ is indeed positive semi-definite. Consider, for instance, Eq. (5.330), which is valid in the neighborhood of equilibrium:

$$\dot{\mathcal{I}} = \frac{V}{\overline{R}} \left(\frac{\hat{\overline{\boldsymbol{\alpha}}}^T}{T}\right) \cdot \mathbf{L} \cdot \left(\frac{\hat{\overline{\boldsymbol{\alpha}}}}{T}\right) \qquad \text{valid only near equilibrium.} \tag{5.389}$$

Recall that by construction $\mathbf{L}$ is positive semi-definite. Now, near equilibrium, $\hat{\overline{\boldsymbol{\alpha}}}$ has a Taylor series expansion

$$\hat{\overline{\boldsymbol{\alpha}}} = \underbrace{\hat{\overline{\boldsymbol{\alpha}}}\big|_{eq}}_{=0} + \left.\frac{\partial \hat{\overline{\boldsymbol{\alpha}}}}{\partial \boldsymbol{\xi}}\right|_{eq} \cdot (\boldsymbol{\xi} - \boldsymbol{\xi}|_{eq}) + ... \tag{5.390}$$

Now, recall that at equilibrium that $\hat{\overline{\boldsymbol{\alpha}}} = 0$. Let us also define the Jacobian of $\hat{\overline{\boldsymbol{\alpha}}}$ as $\mathbf{J}_\alpha$. Thus, Eq. (5.389) can be rewritten as

$$\dot{\mathcal{I}} = \frac{V}{\overline{R}T^2} \left(\mathbf{J}_\alpha \cdot (\boldsymbol{\xi} - \boldsymbol{\xi}|_{eq})\right)^T \cdot \mathbf{L} \cdot \left(\mathbf{J}_\alpha \cdot (\boldsymbol{\xi} - \boldsymbol{\xi}|_{eq})\right), \tag{5.391}$$

$$= \frac{V}{\overline{R}T^2} (\boldsymbol{\xi} - \boldsymbol{\xi}|_{eq})^T \cdot \mathbf{J}_\alpha^T \cdot \mathbf{L} \cdot \mathbf{J}_\alpha \cdot (\boldsymbol{\xi} - \boldsymbol{\xi}|_{eq}). \tag{5.392}$$

By inspection, then we see that the Hessian of $\dot{\mathcal{I}}$ is

$$\mathbf{H}_{\dot{\mathcal{I}}} = \frac{2V}{\overline{R}T^2} \mathbf{J}_\alpha^T \cdot \mathbf{L} \cdot \mathbf{J}_\alpha. \tag{5.393}$$

Moreover, $\mathbf{L}$ has the same eigenvalues as the similar matrix $\mathbf{J}_\alpha^T \cdot \mathbf{L} \cdot \mathbf{J}_\alpha$, so $\mathbf{H}_{\dot{\mathcal{I}}}$ is positive semi-definite.

Returning to the less refined formulation, in Gibbs notation, we can write Eq. (5.388) as

$$\mathbf{H}_{\dot{\mathcal{I}}} = -\frac{2}{T} \mathbf{H}_G \cdot \mathbf{J}, \tag{5.394}$$

where $\mathbf{J}$ is the Jacobian matrix of $\hat{\omega}_k$. Consider the eigenvectors and eigenvalues of the various matrices here. The eigenvalues of $\mathbf{J}$ give the time scales of reaction in the neighborhood of equilibrium. They are guaranteed real and negative. The eigenvectors of $\mathbf{J}$ give the directions of fast and slow modes. Near equilibrium, the dynamics will relax to the slow mode, and the motion towards equilibrium will be along the eigenvector associated with the slowest time scale. Now, in the unlikely circumstance that $\mathbf{H}_G$ were the identity matrix, one would have the eigenvalues of $\mathbf{H}_{\dot{\mathcal{I}}}$ equal to the product of $-2/T$ and the eigenvalues of $\mathbf{H}_G$. So, they would be positive, as expected. Moreover, the eigenvectors of $\mathbf{H}_{\dot{\mathcal{I}}}$ would be identical to those of $\mathbf{J}$, so in this unusual case, the slow dynamics could be inferred from examining the slowest descent down contours of $\dot{I}$. Essentially the same conclusion would be reached if $\mathbf{H}_G$ had a diagonalization with equal eigenvalues on its diagonal. This would correspond to reactions proceeding at the same rate near equilibrium. However, in the usual case, the eigenvalues of $\mathbf{H}_G$ are non-uniform. Thus, the action of $\mathbf{H}_G$ on $\mathbf{J}$ is to stretch it non-uniformly in such a fashion that $\mathbf{H}_{\dot{\mathcal{I}}}$ does not share the same eigenvalues or eigenvectors. Thus, it cannot be used to directly infer the dynamics.

Now, consider the behavior of $\dot{\mathcal{I}}$ in the neighborhood of an equilibrium point. In the neighborhood of a general point $\xi_k = \hat{\xi}_k$, $\dot{\mathcal{I}}$ has a Taylor series expansion

$$\dot{\mathcal{I}} = \dot{\mathcal{I}}\Big|_{\xi_k=\hat{\xi}_k} + \sum_{k=1}^{N-L} \frac{\partial \dot{\mathcal{I}}}{\partial \xi_k}\Big|_{\xi_k=\hat{\xi}_k} \left(\xi_k - \hat{\xi}_k\right) + \frac{1}{2}\sum_{l=1}^{N-L}\sum_{p=1}^{N-L} \left(\xi_l - \hat{\xi}_l\right) \frac{\partial^2 \dot{\mathcal{I}}}{\partial \xi_l \partial \xi_p}\Big|_{\xi_k=\hat{\xi}_k} \left(\xi_p - \hat{\xi}_p\right) + \dots$$

(5.395)

Near equilibrium, the first two terms of this Taylor series are zero, and $\dot{\mathcal{I}}$ has the behavior

$$\dot{\mathcal{I}} = \frac{1}{2}\sum_{l=1}^{N-L}\sum_{p=1}^{N-L} \left(\xi_l - \xi_l^e\right) \frac{\partial^2 \dot{\mathcal{I}}}{\partial \xi_l \partial \xi_p}\Big|_{\xi_k=\xi_k^e} \left(\xi_p - \xi_p^e\right) + \dots$$

(5.396)

Substituting from Eq. (5.388), we find near equilibrium that

$$\dot{\mathcal{I}} = -\frac{1}{T}\sum_{l=1}^{N-L}\sum_{p=1}^{N-L}\sum_{k=1}^{N-L} \left(\xi_l - \xi_l^e\right) \frac{\partial \hat{\omega}_k}{\partial \xi_p}\Big|_{\xi_k=\xi_k^e} \frac{\partial^2 G}{\partial \xi_l \partial \xi_k}\Big|_{\xi_k=\xi_k^e} \left(\xi_p - \xi_p^e\right) + \dots$$

(5.397)

Lastly, let us study whether $\dot{\mathcal{I}}$ is a Lyapunov function. We can show that $\dot{\mathcal{I}} > 0$, $\xi_p \neq \xi_p^e$, and $\dot{\mathcal{I}} = 0$, $\xi_p = \xi_p^e$. Now, to determine whether or not the Lyapunov function exists, we must study $d\dot{\mathcal{I}}/dt$:

$$\frac{d\dot{\mathcal{I}}}{dt} = \sum_{p=1}^{N-L} \frac{\partial \dot{\mathcal{I}}}{\partial \xi_p} \frac{d\xi_p}{dt},$$

(5.398)

$$= \sum_{p=1}^{N-L} \frac{\partial \dot{\mathcal{I}}}{\partial \xi_p} \hat{\omega}_p,$$

(5.399)

$$= \sum_{p=1}^{N-L} \left(-\frac{1}{T} \sum_{k=1}^{N-L} \left(\frac{\partial \hat{\omega}_k}{\partial \xi_p} \frac{\partial G}{\partial \xi_k} + \hat{\omega}_k \frac{\partial^2 G}{\partial \xi_p \partial \xi_k} \right) \right) \hat{\omega}_p, \tag{5.400}$$

$$= -\frac{1}{T} \sum_{p=1}^{N-L} \sum_{k=1}^{N-L} \left(\frac{\partial \hat{\omega}_k}{\partial \xi_p} \frac{\partial G}{\partial \xi_k} \hat{\omega}_p + \hat{\omega}_p \frac{\partial^2 G}{\partial \xi_p \partial \xi_k} \hat{\omega}_k \right). \tag{5.401}$$

At the equilibrium state, $\hat{\omega}_k = 0$, so obviously $d\dot{\mathcal{I}}/dt = 0$, at equilibrium. Away from equilibrium, we know from our uniqueness analysis that the term $\partial^2 G/\partial \xi_p \partial \xi_k$ is positive semi-definite; so this term contributes to rendering $d\dot{\mathcal{I}}/dt < 0$. But the other term does not transparently contribute.

Let us examine the gradient of $d\dot{\mathcal{I}}/dt$. It is

$$\frac{\partial}{\partial \xi_m} \frac{d\dot{\mathcal{I}}}{dt} = -\frac{1}{T} \sum_{p=1}^{N-L} \sum_{k=1}^{N-L} \left(\frac{\partial^2 \hat{\omega}_k}{\partial \xi_m \partial \xi_p} \frac{\partial G}{\partial \xi_k} \hat{\omega}_p + \frac{\partial \hat{\omega}_k}{\partial \xi_p} \frac{\partial^2 G}{\partial \xi_m \partial \xi_k} \hat{\omega}_p + \frac{\partial \hat{\omega}_k}{\partial \xi_p} \frac{\partial G}{\partial \xi_k} \frac{\partial \hat{\omega}_p}{\partial \xi_m} \right.$$
$$\left. + \frac{\partial \hat{\omega}_p}{\partial \xi_m} \frac{\partial^2 G}{\partial \xi_p \partial \xi_k} \hat{\omega}_k + \hat{\omega}_p \frac{\partial^3 G}{\partial \xi_m \partial \xi_p \partial \xi_k} \hat{\omega}_k + \hat{\omega}_p \frac{\partial^2 G}{\partial \xi_p \partial \xi_k} \frac{\partial \hat{\omega}_k}{\partial \xi_m} \right). \tag{5.402}$$

At equilibrium, all terms in the gradient of $d\dot{\mathcal{I}}/dt$ are zero, so it is a critical point.

Let us next study the Hessian of $d\dot{\mathcal{I}}/dt$ to ascertain the nature of this critical point. Because there are so many terms, let us only write those terms which will be non-zero at equilibrium. In this limit, the Hessian is

$$\frac{\partial^2}{\partial \xi_n \partial \xi_m} \frac{d\dot{\mathcal{I}}}{dt} \bigg|_{eq} = -\frac{1}{T} \sum_{p=1}^{N-L} \sum_{k=1}^{N-L} \left(\frac{\partial \hat{\omega}_k}{\partial \xi_p} \frac{\partial^2 G}{\partial \xi_m \partial \xi_k} \frac{\partial \hat{\omega}_p}{\partial \xi_n} + \frac{\partial \hat{\omega}_k}{\partial \xi_p} \frac{\partial^2 G}{\partial \xi_n \partial \xi_k} \frac{\partial \hat{\omega}_p}{\partial \xi_m} \right.$$
$$\left. + \frac{\partial \hat{\omega}_p}{\partial \xi_m} \frac{\partial^2 G}{\partial \xi_p \partial \xi_k} \frac{\partial \hat{\omega}_k}{\partial \xi_n} + \frac{\partial \hat{\omega}_p}{\partial \xi_n} \frac{\partial^2 G}{\partial \xi_p \partial \xi_k} \frac{\partial \hat{\omega}_k}{\partial \xi_m} \right). \tag{5.403}$$

With some effort, it may be possible to show the total sum is negative semi-definite. This would guarantee that $d\dot{\mathcal{I}}/dt < 0$ away from equilibrium. If so, then it is true that $\dot{\mathcal{I}}$ is a Lyapunov function in the neighborhood of equilibrium. Far from equilibrium, it is not clear whether or not a Lyapunov function exists.

5.4.3 Zel'dovich mechanism example

Let us now consider a numerical example, building on the analysis of Sec. 1.1.2; many numerical details have already been presented and will not be repeated here. For the conditions simulated in Sec. 1.1.2, we plot $dS/dt|_{E,V}/V = \dot{\mathcal{I}}/V$ as a function of time as predicted by the full theory of Eq. (5.62), repeated here in slightly modified form

$$\frac{1}{V} \frac{dS}{dt} \bigg|_{E,V} = \frac{\dot{\mathcal{I}}}{V} = \mathbf{r}^T \cdot \left(\frac{\overline{\boldsymbol{\alpha}}}{T} \right), \tag{5.404}$$
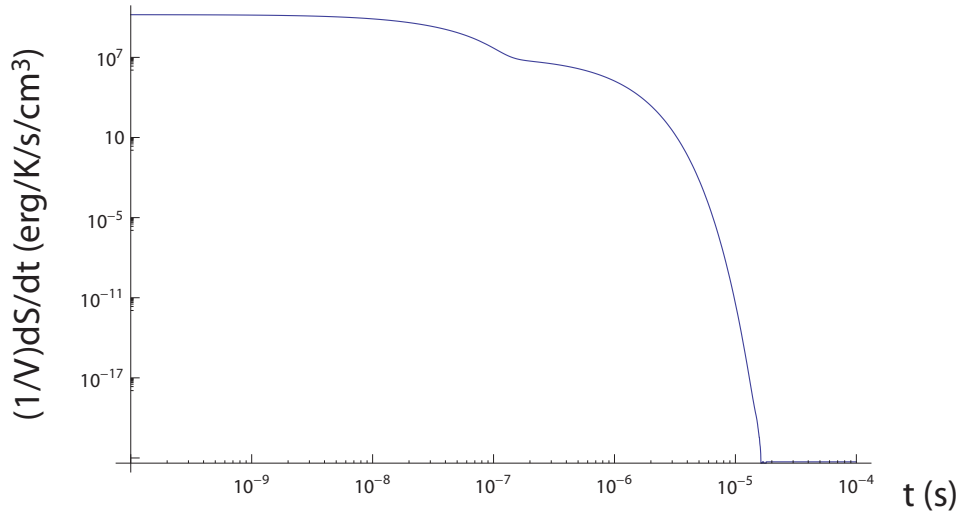
Figure 5.2:   Irreversibility production rate versus time for the Zel'dovich mechanism problem of Sec. 1.1.2.

in Fig. 5.2. Clearly, $\dot{\mathcal{I}}/V$ is always positive and approaches zero as the system approaches equilibrium. Note that we have made no appeal to notions of Onsager nor have we confined ourselves to the neighborhood of equilibrium. The function $\dot{\mathcal{I}}/V$ is non-linear, positive, and decreases to zero by its construction, which is consistent with the Clausius-Duhem results shown earlier on p. 198.

Now, let us consider the system of Sec. 1.1.2 in the language of Onsager reciprocity. We see from Eq. (1.160) that

$$\boldsymbol{\nu}^T = \begin{pmatrix} -1 & -1 & 1 & 1 & 0 \\ 1 & -1 & 0 & 1 & -1 \end{pmatrix}. \tag{5.405}$$

Here, it is easily shown that $\boldsymbol{\nu}^T$ is of full rank, $R = 2$, and thus has two linearly independent column vectors. Following the discussion of Eq. (5.323), let us simply choose the first two column vectors of $\boldsymbol{\nu}^T$ to form the matrix $\mathbf{C}$:

$$\mathbf{C} = \begin{pmatrix} -1 & -1 \\ 1 & -1 \end{pmatrix}. \tag{5.406}$$

Then, by Eq. (5.332), we find the projection matrix $\mathbf{B}$ to be

$$\mathbf{B} = \mathbf{C} \cdot \left(\mathbf{C}^T \cdot \mathbf{C} \right)^{-1} \cdot \mathbf{C}^T, \tag{5.407}$$

$$= \begin{pmatrix} -1 & -1 \\ 1 & -1 \end{pmatrix} \cdot \left(\begin{pmatrix} -1 & 1 \\ -1 & -1 \end{pmatrix} \cdot \begin{pmatrix} -1 & -1 \\ 1 & -1 \end{pmatrix} \right)^{-1} \begin{pmatrix} -1 & 1 \\ -1 & -1 \end{pmatrix}, \tag{5.408}$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{5.409}$$

Remarkably, we recover the identity matrix: $\mathbf{B} = \mathbf{I}$. For more general reaction mechanisms which have $\boldsymbol{\nu}^T$ of less than full rank, this will not be true.

So, from Eq. (5.334), we find one of the Onsager matrices to reduce to

$$\mathsf{L} = \mathbf{B}^T \cdot \mathbf{R}' \cdot \mathbf{B} = \mathbf{I}^T \cdot \mathbf{R}' \cdot \mathbf{I} = \mathbf{R}' = \begin{pmatrix} \mathcal{R}_1' & 0 \\ 0 & \mathcal{R}_2' \end{pmatrix}. \tag{5.410}$$

Since each $\mathcal{R}_j$, $j = 1, \ldots, J$, is positive semi-definite, the matrix $\mathbf{R}'$ is positive semi-definite. We can then cast the entropy production of Eq. (5.333) as

$$\left. \frac{dS}{dt} \right|_{E,V} = \underbrace{\frac{V}{\overline{R}} \left(\frac{\overline{\boldsymbol{\alpha}}^T}{T} \right) \cdot \mathsf{L}}_{\sim \mathbf{j}^T} \cdot \underbrace{\left(\frac{\overline{\boldsymbol{\alpha}}}{T} \right)}_{=\mathbf{x}}. \tag{5.411}$$

Comparing Eqs. (5.411) and (5.65), we see in the Onsager limit that

$$\mathbf{j}^T \sim \frac{V}{\overline{R}} \left(\frac{\overline{\boldsymbol{\alpha}}^T}{T} \right) \cdot \mathsf{L} = \frac{V}{\overline{R}} \mathbf{x}^T \cdot \mathsf{L}. \tag{5.412}$$

Transposing both sides, we can also say

$$\mathbf{j} \sim \frac{V}{\overline{R}} \mathsf{L}^T \cdot \left(\frac{\overline{\boldsymbol{\alpha}}}{T} \right) = \frac{V}{\overline{R}} \mathsf{L}^T \cdot \mathbf{x}. \tag{5.413}$$

We also can recast in the standard form

$$\left. \frac{dS}{dt} \right|_{E,V} = \dot{\mathcal{I}} = \frac{V}{\overline{R}} \mathbf{x}^T \cdot \mathsf{L} \cdot \mathbf{x}. \tag{5.414}$$

For the conditions simulated in Sec. 1.1.2, we plot $\dot{\mathcal{I}}/V$ as a function of time for both the full non-linear model as well as the prediction in the Onsager limit of Eq. (5.411) in Fig. 5.3. Clearly at early time the two theories predict different values, but the Onsager limit become a better approximation as equilibrium is approached.

Numerically, direct substitution of values at equilibrium shows that

$$\mathsf{L} = \begin{pmatrix} 0.573127 & 0 \\ 0 & 0.549134 \end{pmatrix}. \tag{5.415}$$

The units of the entries of L are $mole/cm^3/s$.

Now at equilibrium, Eq. (5.12) tells us the affinity of each reaction must be zero; thus, at equilibrium, we must have $\mathbf{x} = \mathbf{0}$. This then induces the fluxes $\mathbf{j} = \mathbf{0}$ at equilibrium. Near equilibrium, it is possible to perform Prigogine's extremization exercise surrounding Eq. (P6.8). Recognizing that for our problem $\mathsf{L}_{12} = \mathsf{L}_{21} = 0$, which may not hold for more general problems, we slightly extend our analysis to consider the more general case. For such a case, we have near equilibrium that

$$\begin{pmatrix} j_1 \\ j_2 \end{pmatrix} = \frac{V}{\overline{R}} \begin{pmatrix} \mathsf{L}_{11}^T & \mathsf{L}_{12}^T \\ \mathsf{L}_{21}^T & \mathsf{L}_{22}^T \end{pmatrix} \cdot \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}. \tag{5.416}$$
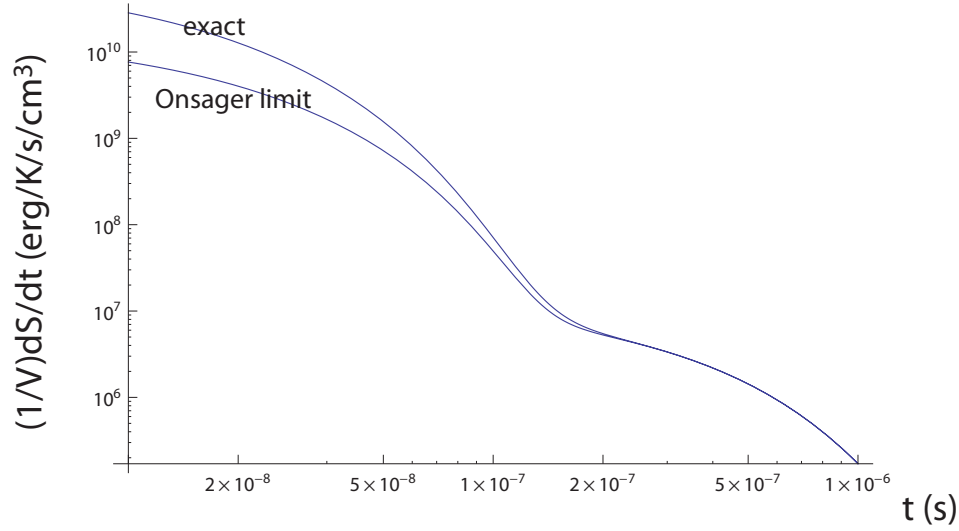
Figure 5.3:   Irreversibility production rate versus time for the Zel'dovich mechanism problem of Sec. 1.1.2 for the full non-linear model and the Onsager limit.

Thus,

$$j_1 \;\; = \;\; \frac{V}{\overline{R}} \left(L_{11}^T x_1 + L_{12}^T x_2 \right), \tag{5.417}$$

$$j_2 \;\; = \;\; \frac{V}{\overline{R}} \left(L_{21}^T x_1 + L_{22}^T x_2 \right), \tag{5.418}$$

$$\tag{5.419}$$

The irreversibility production becomes

$$\dot{\mathcal{I}} = \frac{V}{\overline{R}} \left(L_{11}^T x_1^2 + \left(L_{12}^T + L_{21}^T \right) x_1 x_2 + L_{22}^T x_2^2 \right) \tag{5.420}$$

Let us extremize $\dot{\mathcal{I}}$. We then require at a critical point

$$\frac{\partial \dot{\mathcal{I}}}{\partial x_1} \;\; = \;\; \frac{V}{\overline{R}} \left(2 L_{11}^T x_1 + \left(L_{12}^T + L_{21}^T \right) x_2 \right) = 0, \tag{5.421}$$

$$\frac{\partial \dot{\mathcal{I}}}{\partial x_2} \;\; = \;\; \frac{V}{\overline{R}} \left(\left(L_{12}^T + L_{21}^T \right) x_1 + 2 L_{22}^T x_2 \right) = 0. \tag{5.422}$$

Now by its method of construction, L must be symmetric; thus, $L_{12}^T = L_{21}^T$, and we can thus state at an extreme point that

$$\frac{\partial \dot{\mathcal{I}}}{\partial x_1} \;\; = \;\; \frac{2V}{\overline{R}} \left(L_{11}^T x_1 + L_{12}^T x_2 \right) = 2 j_1 = 0, \tag{5.423}$$

$$\frac{\partial \dot{\mathcal{I}}}{\partial x_2} \;\; = \;\; \frac{2V}{\overline{R}} \left(L_{21}^T x_1 + L_{22}^T x_2 \right) = 2 j_2 = 0. \tag{5.424}$$

Thus, $j_1 = j_2 = 0$ at an extremum of $\dot{\mathcal{I}}$, consistent with Eq. (P6.6).

Away from equilibrium, there is no simple way to formulate $\dot{\mathcal{I}}$ explicitly in terms of affinity. One can however easily formulate $\dot{\mathcal{I}}$ globally in terms of reduced species variables ξ_k as in Eq. (5.382). While the formulation is straightforward, its mathematical form is lengthy, and will not be repeated here. Following the analysis after Eq. (5.382), one can form the gradient and Hessian of $\dot{\mathcal{I}}$, and note that at chemical equilibrium that $\dot{\mathcal{I}} = 0$ and $\nabla \dot{\mathcal{I}} = 0$. Moreover, from Eq. (5.393), we see that the Hessian of $\dot{\mathcal{I}}$ is positive definite, so that in fact $\dot{\mathcal{I}}$ is a minimum at equilibrium.

For our Zel'dovich example problem, the Hessian matrix evaluated at chemical equilibrium is from Eq. (5.388):

$$\left. \frac{\partial^2 \dot{\mathcal{I}}}{\partial \xi_l \partial \xi_p} \right|_{\xi_k = \xi_k^e} = \begin{pmatrix} 6.81073 \times 10^{20} & -1.06440 \times 10^{21} \\ -1.06440 \times 10^{21} & 1.46438 \times 10^{23} \end{pmatrix}. \tag{5.425}$$

The units of each of the entries of the Hessian are $erg/K/s/mole^2$. The eigenvalues of the Hessian are 1.464×10^{23} and 6.733×10^{20}, as expected positive definite.

5.4.4 Extended Zel'dovich mechanism example

The example of the previous section induced a diagonal Onsager matrix because the matrix $\boldsymbol{\nu}$ was full rank. Let us extend the kinetics mechanism so as to induce a $\boldsymbol{\nu}$ which is less than full rank, and thus induce a full Onsager matrix. To do so, we can add N_2 and O_2 dissociation mechanisms to our kinetics laws. We take our extended Zel'dovich reaction mechanism to be

$$N + NO \;\rightleftharpoons\; N_2 + O, \tag{5.426}$$
$$N + O_2 \;\rightleftharpoons\; NO + O, \tag{5.427}$$
$$N_2 + N_2 \;\rightleftharpoons\; 2N + N_2, \tag{5.428}$$
$$O_2 + O_2 \;\rightleftharpoons\; 2O + O_2. \tag{5.429}$$

For this system we have $N = 5$ species composed of $L = 2$ elements reacting in $J = 4$ reactions. We take the reaction constants for the first two reactions from Sec. 1.1.2; the N_2 and O_2 dissociation kinetic rates are those given earlier on p. 167, and in Sec. 1.1.1.2.1.1, respectively.

Applying the extended Zel'dovich model for the same conditions simulated in Sec. 1.1.2, we plot $\overline{\rho}_{NO}$, $\overline{\rho}_N$ and $\overline{\rho}_{O_2}$ as a function of time in Fig. 5.4. We note that the results for NO and N are similar to those for the ordinary Zel'dovich mechanism, see Fig. 1.8, at early time. But at late time there is an additional equilibration with more complicated dynamics, with the relative concentrations of NO and N switching places in importance.

We summarize some of the key vectors and matrices involved in the analysis. We adopt

$\bar\rho_{NO}, \bar\rho_N, \bar\rho_{O_2}$ (mole/cm³)
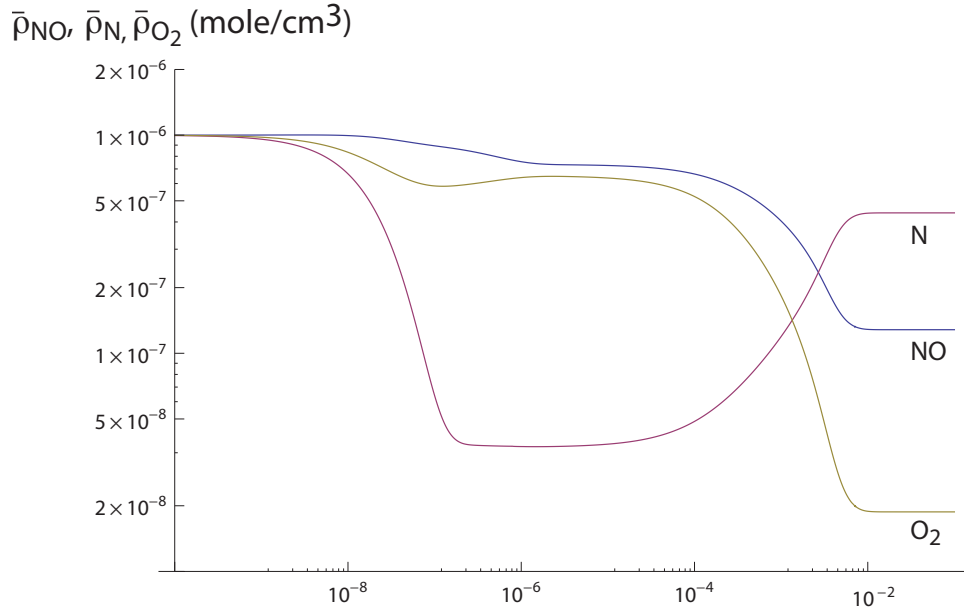
Figure 5.4: NO, N, and O_2 concentrations versus time for $T = 6000\ K$, extended Zel'dovich mechanism.

Eq. (1.154) for our vector of $N = 5$ concentrations:

$$\overline{\boldsymbol{\rho}} = \begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_N \\ \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix}. \tag{5.430}$$

We have $L = 2$ elements, with N, $(l = 1)$ and O, $(l = 2)$. We adopt Eq. (1.155) for the stoichiometric matrix $\boldsymbol{\phi}$, of dimension $L \times N = 2 \times 5$,

$$\boldsymbol{\phi} = \begin{pmatrix} 1 & 1 & 2 & 0 & 0 \\ 1 & 0 & 0 & 1 & 2 \end{pmatrix}. \tag{5.431}$$

The first row of $\boldsymbol{\phi}$ is for the N atom; the second row is for the O atom. For the $J = 4$ reactions, we take

$$\mathbf{r} = \begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \end{pmatrix}, \tag{5.432}$$

where the rates are given by the standard law of mass action kinetics, not shown in detail

here. The matrix $\boldsymbol{\nu}$, of dimension $N \times J = 5 \times 4$ is new for this problem and is

$$\boldsymbol{\nu} = \begin{pmatrix} -1 & 1 & 0 & 0 \\ -1 & -1 & 2 & 0 \\ 1 & 0 & -1 & 0 \\ 1 & 1 & 0 & 2 \\ 0 & -1 & 0 & -1 \end{pmatrix}. \tag{5.433}$$

The matrix $\boldsymbol{\nu}$ has rank $R = N - L = 3$. It is not full rank in this case, in contrast to the previous example. Our stoichiometric constraint on element conservation for each reaction, Eq. (1.22), $\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \mathbf{0}$, holds here:

$$\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \begin{pmatrix} 1 & 1 & 2 & 0 & 0 \\ 1 & 0 & 0 & 1 & 2 \end{pmatrix} \cdot \begin{pmatrix} -1 & 1 & 0 & 0 \\ -1 & -1 & 2 & 0 \\ 1 & 0 & -1 & 0 \\ 1 & 1 & 0 & 2 \\ 0 & -1 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{5.434}$$

With a similar analysis to that given in Sec. 1.1.2, we find that

$$\underbrace{\begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_{N} \\ \overline{\rho}_{N_2} \\ \overline{\rho}_{O} \\ \overline{\rho}_{O_2} \end{pmatrix}}_{\overline{\boldsymbol{\rho}}} = \underbrace{\begin{pmatrix} \widehat{\overline{\rho}}_{NO} \\ \widehat{\overline{\rho}}_{N} \\ \widehat{\overline{\rho}}_{N_2} \\ \widehat{\overline{\rho}}_{O} \\ \widehat{\overline{\rho}}_{O_2} \end{pmatrix}}_{\widehat{\overline{\boldsymbol{\rho}}}} + \underbrace{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -\frac{1}{2} & -\frac{1}{2} & 0 \\ -1 & 0 & -2 \\ 0 & 0 & 1 \end{pmatrix}}_{\mathbf{D}} \underbrace{\begin{pmatrix} \overline{\xi}_{NO} \\ \overline{\xi}_{N} \\ \overline{\xi}_{O_2} \end{pmatrix}}_{=\overline{\boldsymbol{\xi}}}. \tag{5.435}$$

This takes the form of Eq. (1.37):

$$\overline{\boldsymbol{\rho}} = \widehat{\overline{\boldsymbol{\rho}}} + \mathbf{D} \cdot \overline{\boldsymbol{\xi}}. \tag{5.436}$$

Here, the matrix $\mathbf{D}$ is of dimension $N \times R = 5 \times 3$. It spans the same column space as does the $N \times J$ matrix $\boldsymbol{\nu}$ which is of rank R. Note that $\boldsymbol{\phi} \cdot \mathbf{D} = \mathbf{0}$:

$$\boldsymbol{\phi} \cdot \mathbf{D} = \begin{pmatrix} 1 & 1 & 2 & 0 & 0 \\ 1 & 0 & 0 & 1 & 2 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -\frac{1}{2} & -\frac{1}{2} & 0 \\ -1 & 0 & -2 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{5.437}$$

Now let us move to the Onsager analysis. The matrix $\mathbf{C}$ is of dimension $J \times (N-L) = 4 \times 3$ and has in its columns $R = N - L = 3$ linearly independent columns of $\boldsymbol{\nu}^T$. We easily see that $\boldsymbol{\nu}^T$ is

$$\boldsymbol{\nu}^T = \begin{pmatrix} -1 & -1 & 1 & 1 & 0 \\ 1 & -1 & 0 & 1 & -1 \\ 0 & 2 & -1 & 0 & 0 \\ 0 & 0 & 0 & 2 & -1 \end{pmatrix}. \tag{5.438}$$

Now, among many choices, we can take the first, second, and fourth columns of $\boldsymbol{\nu}^T$ to form **C**:

$$\mathbf{C} = \begin{pmatrix} -1 & -1 & 1 \\ 1 & -1 & 1 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}. \tag{5.439}$$

Then, by Eq. (5.332), we find the $J \times J = 4 \times 4$ projection matrix **B** to be

$$\mathbf{B} = \mathbf{C} \cdot \left(\mathbf{C}^T \cdot \mathbf{C} \right)^{-1} \cdot \mathbf{C}^T, \tag{5.440}$$

$$= \begin{pmatrix} \frac{3}{4} & -\frac{1}{4} & -\frac{1}{4} & \frac{1}{4} \\ -\frac{1}{4} & \frac{3}{4} & -\frac{1}{4} & \frac{1}{4} \\ -\frac{1}{4} & -\frac{1}{4} & \frac{3}{4} & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{3}{4} \end{pmatrix}. \tag{5.441}$$

The matrix **B** has rank $N - L = 3$ and is thus not full rank. It has eigenvalues of $1, 1, 1, 0$. The Onsager matrix L is given by

$$\mathsf{L} = \mathbf{B}^T \cdot \mathbf{R}' \cdot \mathbf{B}, \tag{5.442}$$

$$= \frac{1}{16} \begin{pmatrix} 9\mathcal{R}'_1 + \mathcal{R}'_2 + \mathcal{R}'_3 + \mathcal{R}'_4 & -3\mathcal{R}'_1 - 3\mathcal{R}'_2 + \mathcal{R}'_3 + \mathcal{R}'_4 & -3\mathcal{R}'_1 + \mathcal{R}'_2 - 3\mathcal{R}'_3 + \mathcal{R}'_4 & 3\mathcal{R}'_1 - \mathcal{R}'_2 - \mathcal{R}'_3 + 3\mathcal{R}'_4 \\ -3\mathcal{R}'_1 - 3\mathcal{R}'_2 + \mathcal{R}'_3 + \mathcal{R}'_4 & \mathcal{R}'_1 + 9\mathcal{R}'_2 + \mathcal{R}'_3 + \mathcal{R}'_4 & \mathcal{R}'_1 - 3\mathcal{R}'_2 - 3\mathcal{R}'_3 + \mathcal{R}'_4 & -\mathcal{R}'_1 + 3\mathcal{R}'_2 - \mathcal{R}'_3 + 3\mathcal{R}'_4 \\ -3\mathcal{R}'_1 + \mathcal{R}'_2 - 3\mathcal{R}'_3 + \mathcal{R}'_4 & \mathcal{R}'_1 - 3\mathcal{R}'_2 - 3\mathcal{R}'_3 + \mathcal{R}'_4 & \mathcal{R}'_1 + \mathcal{R}'_2 + 9\mathcal{R}'_3 + \mathcal{R}'_4 & -\mathcal{R}'_1 - \mathcal{R}'_2 + 3\mathcal{R}'_3 + 3\mathcal{R}'_4 \\ 3\mathcal{R}'_1 - \mathcal{R}'_2 - \mathcal{R}'_3 + 3\mathcal{R}'_4 & -\mathcal{R}'_1 + 3\mathcal{R}'_2 - \mathcal{R}'_3 + 3\mathcal{R}'_4 & -\mathcal{R}'_1 - \mathcal{R}'_2 + 3\mathcal{R}'_3 + 3\mathcal{R}'_4 & \mathcal{R}'_1 - \mathcal{R}'_2 + \mathcal{R}'_3 + 9\mathcal{R}'_4 \end{pmatrix}. \tag{5.443}$$

One can estimate the behavior of $\dot{\mathcal{I}}$ with both the full non-linear model and its Onsager approximation. As expected, the Onsager approximation works well near equilibrium. Meaningful graphical display of the comparison of the two approximations is difficult due to numerical precision issues. As expected, the Hessian matrix of $\dot{\mathcal{I}}$ is symmetric and positive definite at equilibrium with eigenvalues of 9.245×10^{22}, 1.50×10^{22} and 4.025×10^{17}.

For variety, let us work with a different Onsager matrix. Let us first get the reduced affinity by Eq. (5.326):

$$\hat{\overline{\boldsymbol{\alpha}}} = \left(\mathbf{C}^T \cdot \mathbf{C} \right)^{-1} \cdot \mathbf{C}^T \cdot \overline{\boldsymbol{\alpha}}, \tag{5.444}$$

$$\begin{pmatrix} \hat{\overline{\alpha}}_1 \\ \hat{\overline{\alpha}}_2 \\ \hat{\overline{\alpha}}_3 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{1}{2} & 0 & 0 \\ -\frac{1}{8} & -\frac{1}{8} & \frac{3}{8} & \frac{1}{8} \\ \frac{1}{8} & \frac{1}{8} & \frac{1}{8} & \frac{3}{8} \end{pmatrix} \cdot \begin{pmatrix} \overline{\alpha}_1 \\ \overline{\alpha}_2 \\ \overline{\alpha}_3 \\ \overline{\alpha}_4 \end{pmatrix}, \tag{5.445}$$

$$= \begin{pmatrix} -\frac{\overline{\alpha}_1}{2} + \frac{\overline{\alpha}_2}{2} \\ -\frac{\overline{\alpha}_1}{8} - \frac{\overline{\alpha}_2}{8} + \frac{3\overline{\alpha}_3}{8} + \frac{\overline{\alpha}_4}{8} \\ \frac{\overline{\alpha}_1}{8} + \frac{\overline{\alpha}_2}{8} + \frac{\overline{\alpha}_3}{8} + \frac{3\overline{\alpha}_4}{8} \end{pmatrix}. \tag{5.446}$$

The $(N - L) \times (N - L) = 3 \times 3$ Onsager matrix **L** is given by Eq. (5.331):

$$\mathbf{L} = \mathbf{C}^T \cdot \mathbf{R}' \cdot \mathbf{C}, \tag{5.447}$$

$$
= \begin{pmatrix} -1 & 1 & 0 & 0 \\ -1 & -1 & 2 & 0 \\ 1 & 1 & 0 & 2 \end{pmatrix} \cdot \begin{pmatrix} \mathcal{R}'_1 & 0 & 0 & 0 \\ 0 & \mathcal{R}'_2 & 0 & 0 \\ 0 & 0 & \mathcal{R}'_3 & 0 \\ 0 & 0 & 0 & \mathcal{R}'_4 \end{pmatrix} \cdot \begin{pmatrix} -1 & -1 & 1 \\ 1 & -1 & 1 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad (5.448)
$$

$$
= \begin{pmatrix} \mathcal{R}'_1 + \mathcal{R}'_2 & \mathcal{R}'_1 - \mathcal{R}'_2 & -\mathcal{R}'_1 + \mathcal{R}'_2 \\ \mathcal{R}'_1 - \mathcal{R}'_2 & \mathcal{R}'_1 + \mathcal{R}'_2 + 4\mathcal{R}'_3 & -\mathcal{R}'_1 - \mathcal{R}'_2 \\ -\mathcal{R}'_1 + \mathcal{R}'_2 & -\mathcal{R}'_1 - \mathcal{R}'_2 & \mathcal{R}'_1 + \mathcal{R}'_2 + 4\mathcal{R}'_4 \end{pmatrix}. \quad (5.449)
$$

Then, we can write Eq. (5.330) as

$$
\left. \frac{dS}{dt} \right|_{E,V} = \frac{V}{T} \begin{pmatrix} \hat{\alpha}_1 & \hat{\alpha}_2 & \hat{\alpha}_3 \end{pmatrix} \cdot \begin{pmatrix} \mathcal{R}'_1 + \mathcal{R}'_2 & \mathcal{R}'_1 - \mathcal{R}'_2 & -\mathcal{R}'_1 + \mathcal{R}'_2 \\ \mathcal{R}'_1 - \mathcal{R}'_2 & \mathcal{R}'_1 + \mathcal{R}'_2 + 4\mathcal{R}'_3 & -\mathcal{R}'_1 - \mathcal{R}'_2 \\ -\mathcal{R}'_1 + \mathcal{R}'_2 & -\mathcal{R}'_1 - \mathcal{R}'_2 & \mathcal{R}'_1 + \mathcal{R}'_2 + 4\mathcal{R}'_4 \end{pmatrix} \cdot \begin{pmatrix} \hat{\alpha}_1 \\ \hat{\alpha}_2 \\ \hat{\alpha}_3 \end{pmatrix}.
$$
$$(5.450)$$

In summary, we have spent considerable time exposing notions of production of irreversibility because it is associated with an ongoing debate on whether additional principles beyond the traditional laws of thermodynamics reflect nature. One of the more common contentions is given by Prigogine,[11] who notes

> "We shall see that stationary states may be characterized by an extremum principle which states that in the stationary state, the entropy production has its minimum value compatible with some auxiliary conditions to be specified in each case."

Notions such as these have spurred much activity in a variety of disciplines, including combustion, with the goal of using new principles to better codify observed behaviors. One must note, however, that these notions have also attracted widespread skepticism. A thorough review and discussion is given by Grandy,[12] who notes on p. 170,

> "...these observations do not in themselves seem to support the notion of a *general* extremum principle for dissipation rates in steady-state processes, either linear or nonlinear, near or far from equilibrium."

Grandy concludes on p. 172 that

> "After all is said and done, the issue with which we began this discussion—the role of additional principles in non equilibrium thermodynamics—does not appear to be much closer to a definite resolution. In those cases where we are able to apply a principle of minimum (or maximum) rate of energy dissipation, it seems that we already have sufficient tools in the conservation laws and constitutive equations. Although the conservation laws are exact, the constitutive

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[11]Prigogine, I., 1967, *Introduction to Thermodynamics of Irreversible Processes*, Interscience, New York, p. 75.
[12]Grandy, W. T., 2008, *Entropy and the Time Evolution of Macroscopic Systems*, Oxford, Oxford.

relations are of necessity approximated to some degree, so it may be that the choice of which route to follow very much depends on the details of any specific problem. Rather than focus on some general and improbable principle, it may be more reasonable to search for general conditions or classes of problems for which extremum rate principles might be both valid and productive."

Consistent with Grandy, the analysis presented in these notes does not explicitly rely on invocation of additional extremum principles beyond the ordinary laws of thermodynamics, though one cannot ignore the possibility that such principles may be in play at a deeper level in the construction of constitutive models. But at this stage, we are not prepared to accept as proven that additional laws of nature based on extremizing entropy production rates have been firmly established.

Chapter 6

Reactive Navier-Stokes equations

Double, double toil and trouble;
Fire burn, and caldron bubble.
William Shakespeare (1564-1616), *Macbeth*, Act IV, § i, ll. 10-11.

———————————————-

Up to this point we have exclusively focused on systems which are spatially homogeneous. We now turn to important systems for which the state variables are functions of both time and space. Here, we will focus on a general model for a mixture of gases which are allowed to react, advect, and diffuse. As such, we will present the compressible reactive Navier[1]-Stokes[2] equations for an ideal mixture of N ideal gases. We will not give detailed derivations. We are guided in part by the excellent derivations given by Aris[3] and Merk.[4]

6.1 Evolution axioms

6.1.1 Conservative form

The conservation of mass, linear momenta, and energy, and the entropy inequality for the mixture are expressed in conservative form as

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (6.1)$$

$$\frac{\partial}{\partial t} (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \mathbf{u} + P\mathbf{I} - \boldsymbol{\tau}) = \mathbf{0}, \quad (6.2)$$

$$\frac{\partial}{\partial t} \left(\rho \left(e + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \right) \right) + \nabla \cdot \left(\rho \mathbf{u} \left(e + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \right) + \mathbf{j}^q + (P\mathbf{I} - \boldsymbol{\tau}) \cdot \mathbf{u} \right) = 0, \quad (6.3)$$

[1]Claude-Louis Navier, 1785-1836, French engineer.
[2]George Gabriel Stokes, 1819-1903, Anglo-Irish mathematician.
[3]R. Aris, 1962, *Vectors, Tensors, and the Basic Equations of Fluid Mechanics*, Dover, New York.
[4]H. J. Merk, 1959, "The Macroscopic Equations for Simultaneous Heat and Mass Transfer in Isotropic Continuous and Closed Systems," *Applied Scientific Research*, 8(1): 73-99.

$$\frac{\partial}{\partial t}(\rho s) + \nabla \cdot \left(\rho s \mathbf{u} + \frac{\mathbf{j}^q}{T} \right) \;\geq\; 0. \qquad (6.4)$$

New variables here are the velocity vector $\mathbf{u}$, the viscous shear tensor $\boldsymbol{\tau}$, and the diffusive heat flux vector $\mathbf{j}^q$. Note that these equations are precisely the same one would use for a single fluid. We have neglected body forces.

The evolution of molecular species is dictated by an evolution axiom, an extension of Eq. (5.23) to account for reaction, and now additionally, advection and diffusion:

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho Y_i \mathbf{u} + \mathbf{j}_i^m) \;=\; M_i \dot{\omega}_i, \qquad i = 1, \ldots, N - 1. \qquad (6.5)$$

Here, the diffusive mass flux vector of species i is $\mathbf{j}_i^m$. Note that together, Eqs. (6.1) and $N - 1$ of Eq. (6.5) form N equations for the evolution of the N species. We insist that the species diffusive mass flux be constrained by

$$\sum_{i=1}^{N} \mathbf{j}_i^m = \mathbf{0}. \qquad (6.6)$$

Recalling our earlier definitions of M_i and $\dot{\omega}_i$, Eqs. (5.1) and (5.20), respectively, Eq. (6.5) can be rewritten as

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho Y_i \mathbf{u} + \mathbf{j}_i^m) \;=\; \left(\sum_{l=1}^{L} \mathcal{M}_l \phi_{li} \right) \sum_{j=1}^{J} \nu_{ij} r_j. \qquad (6.7)$$

Let us sum Eq. (6.7) over all species to get

$$\sum_{i=1}^{N} \frac{\partial}{\partial t}(\rho Y_i) + \sum_{i=1}^{N} \nabla \cdot (\rho Y_i \mathbf{u} + \mathbf{j}_i^m) \;=\; \sum_{i=1}^{N} \left(\sum_{l=1}^{L} \mathcal{M}_l \phi_{li} \right) \sum_{j=1}^{J} \nu_{ij} r_j, \qquad (6.8)$$

$$\frac{\partial}{\partial t} \left(\rho \underbrace{\sum_{i=1}^{N} Y_i}_{=1} \right) + \nabla \cdot \left(\rho \mathbf{u} \underbrace{\sum_{i=1}^{N} Y_i}_{=1} + \underbrace{\sum_{i=1}^{N} \mathbf{j}_i^m}_{=0} \right) \;=\; \sum_{i=1}^{N} \sum_{l=1}^{L} \sum_{j=1}^{J} \mathcal{M}_l \phi_{li} \nu_{ij} r_j, \qquad (6.9)$$

$$\;=\; \sum_{j=1}^{J} r_j \sum_{l=1}^{L} \mathcal{M}_l \sum_{i=1}^{N} \underbrace{\phi_{li} \nu_{ij}}_{=0}, \qquad (6.10)$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) \;=\; 0. \qquad (6.11)$$

This is the extension of the spatially homogeneous Eq. (4.399). So, the summation over all species gives a redundancy with Eq. (6.1).

We can get a similar relation for the elements. Let us multiply Eq. (6.5) by our stoichiometric matrix ϕ_{li} to get

$$\phi_{li} \frac{\partial}{\partial t} (\rho Y_i) + \phi_{li} \nabla \cdot (\rho Y_i \mathbf{u} + \mathbf{j}_i^m) = \phi_{li} M_i \dot{\omega}_i, \qquad (6.12)$$

$$\frac{\partial}{\partial t} \left(\frac{\rho \phi_{li} Y_i}{M_i} \right) + \nabla \cdot \left(\frac{\rho \phi_{li} Y_i}{M_i} \mathbf{u} + \phi_{li} \frac{\mathbf{j}_i^m}{M_i} \right) = \phi_{li} \sum_{j=1}^{J} \nu_{ij} r_j. \qquad (6.13)$$

Now sum over all species to get

$$\sum_{i=1}^{N} \frac{\partial}{\partial t} \left(\frac{\rho \phi_{li} Y_i}{M_i} \right) + \sum_{i=1}^{N} \nabla \cdot \left(\frac{\rho \phi_{li} Y_i}{M_i} \mathbf{u} + \phi_{li} \frac{\mathbf{j}_i^m}{M_i} \right) = \sum_{i=1}^{N} \phi_{li} \sum_{j=1}^{J} \nu_{ij} r_j, \qquad (6.14)$$

$$\frac{\partial}{\partial t} \left(\rho \sum_{i=1}^{N} \frac{\phi_{li} Y_i}{M_i} \right) + \nabla \cdot \left(\rho \sum_{i=1}^{N} \frac{\phi_{li} Y_i}{M_i} \mathbf{u} + \sum_{i=1}^{N} \phi_{li} \frac{\mathbf{j}_i^m}{M_i} \right) = \sum_{j=1}^{J} r_j \underbrace{\sum_{i=1}^{N} \phi_{li} \nu_{ij}}_{=0}, \qquad (6.15)$$

$$\frac{\partial}{\partial t} \left(\rho \sum_{i=1}^{N} \frac{\phi_{li} Y_i}{M_i} \right) + \nabla \cdot \left(\rho \sum_{i=1}^{N} \frac{\phi_{li} Y_i}{M_i} \mathbf{u} + \sum_{i=1}^{N} \phi_{li} \frac{\mathbf{j}_i^m}{M_i} \right) = 0, \qquad (6.16)$$

$$\mathcal{M}_l \frac{\partial}{\partial t} \left(\rho \sum_{i=1}^{N} \frac{\phi_{li} Y_i}{M_i} \right) + \mathcal{M}_l \nabla \cdot \left(\rho \sum_{i=1}^{N} \frac{\phi_{li} Y_i}{M_i} \mathbf{u} + \sum_{i=1}^{N} \phi_{li} \frac{\mathbf{j}_i^m}{M_i} \right) = 0, \quad l = 1, \dots, L, \qquad (6.17)$$

$$\frac{\partial}{\partial t} \left(\rho \mathcal{M}_l \sum_{i=1}^{N} \frac{\phi_{li} Y_i}{M_i} \right) + \nabla \cdot \left(\rho \mathcal{M}_l \sum_{i=1}^{N} \frac{\phi_{li} Y_i}{M_i} \mathbf{u} + \mathcal{M}_l \sum_{i=1}^{N} \phi_{li} \frac{\mathbf{j}_i^m}{M_i} \right) = 0, \quad l = 1, \dots, L, \qquad (6.18)$$

Let us now define the element mass fraction Y_l^e, $l = 1, \dots, L$, as

$$Y_l^e \equiv \mathcal{M}_l \sum_{i=1}^{N} \frac{\phi_{li} Y_i}{M_i}. \qquad (6.19)$$

Note that this can be expressed as

$$Y_l^e = \underbrace{\frac{mass\ element\ l}{moles\ element\ l}}_{=\mathcal{M}_l} \sum_{i=1}^{N} \underbrace{\frac{moles\ element\ l}{moles\ species\ i}}_{=\phi_{li}} \underbrace{\frac{mass\ species\ i}{total\ mass}}_{=Y_i} \underbrace{\frac{mole\ species\ i}{mass\ species\ i}}_{=1/M_i}, \qquad (6.20)$$

$$= \frac{mass\ element\ l}{total\ mass}. \qquad (6.21)$$

Similarly, we take the diffusive element mass flux to be

$$\mathbf{j}_l^e \equiv \mathcal{M}_l \sum_{i=1}^{N} \phi_{li} \frac{\mathbf{j}_i^m}{M_i}, \qquad l = 1, \ldots, L. \tag{6.22}$$

Substitute Eqs. (6.19,6.22) into Eq. (6.18) to get

$$\frac{\partial}{\partial t}\left(\rho Y_l^e\right) + \nabla \cdot \left(\rho Y_l^e \mathbf{u} + \mathbf{j}_l^e\right) = 0. \tag{6.23}$$

We also insist that

$$\sum_{l=1}^{L} \mathbf{j}_l^e = \mathbf{0}, \tag{6.24}$$

so as to keep the total mass of each element constant. This is easily seen to be guaranteed. Sum Eq. (6.22) over all elements to get

$$\sum_{l=1}^{L} \mathbf{j}_l^e = \sum_{l=1}^{L} \mathcal{M}_l \sum_{i=1}^{N} \phi_{li} \frac{\mathbf{j}_i^m}{M_i}, \tag{6.25}$$

$$= \sum_{i=1}^{N} \sum_{l=1}^{L} \mathcal{M}_l \phi_{li} \frac{\mathbf{j}_i^m}{M_i}, \tag{6.26}$$

$$= \sum_{i=1}^{N} \frac{\mathbf{j}_i^m}{M_i} \underbrace{\sum_{l=1}^{L} \mathcal{M}_l \phi_{li}}_{=M_i}, \tag{6.27}$$

$$= \sum_{i=1}^{N} \frac{\mathbf{j}_i^m}{M_i} M_i, \tag{6.28}$$

$$= \sum_{i=1}^{N} \mathbf{j}_i^m, \tag{6.29}$$

$$= \mathbf{0}. \tag{6.30}$$

In summary, we have $L-1$ conservation equations for the elements, one global mass conservation equation, and $N-L$ species evolution equations, in general. These add to form N equations for the overall species evolution.

6.1.2 Non-conservative form

It is often convenient to have an alternative non-conservative form of the governing equations.

Let us define the material derivative as

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla. \tag{6.31}$$

6.1.2.1 Mass

Using the product rule to expand the mass equation, Eq. (6.1), we get

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) \;=\; 0, \tag{6.32}$$

$$\underbrace{\frac{\partial \rho}{\partial t} + \mathbf{u} \cdot \nabla \rho}_{=d\rho/dt} + \rho \nabla \cdot \mathbf{u} \;=\; 0, \tag{6.33}$$

$$\frac{d\rho}{dt} + \rho \nabla \cdot \mathbf{u} \;=\; 0. \tag{6.34}$$

6.1.2.2 Linear momentum

We again use the product rule to expand the linear momentum equation, Eq. (6.2):

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \frac{\partial \rho}{\partial t} + \mathbf{u} \nabla \cdot (\rho \mathbf{u}) + \rho \mathbf{u} \cdot \nabla \mathbf{u} + \nabla P - \nabla \cdot \boldsymbol{\tau} \;=\; \mathbf{0}, \tag{6.35}$$

$$\rho \underbrace{\left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right)}_{=d\mathbf{u}/dt} + \mathbf{u} \underbrace{\left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) \right)}_{=0} + \nabla P - \nabla \cdot \boldsymbol{\tau} \;=\; \mathbf{0}, \tag{6.36}$$

$$\rho \frac{d\mathbf{u}}{dt} + \nabla P - \nabla \cdot \boldsymbol{\tau} \;=\; \mathbf{0}. \tag{6.37}$$

The key simplification was effected by using the mass equation Eq. (6.1).

6.1.2.3 Energy

Now, use the product rule to expand the energy equation, Eq. (6.3).

$$\rho \frac{\partial}{\partial t} \left(e + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \right) + \rho \mathbf{u} \cdot \nabla \left(e + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \right) + \left(e + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \right) \underbrace{\left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) \right)}_{=0}$$
$$+ \nabla \cdot \mathbf{j}^q + \nabla \cdot (P\mathbf{u}) - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{u}) = 0, \quad \tag{6.38}$$

$$\rho \frac{\partial}{\partial t} \left(e + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \right) + \rho \mathbf{u} \cdot \nabla \left(e + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \right) + \nabla \cdot \mathbf{j}^q + \nabla \cdot (P\mathbf{u}) - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{u}) = 0. \quad \tag{6.39}$$

We have once again used the mass equation, Eq. (6.1), to simplify. Let us expand more using the product rule:

$$\rho \underbrace{\left(\frac{\partial e}{\partial t} + \mathbf{u} \cdot \nabla e \right)}_{=de/dt} + \rho \mathbf{u} \cdot \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) + \nabla \cdot \mathbf{j}^q + \nabla \cdot (P\mathbf{u}) - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{u}) = 0, \quad \tag{6.40}$$

$$\rho\frac{de}{dt} + \mathbf{u} \cdot \underbrace{\left(\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) + \nabla P - \nabla \cdot \boldsymbol{\tau} \right)}_{=0} + \nabla \cdot \mathbf{j}^q + P\nabla \cdot \mathbf{u} - \boldsymbol{\tau} : \nabla \mathbf{u} = 0, \quad (6.41)$$

$$\rho\frac{de}{dt} + \nabla \cdot \mathbf{j}^q + P\nabla \cdot \mathbf{u} - \boldsymbol{\tau} : \nabla \mathbf{u} = 0. \quad (6.42)$$

We have used the linear momentum equation, Eq. (6.37), to simplify.

From the mass equation, Eq. (6.34), we have $\nabla \cdot \mathbf{u} = -(1/\rho)d\rho/dt$, so the energy equation, Eq. (6.42), can also be written as

$$\rho\frac{de}{dt} + \nabla \cdot \mathbf{j}^q - \frac{P}{\rho}\frac{d\rho}{dt} - \boldsymbol{\tau} : \nabla \mathbf{u} = 0. \quad (6.43)$$

This energy equation can be formulated in terms of enthalpy. Use the definition, Eq. (3.78), $h = e + P/\rho$ to get an expression for dh/dt:

$$dh = de - \frac{P}{\rho^2}d\rho + \frac{1}{\rho}dP, \quad (6.44)$$

$$\frac{dh}{dt} = \frac{de}{dt} - \frac{P}{\rho^2}\frac{d\rho}{dt} + \frac{1}{\rho}\frac{dP}{dt}, \quad (6.45)$$

$$\frac{de}{dt} - \frac{P}{\rho^2}\frac{d\rho}{dt} = \frac{dh}{dt} - \frac{1}{\rho}\frac{dP}{dt}, \quad (6.46)$$

$$\rho\frac{de}{dt} - \frac{P}{\rho}\frac{d\rho}{dt} = \rho\frac{dh}{dt} - \frac{dP}{dt}. \quad (6.47)$$

So, the energy equation, Eq. (6.43), in terms of enthalpy is

$$\rho\frac{dh}{dt} + \nabla \cdot \mathbf{j}^q - \frac{dP}{dt} - \boldsymbol{\tau} : \nabla \mathbf{u} = 0. \quad (6.48)$$

6.1.2.4   Second law

Let us expand Eq. (6.4) to write the second law in non-conservative form.

$$\frac{\partial}{\partial t}(\rho s) + \nabla \cdot \left(\rho s \mathbf{u} + \frac{\mathbf{j}^q}{T} \right) \geq 0, \quad (6.49)$$

$$\rho \underbrace{\left(\frac{\partial s}{\partial t} + \mathbf{u} \cdot \nabla s \right)}_{=ds/dt} + s \underbrace{\left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) \right)}_{=0} + \nabla \cdot \left(\frac{\mathbf{j}^q}{T} \right) \geq 0, \quad (6.50)$$

$$\rho\frac{ds}{dt} + \nabla \cdot \left(\frac{\mathbf{j}^q}{T} \right) \geq 0. \quad (6.51)$$

6.1.2.5 Species

Let us expand Eq. (6.5) to write species evolution in non-conservative form.

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho Y_i \mathbf{u} + \mathbf{j}_i^m) = M_i \dot{\omega}_i, \quad i = 1, \ldots, N-1, \quad (6.52)$$

$$\rho \underbrace{\left(\frac{\partial Y_i}{\partial t} + \mathbf{u} \cdot \nabla Y_i\right)}_{=dY_i/dt} + Y_i \underbrace{\left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u})\right)}_{=0} + \nabla \cdot \mathbf{j}_i^m = M_i \dot{\omega}_i, \quad i = 1, \ldots, N-1, \quad (6.53)$$

$$\rho \frac{dY_i}{dt} + \nabla \cdot \mathbf{j}_i^m = M_i \dot{\omega}_i, \quad i = 1, \ldots, N-1. \quad (6.54)$$

6.1.2.6 Elements

Let us expand Eq. (6.23) to write element conservation in non-conservative form.

$$\frac{\partial}{\partial t}(\rho Y_l^e) + \nabla \cdot (\rho Y_l^e \mathbf{u} + \mathbf{j}_l^e) = 0, \quad l = 1, \ldots, L, \quad (6.55)$$

$$\rho \underbrace{\left(\frac{\partial Y_l^e}{\partial t} + \mathbf{u} \cdot \nabla Y_l^e\right)}_{=dY_l^e/dt} + Y_l^e \underbrace{\left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u})\right)}_{=0} + \nabla \cdot \mathbf{j}_l^e = 0, \quad l = 1, \ldots, L, \quad (6.56)$$

$$\rho \frac{dY_l^e}{dt} + \nabla \cdot \mathbf{j}_l^e = 0, \quad l = 1, \ldots, L. \quad (6.57)$$

6.2 Mixture rules

We adopt the following rules for the ideal mixture:

$$P = \sum_{i=1}^{N} P_i, \quad (6.58)$$

$$1 = \sum_{i=1}^{N} Y_i, \quad (6.59)$$

$$\rho = \sum_{i=1}^{N} \rho_i = \sum_{i=1}^{N} \frac{\overline{\rho}_i}{M_i}, \quad (6.60)$$

$$e = \sum_{i=1}^{N} Y_i e_i, \quad (6.61)$$

$$h = \sum_{i=1}^{N} Y_i h_i, \quad (6.62)$$

$$s = \sum_{i=1}^{N} Y_i s_i, \tag{6.63}$$

$$c_v = \sum_{i=1}^{N} Y_i c_{vi}, \tag{6.64}$$

$$c_P = \sum_{i=1}^{N} Y_i c_{Pi}, \tag{6.65}$$

$$V = V_i, \tag{6.66}$$

$$T = T_i. \tag{6.67}$$

6.3   Constitutive models

The evolution axioms do not form a complete set of equations. Let us supplement these by a set of constitutive model equations appropriate for a mixture of calorically perfect ideal gases that react according the to the law of mass action with an Arrhenius kinetic reaction rate. We have seen many of these models before, and repeat them here for completeness.

For the thermal equation of state, we take the ideal gas law for the partial pressures:

$$P_i = \overline{R}T\overline{\rho}_i = \overline{R}T\frac{\rho Y_i}{M_i} = \overline{R}T\frac{\rho_i}{M_i} = R_i T\rho_i. \tag{6.68}$$

So, the mixture pressure is

$$P = \overline{R}T\sum_{i=1}^{N}\overline{\rho}_i = \overline{R}T\sum_{i=1}^{N}\frac{\rho Y_i}{M_i} = \overline{R}T\sum_{i=1}^{N}\frac{\rho_i}{M_i}. \tag{6.69}$$

For the ideal gas, the enthalpy and internal energy of each component is a function of T at most. We have for the enthalpy of a component

$$h_i = h^o_{T_o,i} + \int_{T_o}^{T} c_{Pi}(\hat{T})d\hat{T}. \tag{6.70}$$

So, the mixture enthalpy is

$$h = \sum_{i=1}^{N} Y_i \left(h^o_{T_o,i} + \int_{T_o}^{T} c_{Pi}(\hat{T})d\hat{T} \right). \tag{6.71}$$

We then use the definition of enthalpy to recover the internal energy of component i:

$$e_i = h_i - \frac{P_i}{\rho_i} = h_i - R_i T. \tag{6.72}$$

So, the mixture internal energy is

$$
\begin{aligned}
e &= \sum_{i=1}^{N} Y_i \left(h_{T_o,i}^o - R_i T + \int_{T_o}^{T} c_{Pi}(\hat{T}) d\hat{T} \right), & (6.73) \\
&= \sum_{i=1}^{N} Y_i \left(h_{T_o,i}^o - R_i(T - T_o) - R_i T_o + \int_{T_o}^{T} c_{Pi}(\hat{T}) d\hat{T} \right), & (6.74) \\
&= \sum_{i=1}^{N} Y_i \left(h_{T_o,i}^o - R_i T_o + \int_{T_o}^{T} (c_{Pi}(\hat{T}) - R_i) d\hat{T} \right), & (6.75) \\
&= \sum_{i=1}^{N} Y_i \left(h_{T_o,i}^o - R_i T_o + \int_{T_o}^{T} c_{vi}(\hat{T}) d\hat{T} \right), & (6.76) \\
&= \sum_{i=1}^{N} Y_i \left(e_{T_o,i}^o + \int_{T_o}^{T} c_{vi}(\hat{T}) d\hat{T} \right). & (6.77)
\end{aligned}
$$

The mixture entropy is

$$
s = \sum_{i=1}^{N} Y_i s_{T_o,i}^o + \int_{T_o}^{T} \frac{c_P(\hat{T})}{\hat{T}} d\hat{T} - \sum_{i=1}^{N} Y_i R_i \ln\left(\frac{P_i}{P_o}\right). \tag{6.78}
$$

The viscous shear stress for an isotropic Newtonian fluid which satisfies Stokes' assumption is

$$
\boldsymbol{\tau} = 2\hat{\mu} \left(\frac{\nabla \mathbf{u} + (\nabla \mathbf{u})^T}{2} - \frac{1}{3}(\nabla \cdot \mathbf{u})\mathbf{I} \right). \tag{6.79}
$$

Here, $\hat{\mu}$ is the mixture viscosity coefficient which is determined from a suitable mixture rule averaging over each component.

The energy flux vector $\mathbf{j}^q$ is written as

$$
\mathbf{j}^q = -\mathsf{k}\nabla T + \sum_{i=1}^{N} \mathbf{j}_i^m h_i - \overline{R}T \sum_{i=1}^{N} \frac{D_i^T}{M_i} \left(\frac{\nabla y_i}{y_i} + \left(1 - \frac{M_i}{M}\right) \frac{\nabla P}{P} \right). \tag{6.80}
$$

Here, k is a suitably mixture averaged thermal conductivity. The parameter D_i^T is the so-called thermal diffusion coefficient. Recall y_i is the mole fraction.

We consider a mass diffusion vector with multicomponent diffusion coefficient D_{ik}:

$$
\mathbf{j}_i^m = \rho \sum_{k=1,\ k\neq i}^{N} \frac{M_i D_{ik} Y_k}{M} \left(\frac{\nabla y_k}{y_k} - \left(1 - \frac{M_k}{M}\right) \frac{\nabla P}{P} \right) - D_i^T \frac{\nabla T}{T}. \tag{6.81}
$$

We adopt, as before, the reaction rate of creation of species i, Eq. (5.20):

$$
\dot{\omega}_i = \sum_{j=1}^{J} \nu_{ij} r_j. \tag{6.82}
$$

Here, r_j is given by the law of mass action, Eq. (5.16):

$$r_j = k_j \prod_{k=1}^{N} \overline{\rho}_k^{\nu'_{kj}} \left(1 - \frac{1}{K_{c,j}} \prod_{k=1}^{N} \overline{\rho}_k^{\nu_{kj}}. \right),$$

(6.83)

The term k_j is given by the Arrhenius kinetics rule, Eq. (5.19):

$$k_j = a_j T^{\beta_j} \exp\left(\frac{-\overline{\mathcal{E}}_j}{\overline{R}T} \right),$$

(6.84)

and the equilibrium constant $K_{c,j}$ for the ideal gas mixture is given by Eq. (5.7):

$$K_{c,j} = \left(\frac{P_o}{\overline{R}T} \right)^{\sum_{i=1}^{N} \nu_{ij}} \exp\left(-\frac{\Delta G_j^o}{\overline{R}T} \right).$$

(6.85)

6.4   Temperature evolution

Because temperature T has an important role in many discussions of combustion, let us formulate our energy conservation principle as a temperature evolution equation by employing a variety of constitutive laws.

Let us begin with Eq. (6.48) coupled with our constitutive rule for h, Eq. (6.71):

$$\rho \frac{d}{dt} \left(\underbrace{\sum_{i=1}^{N} Y_i \underbrace{\left(h_{T_o,i}^o + \int_{T_o}^{T} c_{Pi}(\hat{T}) d\hat{T} \right)}_{=h_i}}_{=h} \right) + \nabla \cdot \mathbf{j}^q - \frac{dP}{dt} - \boldsymbol{\tau} : \nabla \mathbf{u} = 0,$$

(6.86)

$$\rho \frac{d}{dt} \sum_{i=1}^{N} Y_i h_i + \nabla \cdot \mathbf{j}^q - \frac{dP}{dt} - \boldsymbol{\tau} : \nabla \mathbf{u} = 0,$$

(6.87)

$$\sum_{i=1}^{N} \left(\rho Y_i \frac{dh_i}{dt} + \rho h_i \frac{dY_i}{dt} \right) + \nabla \cdot \mathbf{j}^q - \frac{dP}{dt} - \boldsymbol{\tau} : \nabla \mathbf{u} = 0,$$

(6.88)

$$\sum_{i=1}^{N} \left(\rho Y_i c_{Pi} \frac{dT}{dt} + \rho h_i \frac{dY_i}{dt} \right) + \nabla \cdot \mathbf{j}^q - \frac{dP}{dt} - \boldsymbol{\tau} : \nabla \mathbf{u} = 0,$$

(6.89)

$$\rho \frac{dT}{dt} \underbrace{\sum_{i=1}^{N} Y_i c_{Pi}}_{=c_P} + \sum_{i=1}^{N} h_i \underbrace{\rho \frac{dY_i}{dt}}_{=M_i \dot{\omega}_i - \nabla \cdot \mathbf{j}_i^m} + \nabla \cdot \mathbf{j}^q - \frac{dP}{dt} - \boldsymbol{\tau} : \nabla \mathbf{u} = 0,$$

(6.90)

$$\rho c_P \frac{dT}{dt} + \sum_{i=1}^{N} h_i \left(M_i \dot{\omega}_i - \nabla \cdot \mathbf{j}_i^m \right) + \nabla \cdot \mathbf{j}^q - \frac{dP}{dt} - \boldsymbol{\tau} : \nabla \mathbf{u} = 0.$$

(6.91)

Now, let us define the "thermal diffusion" flux $\mathbf{j}^T$ as

$$\mathbf{j}^T \equiv -\overline{R}T \sum_{i=1}^{N} \frac{D_i^T}{M_i} \left(\frac{\nabla y_i}{y_i} + \left(1 - \frac{M_i}{M} \right) \frac{\nabla P}{P} \right). \tag{6.92}$$

With this, our total energy diffusion flux vector $\mathbf{j}^q$, Eq. (6.80), becomes

$$\mathbf{j}^q = -\mathsf{k}\nabla T + \sum_{i=1}^{N} \mathbf{j}_i^m h_i + \mathbf{j}^T. \tag{6.93}$$

Now, substitute Eq. (6.93) into Eq. (6.91) and rearrange to get

$$\rho c_P \frac{dT}{dt} + \sum_{i=1}^{N} h_i \left(M_i \dot{\omega}_i - \nabla \cdot \mathbf{j}_i^m \right) + \nabla \cdot \left(-\mathsf{k}\nabla T + \sum_{i=1}^{N} \mathbf{j}_i^m h_i + \mathbf{j}^T \right)$$
$$= \frac{dP}{dt} + \boldsymbol{\tau} : \nabla \mathbf{u}, \tag{6.94}$$

$$\rho c_P \frac{dT}{dt} + \sum_{i=1}^{N} \left(h_i M_i \dot{\omega}_i - h_i \nabla \cdot \mathbf{j}_i^m + \nabla \cdot (\mathbf{j}_i^m h_i) \right) = \nabla \cdot (\mathsf{k}\nabla T) - \nabla \cdot \mathbf{j}^T + \frac{dP}{dt} + \boldsymbol{\tau} : \nabla \mathbf{u}, \tag{6.95}$$

$$\rho c_P \frac{dT}{dt} + \sum_{i=1}^{N} \left(h_i M_i \dot{\omega}_i + \mathbf{j}_i^m \cdot \nabla h_i \right) = \nabla \cdot (\mathsf{k}\nabla T) - \nabla \cdot \mathbf{j}^T + \frac{dP}{dt} + \boldsymbol{\tau} : \nabla \mathbf{u}, \tag{6.96}$$

$$\rho c_P \frac{dT}{dt} + \sum_{i=1}^{N} \left(h_i M_i \dot{\omega}_i + c_{Pi} \mathbf{j}_i^m \cdot \nabla T \right) = \nabla \cdot (\mathsf{k}\nabla T) - \nabla \cdot \mathbf{j}^T + \frac{dP}{dt} + \boldsymbol{\tau} : \nabla \mathbf{u}. \tag{6.97}$$

So, the equation for the evolution of a material fluid particle is

$$\rho c_P \frac{dT}{dt} = -\sum_{i=1}^{N} \left(h_i M_i \dot{\omega}_i + c_{Pi} \mathbf{j}_i^m \cdot \nabla T \right) + \nabla \cdot (\mathsf{k}\nabla T) - \nabla \cdot \mathbf{j}^T + \frac{dP}{dt} + \boldsymbol{\tau} : \nabla \mathbf{u}. \tag{6.98}$$

Let us impose some more details from the reaction law. First, we recall that $\overline{h}_i = h_i M_i$, so

$$\rho c_P \frac{dT}{dt} = -\sum_{i=1}^{N} \overline{h}_i \dot{\omega}_i - \sum_{i=1}^{N} c_{Pi} \mathbf{j}_i^m \cdot \nabla T + \nabla \cdot (\mathsf{k}\nabla T) - \nabla \cdot \mathbf{j}^T + \frac{dP}{dt} + \boldsymbol{\tau} : \nabla \mathbf{u}. \tag{6.99}$$

Impose now Eq. (6.82) to expand $\dot{\omega}_i$

$$\rho c_P \frac{dT}{dt} = -\sum_{i=1}^{N} \overline{h}_i \sum_{j=1}^{J} \nu_{ij} r_j - \sum_{i=1}^{N} c_{Pi} \mathbf{j}_i^m \cdot \nabla T + \nabla \cdot (\mathsf{k}\nabla T) - \nabla \cdot \mathbf{j}^T + \frac{dP}{dt} + \boldsymbol{\tau} : \nabla \mathbf{u}, \tag{6.100}$$

$$\rho c_P \frac{dT}{dt} = -\sum_{j=1}^{J} r_j \sum_{i=1}^{N} \overline{h}_i \nu_{ij} - \sum_{i=1}^{N} c_{Pi} \mathbf{j}_i^m \cdot \nabla T + \nabla \cdot (\mathsf{k}\nabla T) - \nabla \cdot \mathbf{j}^T + \frac{dP}{dt} + \boldsymbol{\tau} : \nabla \mathbf{u}. \tag{6.101}$$

Now, recall Eq. (5.34):

$$\Delta H_j \equiv \sum_{i=1}^{N} \overline{h}_i \nu_{ij}. \tag{6.102}$$

With this, Eq. (6.101) becomes, after small rearrangement,

$$\rho c_P \frac{dT}{dt} = -\sum_{j=1}^{J} r_j \Delta H_j + \frac{dP}{dt} \underbrace{- \sum_{i=1}^{N} c_{Pi} \mathbf{j}_i^m \cdot \nabla T + \nabla \cdot (\mathsf{k}\nabla T) - \nabla \cdot \mathbf{j}^T + \boldsymbol{\tau} : \nabla \mathbf{u}}_{\text{diffusion effects}}. \tag{6.103}$$

By comparing Eq. (6.103) with Eq. (5.33), it is easy to see the effects of variable pressure and diffusion on how temperature evolves. Interestingly, mass, momentum, and energy diffusion all influence temperature evolution. The non-diffusive terms are combinations of advection, reaction, and spatially homogeneous effects.

6.5   Shvab-Zel'dovich formulation

Under some restrictive assumptions, we can simplify the energy equation considerably. Let us assume

- the low Mach[5] number limit is applicable, which can be shown to imply that pressure changes and work work due to viscous dissipation are negligible at leading order, $dP/dt \sim 0$, $\boldsymbol{\tau} : \nabla \mathbf{u} \sim 0$,

- the incompressible limit applies, $d\rho/dt = 0$,

- thermal diffusion is negligible, $D_i^T \sim 0$,

- all species have identical molecular masses, so that $M_i = M$,

- the multicomponent diffusion coefficients of all species are equal, $D_{ij} = \mathcal{D}$,

- all species possess identical specific heats, $c_{Pi} = c_P$, which is itself a constant, and

- energy diffuses at the same rate as mass so that $\mathsf{k}/c_P = \rho \mathcal{D}$.

With the low Mach number limit, the energy equation, Eq. (6.48), reduces to

$$\rho \frac{dh}{dt} + \nabla \cdot \mathbf{j}^q = 0. \tag{6.104}$$

---

[5]Ernst Mach, 1838-1916, Austrian physicist.

With $D_i^T = 0$, the diffusive energy flux vector, Eq. (6.80), reduces to

$$\mathbf{j}^q = -\mathsf{k}\nabla T + \sum_{i=1}^{N} \mathbf{j}_i^m h_i. \tag{6.105}$$

Substituting Eq. (6.105) into Eq. (6.104), we get

$$\rho\frac{dh}{dt} + \nabla \cdot \left(-\mathsf{k}\nabla T + \sum_{i=1}^{N} \mathbf{j}_i^m h_i\right) = 0. \tag{6.106}$$

With all component specific heats equal and constant, $c_{Pi} = c_P$, Eq. (6.71) for the mixture enthalpy reduces to

$$h = \sum_{i=1}^{N} Y_i\left(h_{T_o,i}^o + c_P(T - T_o)\right), \tag{6.107}$$

$$= c_P(T - T_o) + \sum_{i=1}^{N} Y_i h_{T_o,i}^o. \tag{6.108}$$

Similarly for a component, Eq. (6.70) reduces to

$$h_i = h_{T_o,i}^o + c_P(T - T_o). \tag{6.109}$$

With Eqs. (6.108,6.109), Eq. (6.106) transforms to

$$\rho c_P\frac{dT}{dt} + \rho\frac{d}{dt}\left(\sum_{i=1}^{N} Y_i h_{T_o,i}^o\right) - \nabla \cdot \left(\mathsf{k}\nabla T - \sum_{i=1}^{N} \mathbf{j}_i^m\left(h_{T_o,i}^o + c_P(T - T_o)\right)\right) = 0, \tag{6.110}$$

$$\rho c_P\frac{dT}{dt} + \rho\frac{d}{dt}\left(\sum_{i=1}^{N} Y_i h_{T_o,i}^o\right) - \nabla \cdot \left(\mathsf{k}\nabla T - \sum_{i=1}^{N} \mathbf{j}_i^m h_{T_o,i}^o - c_P(T - T_o)\underbrace{\sum_{i=1}^{N} \mathbf{j}_i^m}_{=0}\right) = 0, \tag{6.111}$$

$$\rho c_P\frac{dT}{dt} + \rho\frac{d}{dt}\left(\sum_{i=1}^{N} Y_i h_{T_o,i}^o\right) - \nabla \cdot \left(\mathsf{k}\nabla T - \sum_{i=1}^{N} \mathbf{j}_i^m h_{T_o,i}^o\right) = 0, \tag{6.112}$$

$$\rho c_P\frac{d}{dt}\left(T + \frac{\sum_{i=1}^{N} Y_i h_{T_o,i}^o}{c_P}\right) - \nabla \cdot \left(\mathsf{k}\nabla T - \sum_{i=1}^{N} \mathbf{j}_i^m h_{T_o,i}^o\right) = 0, \tag{6.113}$$

With $M = M_i$, we recover mass fractions to be identical to mole fractions, $Y_k = y_k$. Using this along with our assumptions of negligible thermal diffusion, $D_i^T = 0$ and equal multicomponent diffusion coefficients, $D_{ij} = \mathcal{D}$, the mass diffusion flux vector, Eq. (6.81), reduces to

$$\mathbf{j}_i^m = \rho \sum_{k=1, k \neq i}^{N} \mathcal{D} \nabla Y_k, \tag{6.114}$$

$$= \rho \mathcal{D} \sum_{k=1, k \neq i}^{N} \nabla Y_k, \tag{6.115}$$

$$= \rho \mathcal{D} \nabla \sum_{k=1, k \neq i}^{N} Y_k, \tag{6.116}$$

$$= \rho \mathcal{D} \nabla \left(-Y_i + \underbrace{\sum_{k=1}^{N} Y_k}_{=1} \right), \tag{6.117}$$

$$= \rho \mathcal{D} \nabla \left(-Y_i + 1 \right), \tag{6.118}$$

$$= -\rho \mathcal{D} \nabla Y_i. \tag{6.119}$$

Now, substitute Eq. (6.119) into Eq. (6.113) and use our equidiffusion rate assumption, $\rho \mathcal{D} = \mathsf{k}/c_P$, to get

$$\rho c_P \frac{d}{dt} \left(T + \frac{\sum_{i=1}^{N} Y_i h_{T_o,i}^o}{c_P} \right) - \nabla \cdot \left(\mathsf{k} \nabla T + \rho \mathcal{D} \sum_{i=1}^{N} \nabla Y_i h_{T_o,i}^o \right) = 0, \tag{6.120}$$

$$\rho c_P \frac{d}{dt} \left(T + \frac{\sum_{i=1}^{N} Y_i h_{T_o,i}^o}{c_P} \right) - \nabla \cdot \left(\mathsf{k} \nabla T + \frac{\mathsf{k}}{c_P} \sum_{i=1}^{N} \nabla Y_i h_{T_o,i}^o \right) = 0, \tag{6.121}$$

$$\frac{d}{dt} \left(T + \frac{\sum_{i=1}^{N} Y_i h_{T_o,i}^o}{c_P} \right) - \frac{\mathsf{k}}{\rho c_P} \nabla \cdot \left(\nabla \left(T + \frac{\sum_{i=1}^{N} Y_i h_{T_o,i}^o}{c_P} \right) \right) = 0. \tag{6.122}$$

Now, iff

- there is a spatially uniform distribution of the quantity $T + (1/c_P) \sum_{i=1}^{N} Y_i h_{T_o,i}^o$ at $t = 0$, and

- there is no flux of $T + (1/c_P) \sum_{i=1}^{N} Y_i h_{T_o,i}^o$ at the boundary of the spatial domain for all time,

then, Eq. (6.122) can be satisfied for all time by the algebraic relation

$$T + \frac{\sum_{i=1}^{N} Y_i h_{T_o,i}^o}{c_P} = T(0) + \frac{\sum_{i=1}^{N} Y_i(0) h_{T_o,i}^o}{c_P}, \tag{6.123}$$

where $T(0)$ and $Y_i(0)$ are constants at the spatially uniform initial state. We can slightly rearrange to write

$$\underbrace{c_P(T - T_o) + \sum_{i=1}^{N} Y_i h_{T_o,i}^o}_{=h(T,Y_i)} = \underbrace{c_P(T(0) - T_o) + \sum_{i=1}^{N} Y_i(0) h_{T_o,i}^o}_{=h(T(0),Y_i(0))}, \qquad (6.124)$$

$$h(T, Y_i) = h(T(0), Y_i(0)). \qquad (6.125)$$

This simply says the enthalpy function is a constant, which can be evaluated at the initial state.

Chapter 7

Linear combustion: advection-reaction-diffusion

In order to acquire a better understanding of the fundaments of combustion, a model problem is employed here to illustrate the basic ideas. Consider the following linear advection-diffusion-reaction problem:

$$\frac{\partial}{\partial t}\psi(x,t) + u\frac{\partial}{\partial x}\psi(x,t) = \mathcal{D}\frac{\partial^2}{\partial x^2}\psi(x,t) - a\psi(x,t), \tag{7.1a}$$

$$\psi(x,0) = \psi_u, \tag{7.1b}$$

$$\psi(0,t) = \psi_u, \tag{7.1c}$$

$$\frac{\partial \psi}{\partial x}(\infty,t) \rightarrow 0, \tag{7.1d}$$

where the independent variables are $t > 0$ and $x \in (0,\infty)$. Here, $\psi(x,t)$ is a general scalar, $u > 0$ is a constant advective wave speed, $\mathcal{D} > 0$ is a constant diffusion coefficient, and $a > 0$ is the chemical consumption rate constant.

The spatially homogeneous version of Eqs. (7.1) is

$$\frac{d\psi_h(t)}{dt} = -a\psi_h(t), \qquad \psi_h|_{t=0} = \psi_u, \tag{7.2a}$$

which has the solution

$$\psi_h(t) = \exp\left(-at\right)\psi_u. \tag{7.2b}$$

The time scale τ over which ψ_h evolves is

$$\tau = \frac{1}{a}. \tag{7.3}$$

This time scale serves as an upper bound for the required time step to capture the dynamics in a numerical simulation. Since there is only one dependent variable in this problem, the temporal spectrum contains only one time scale. Consequently, this formulation of the system is not temporally stiff.

A simple means to determine the relevant length scales, and consequently, an upper bound for the required spatial grid resolution, is to obtain the steady structure $\psi_s(x)$, which is governed by the time-independent version of Eqs. (7.1):

$$u\frac{d\psi_s(x)}{dx} = \mathcal{D}\frac{d^2\psi_s(x)}{dx^2} - a\psi_s(x), \qquad \psi_s|_{x=0} = \psi_u, \quad \frac{d\psi_s}{dx}\bigg|_{x\to\infty} \to 0. \tag{7.4a}$$

Assuming solutions of the form $\psi_s = Ce^{\lambda x}$, we are led to a characteristic polynomial of

$$u\lambda = \mathcal{D}\lambda^2 - a, \tag{7.4b}$$

which has roots

$$\lambda = \frac{u}{2\mathcal{D}}\left(1 \pm \sqrt{1 + \frac{4a\mathcal{D}}{u^2}}\right). \tag{7.4c}$$

Taking λ_+ to denote the + root, for which $\lambda_+ > 0$, and λ_- to denote the minus root, for which $\lambda_- < 0$, the solution takes the form

$$\psi_s(x) = C_1 e^{\lambda_+ x} + C_2 e^{\lambda_- x}, \tag{7.4d}$$

where C_1 and C_2 are constants. Thus, taking the spatial derivative, we get

$$\frac{d\psi_s}{dx} = C_1\lambda_+ e^{\lambda_+ x} + C_2\lambda_- e^{\lambda_- x}, \tag{7.4e}$$

In the limit of large positive x, the boundary condition requires the derivative to vanish giving

$$\lim_{x\to\infty} \frac{d\psi_s}{dx} = 0 = \lim_{x\to\infty}\left(C_1\lambda_+ e^{\lambda_+ x} + C_2\lambda_- e^{\lambda_- x}\right). \tag{7.4f}$$

Because $\lambda_+ > 0$, we must insist that $C_1 = 0$ in order to satisfy the far field boundary condition. Then, enforcing that $\psi_s(0) = \psi_u$, we find the solution of Eq. (7.4a) is

$$\psi_s(x) = \exp(\lambda_- x)\,\psi_u, \tag{7.4g}$$

where

$$\lambda_- = \frac{u}{2\mathcal{D}}\left(1 - \sqrt{1 + \frac{4a\mathcal{D}}{u^2}}\right). \tag{7.4h}$$

Here, there is one length scale in the system, $\ell \equiv 1/|\lambda_-|$; this formulation of the system is not spatially stiff. By examining Eq. (7.4h) in the limit $a\mathcal{D}/u^2 \gg 1$, one finds that

$$\ell \approx \sqrt{\frac{\mathcal{D}}{a}} = \sqrt{\mathcal{D}\tau}, \tag{7.5}$$

where $\tau = 1/a$ is the time scale from spatially homogeneous reaction. So, this length scale ℓ reflects the inherent physics of coupled reaction-advection-diffusion. In the opposite limit of $a\mathcal{D}/u^2 \ll 1$, one finds $\lambda \to 0$, $\ell \to \infty$, and $\psi_s(x) \to \psi_u$, a constant.

Now, for Eqs. (7.1), it is possible to find a simple analytic expression for the continuous spectrum of time scales τ associated with a particular linearly independent mode of wavenumber $\hat{k}$. A linearly independent mode with wavenumber $\hat{k}$ has wavelength $\Lambda = 2\pi/\hat{k}$. Assume a solution of the form

$$\psi(x,t) = \exp\left(i\hat{k}x\right)\Psi(t), \tag{7.6}$$

where $\Psi(t)$ is the time-dependent amplitude of the chosen linearly independent mode. Substituting this into Eq. (7.1a) gives

$$\frac{d\Psi(t)}{dt} = -\lambda\Psi(t), \qquad \Psi(0) = \Psi_o, \tag{7.7}$$

where

$$\lambda = a\left(1 + \frac{\mathcal{D}\hat{k}^2}{a} + \frac{i\hat{k}u}{a}\right). \tag{7.8}$$

This has a solution of the form

$$\Psi(t) = \exp\left(-\lambda t\right)\Psi_o. \tag{7.9}$$

We see that the continuous time scale spectrum for amplitude growth or decay is given by

$$\tau = \frac{1}{|\text{Re}(\lambda)|} = \frac{1}{a\left(1 + \frac{\mathcal{D}\hat{k}^2}{a}\right)}, \qquad 0 < \hat{k} \in \mathbb{R}. \tag{7.10}$$

From Eq. (7.10), it is clear that for $\mathcal{D}\hat{k}^2/a \ll 1$, *i.e.* for sufficiently small wavenumbers or long wavelengths, the time scales of amplitude growth or decay will be dominated by reaction:

$$\lim_{\hat{k}\to 0} \tau = \frac{1}{a}. \tag{7.11a}$$

However, for $\mathcal{D}\hat{k}^2/a \gg 1$, *i.e.* for sufficiently large wavenumbers or small wavelengths, the amplitude growth/decay time scales are dominated by diffusion:

$$\lim_{\hat{k}\to\infty} \tau = \frac{1}{\mathcal{D}\hat{k}^2} = \frac{1}{\mathcal{D}}\left(\frac{\Lambda}{2\pi}\right)^2. \tag{7.11b}$$

From Eq. (7.10), we see that a balance between reaction and diffusion exists for $\hat{k} = \sqrt{a/\mathcal{D}}$. In terms of wavelength, and recalling Eqs. (7.5), we see the balance at

$$\frac{\Lambda}{2\pi} = \frac{1}{\hat{k}} = \sqrt{\frac{\mathcal{D}}{a}} = \sqrt{\mathcal{D}\tau} = \ell, \tag{7.12}$$

where $\ell = 1/\hat{k}$ is proportional to the wavelength.

The oscillatory behavior is of lesser importance. The continuous time scale spectrum for oscillatory mode, τ_O is given by

$$\tau_O = \frac{1}{|\mathrm{Im}(\lambda)|} = \frac{1}{\hat{k}u}. \tag{7.13}$$

As $\hat{k} \to 0$, $\tau_O \to \infty$. While $\tau_O \to 0$ as $\hat{k} \to \infty$, it approaches at a rate $\sim 1/\hat{k}$, in contrast to the more demanding time scale of diffusion which approaches zero at a faster rate $\sim 1/\hat{k}^2$. Thus, it is clear that advection does not play a role in determining the limiting values of the time scale spectrum; reaction and diffusion are the major players. Lastly, it is easy to show in the absence of diffusion, that the length scale where reaction effects balance advection effects is found at

$$\ell = \frac{u}{a} = u\tau, \tag{7.14}$$

where $\tau = 1/a$ is the time scale from spatially homogeneous chemistry.

As an illustration, we examine the behavior of the system quantitatively by choosing arbitrary numerical values, loosely motivated by parameters of gas phase systems, of $a = 10^8 \ 1/s$, $\mathcal{D} = 10^1 \ cm^2/s$, $u = 10^2 \ cm/s$. For these values, we find the estimate from Eq. (7.5) for the length scale where reaction balances diffusion as $\ell = \Lambda/(2\pi) = 3.16228 \times 10^{-4} \ cm$. A plot of τ versus $\ell = \Lambda/(2\pi)$ from Eq. (7.10) is given in Fig. 7.1. For long wavelengths, the time scales are determined by reaction; for fine wavelengths, the time scale's falloff is dictated by diffusion, and our simple formula for the critical $\ell = \sqrt{\mathcal{D}\tau}$, illustrated as a dashed line, predicts the transition well. For large $\hat{k}$, it is seen that a one decade decrease in ℓ induces a two decade decrease in τ, consistent with the prediction of Eq. (7.11b): $\lim_{\hat{k}\to\infty} (\ln \tau) \sim 2\ln(\ell) - \ln(\mathcal{D})$. Lastly, over the same range of ℓ, the oscillatory time scales induced by advection are orders of magnitude less demanding, and are thus not included in the plot.

The results of this simple analysis can be summarized as follows:

- *Long wavelength spatial disturbances have early time dynamics which are dominated by chemistry; each spatial point behaves as an isolated spatially homogeneous reactor. Late time dynamics are dictated by diffusion.*

- *Short wavelength spatial disturbances have early time dynamics which are dominated by diffusion; diffusion first smears the disturbance and then reaction acts over late time scales, such that at late time the reaction is spatially homogeneous over the entire spatial domain.*

- *Intermediate wavelength spatial disturbances have time dynamics determined by fully coupled combination diffusion and chemistry. The critical intermediate length scale where this balance exists is given by $\ell = \sqrt{\mathcal{D}\tau}$.*
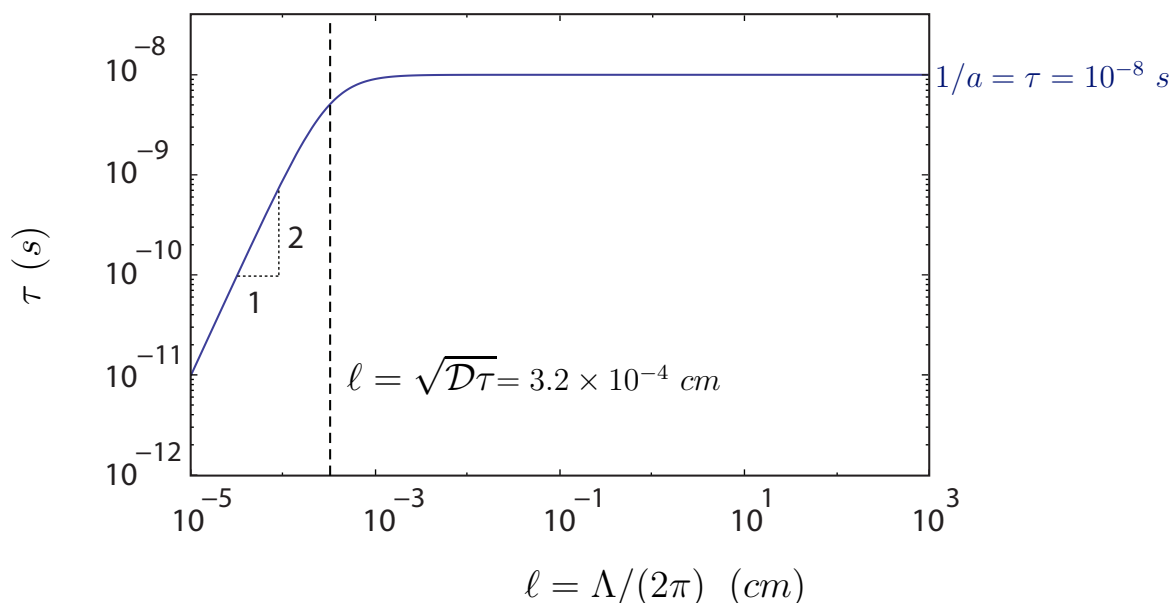
Figure 7.1: Time scale spectrum versus wavelength for the simple reaction-advection-diffusion model.

- *A fully resolved computation of a combustion process with advection-reaction-diffusion requires*

$$\Delta t \quad < \quad \tau, \tag{7.15}$$
$$\Delta x \quad < \quad \sqrt{\mathcal{D}\tau}. \tag{7.16}$$

Less restrictive choices will not capture time dynamics and spatial structures inherent in the continuum model.

- *Advection usually plays a secondary role in determining time dynamics.*

We show analogous results for a detailed kinetics reaction-advection-diffusion combustion system in Fig. 7.2. The analysis necessary to generate these results is detailed and given by Al-Khateeb, and Powers, *et al.*[1] Fig. 7.2 has an analog in Al-Khateeb and Powers, but was analyzed in a slightly different fashion. This is inconsequential for our present discussion.

The results of Fig. 7.2 were obtained for an $N = 9$-species, $L = 3$-element, $J = 19$-reaction model of hydrogen-air kinetics augmented by both advection and multi-component mass and energy diffusion. To obtain the figure, an equilibrium state was subjected to linear perturbation, and the corresponding eigenvalues and eigenfunctions were determined. The time scales are the reciprocals of the real parts of the eigenvalues.

---

[1] Al-Khateeb, A. N. and Powers, J. M., 2010, "Analysis of the Reaction-Advection-Diffusion Spectrum of Laminar Premixed Flames," 48th AIAA Aerospace Sciences Meeting, Orlando, Florida, AIAA-2010-0954.
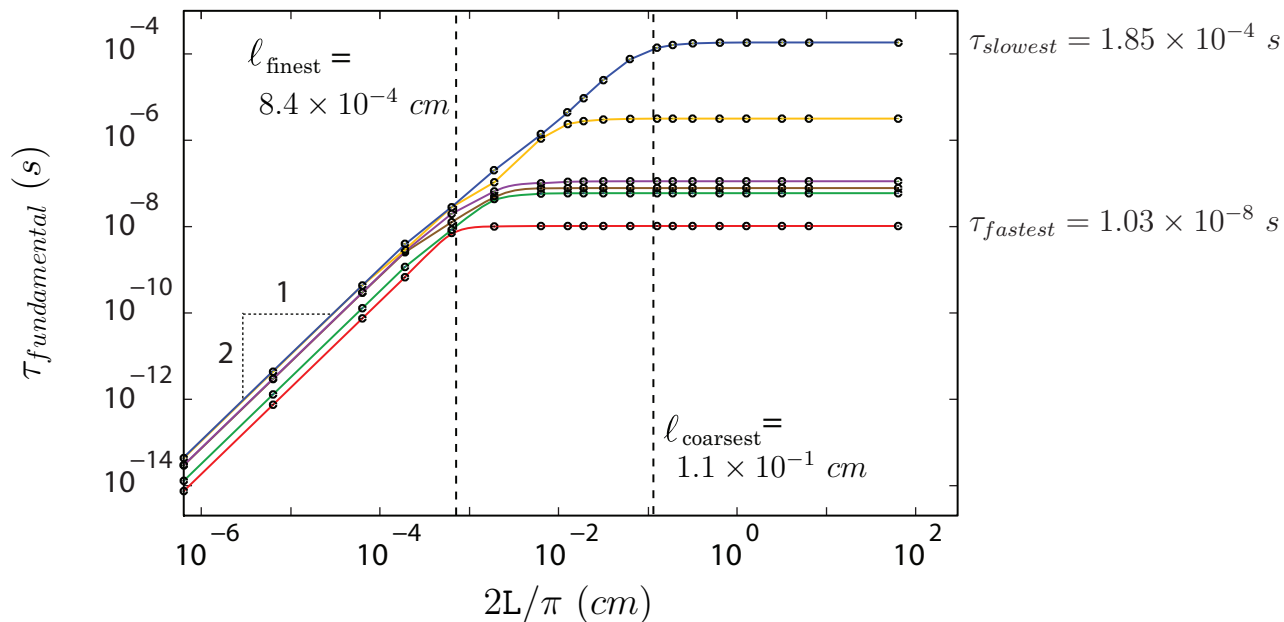
Figure 7.2: Time scales associated with the fundamental modes for a nine-species, nineteen step stoichiometric, $p = 1\ atm$, $T_o = 800\ K$ hydrogen–air reaction-advection-diffusion system versus the length $2L/\pi$.

For long length scales, the time scales are effectively identical to those obtained by analysis of a spatially homogeneous system. Thus we see clearly $N - L = 6$ independent time scales. The fastest is $\tau_{fastest} = 1.03 \times 10^{-8}\ s$ and the slowest is $\tau_{slowest} = 1.85 \times 10^{-4}\ s$. As the length scale is decreased, one finds that diffusive effects first become important in describing dynamics associated with the slowest reaction model. As the length scale continues to decrease, diffusion becomes more and more important for each progressively faster reaction mode, until the fastest reaction mode is reached. With the diffusion coefficient estimated independently as $\mathcal{D}_{mix} = 68.91\ cm^2/s$, the coarsest and finest transition length scale, $\ell_{coarsest}$ and ℓ_{finest} are found to be

$$
\begin{aligned}
\ell_{coarsest} &= \sqrt{\mathcal{D}_{mix}\tau_{slowest}} = 1.1 \times 10^{-1}\ cm, & (7.17) \\
\ell_{finest} &= \sqrt{\mathcal{D}_{mix}\tau_{fastest}} = 8.4 \times 10^{-4}\ cm. & (7.18)
\end{aligned}
$$

Chapter 8

Simple solid combustion: reaction-diffusion

Here, we will modify the simple thermal explosion theory of Sec. 1.2.1 which balanced unsteady evolution against reaction to include the effects of diffusion. Starting from a fully unsteady formulation, we will focus on cases which are steady, resulting in a balance between reaction and diffusion; however, we will briefly consider a balance between all three effects. Such a theory is known after its founder as Frank-Kamenetskii[1] theory. In particular, we will look for transitions from a low temperature reaction to a high temperature reaction, mainly in the context of steady state solutions, i.e. solutions with no time dependence. We draw upon the work of Buckmaster and Ludford for guidance.[2]

8.1 Simple planar model

Let us consider a slab of *solid* fuel/oxidizer mixture. The material is modelled to be of infinite extent in the y and z directions and has length $2L$ in the x direction. The temperature at each end, $x = \pm L$, is held fixed at $T = T_o$.

The slab is initially unreacted. Exothermic conversion of solid material from reactants to products will generate an elevated temperature within the slab $T > T_o$, for $x \in (-L, L)$. If the thermal energy generated diffuses rapidly enough, the temperature within the slab will be $T \sim T_o$, and the reaction rate will be low. If the energy generated by local reaction diffuses slowly, it will accumulate in the interior, accelerate the local reaction rate, and induce rapid energy release and high temperature.

Let us assume

- The material is an immobile, incompressible solid with constant specific heat,

  - Thus, ρ is constant,

---

[1]David Albertovich Frank-Kamenetskii, 1910-1970, Soviet physicist.
[2]Buckmaster, J. D., and Ludford, G. S. S., 1983, *Lectures on Mathematical Combustion*, SIAM, Philadelphia. See Chapter 1.

- – Thus, $c_P = c_v$ is a constant,

  – Thus, there is no advective transport of mass, momentum, or energy: $\mathbf{u} = \mathbf{0}$.

- The material has variation only with x and t,

- The reaction can be modelled as

$$A \rightarrow B, \tag{8.1}$$

  where A and B have identical molecular masses.

- The reaction is irreversible,

- The reaction is exothermic,

- Initially only A is present,

- The thermal conductivity, k is constant.

Let us take, as we did in thermal explosion theory, Sec. 1.2.1

$$
\begin{aligned}
Y_A &= 1 - \lambda, \tag{8.2} \\
Y_B &= \lambda. \tag{8.3}
\end{aligned}
$$

We interpret λ as a *reaction progress variable* which has $\lambda \in [0, 1]$. For $\lambda = 0$, the material is all A; when $\lambda = 1$, the material is all B.

8.1.1   Model equations

Our simple model for reaction is

$$
\begin{aligned}
\frac{\partial \lambda}{\partial t} &= a e^{-\overline{\mathcal{E}}/\overline{R}/T}(1 - \lambda), \tag{8.4} \\
\rho \frac{\partial e}{\partial t} &= -\frac{\partial \mathsf{q}}{\partial x}, \tag{8.5} \\
\mathsf{q} &= -\mathsf{k}\frac{\partial T}{\partial x}, \tag{8.6} \\
e &= c_v T - \lambda q. \tag{8.7}
\end{aligned}
$$

Equation (8.4) is our reaction kinetics law. It is the equivalent of the earlier derived Eq. (1.281) in the irreversible limit, $K_c \rightarrow \infty$. Equation (8.5) is our energy conservation expression. It amounts to Eq. (6.42), with q playing the role of the heat flux $\mathbf{j}^q$. Equation (8.6) is the constitutive law for heat flux; it is the equivalent of Eq. (6.80) when mass diffusion is neglected and amounts to Fourier's[3] law. Equation (8.7) is our caloric equation of state; it is Eq. (1.314) with $q = \overline{e}^o_{T_o,A} - \overline{e}^o_{T_o,B}$ and $Y_B = \lambda$. Equations (8.4-8.7) are completed by initial and boundary conditions, which are

$$T(-L, t) = T(L, t) = T_o, \qquad T(x, 0) = T_o, \qquad \lambda(x, 0) = 0. \tag{8.8}$$

[3]Jean Baptiste Joseph Fourier, 1768-1830, French mathematician.

8.1.2 Simple planar derivation

Let us perform a simple "control volume" derivation of the planar energy equation, Eq. (8.7). Consider a small volume of dimension A by Δx. At the left boundary x, we have heat flux q, in which we notate as q_x. At the right boundary, $x + \Delta x$, we have heat flux out of $\mathsf{q}_{x+\Delta x}$. Recall the units of heat flux are $J/m^2/s$.

The first law of thermodynamics is

$$\text{change in total energy} = \text{heat in} - \underbrace{\text{work out}}_{=0}. \tag{8.9}$$

There is no work for our system. But there is heat flux over system boundaries. In a combination of symbols and words, we can say

$$\underbrace{\text{total energy @ } t + \Delta t - \text{total energy @ } t}_{\text{unsteady}} = \underbrace{\text{energy flux in} - \text{energy flux out}}_{\underbrace{\text{advection}_{=0} \text{ and diffusion}}}. \tag{8.10}$$

Mathematically, we can say

$$E|_{t+\Delta t} - E|_t = -\left(E_{flux\ out} - E_{flux\ in}\right), \tag{8.11}$$

$$\underbrace{\rho A \Delta x}_{kg} \underbrace{\left(e|_{t+\Delta t} - e|_t\right)}_{J/kg} = -\underbrace{\left(\mathsf{q}_{x+\Delta x} - \mathsf{q}_x\right)}_{J/m^2/s} \underbrace{A \Delta t}_{(m^2\ s)}, \tag{8.12}$$

$$\rho \frac{e|_{t+\Delta t} - e|_t}{\Delta t} = -\left(\frac{\mathsf{q}_{x+\Delta x} - \mathsf{q}_x}{\Delta x}\right) \tag{8.13}$$

Now, let $\Delta x \to 0$ and $\Delta t \to 0$, and we get

$$\rho \frac{\partial e}{\partial t} = -\frac{\partial \mathsf{q}_x}{\partial x}. \tag{8.14}$$

Now, standard constitutive theory gives Fourier's law to specify the heat flux:

$$\mathsf{q} = -\mathsf{k}\frac{\partial T}{\partial x}. \tag{8.15}$$

So, Eq. (8.15) along with the thermal state equation, (8.7) when substituted into Eq. (8.14) yield

$$\rho \frac{\partial}{\partial t}\left(c_v T - \lambda q\right) = \mathsf{k}\frac{\partial^2 T}{\partial x^2}, \tag{8.16}$$

$$\rho c_v \frac{\partial T}{\partial t} - \rho q \frac{\partial \lambda}{\partial t} = \mathsf{k}\frac{\partial^2 T}{\partial x^2}, \tag{8.17}$$

$$\rho c_v \frac{\partial T}{\partial t} - \rho q a e^{-\overline{\mathcal{E}}/\overline{R}/T}(1 - \lambda) = \mathsf{k}\frac{\partial^2 T}{\partial x^2}, \tag{8.18}$$

$$\rho c_v \frac{\partial T}{\partial t} = \mathsf{k}\frac{\partial^2 T}{\partial x^2} + \rho q a e^{-\overline{\mathcal{E}}/\overline{R}/T}(1 - \lambda). \tag{8.19}$$

So, our complete system is two equations in two unknowns with appropriate initial and boundary conditions:

$$\rho c_v \frac{\partial T}{\partial t} = \mathsf{k}\frac{\partial^2 T}{\partial x^2} + \rho q a e^{-\overline{\mathcal{E}}/\overline{R}/T}(1-\lambda), \qquad (8.20)$$

$$\frac{\partial \lambda}{\partial t} = a e^{-\overline{\mathcal{E}}/\overline{R}/T}(1-\lambda), \qquad (8.21)$$

$$T(-L,t) = T(L,t) = T_o, \qquad T(x,0) = T_o, \qquad \lambda(x,0) = 0. \qquad (8.22)$$

8.1.3   *Ad hoc* approximation

Let us consider an *ad hoc* approximation to a system much like Eqs. (8.20-8.22), but which has the advantage of being one equation and one unknown.

8.1.3.1   Planar formulation

If there were no diffusion, Eq. (8.14) would yield $\partial e/\partial t = 0$ and would lead us to conclude that $e(x,t) = e(x)$. And because we have nothing now to introduce a spatial inhomogeneity, there is no reason to take $e(x)$ to be anything other than a constant e_o. That would lead us to

$$e(x,t) = e_o, \qquad (8.23)$$

so

$$e_o = c_v T - \lambda q. \qquad (8.24)$$

Now, at $t = 0$, $\lambda = 0$, and $T = T_o$, so $e_o = c_v T_o$; thus,

$$c_v T_o = c_v T - \lambda q, \qquad (8.25)$$

$$\lambda = \frac{c_v(T-T_o)}{q}. \qquad (8.26)$$

We also get the final temperature at $\lambda = 1$ to be

$$T(\lambda = 1) = T_o + \frac{q}{c_v}. \qquad (8.27)$$

We shall adopt Eq. (8.26) as our model for λ in place of Eq. (8.21). Had we admitted species diffusion, we could more rigorously have arrived at a similar result, but it would be more difficult to justify treating the material as a solid.

Let us use Eq. (8.26) to eliminate λ in Eq. (8.20) so as to get a single equation for T:

$$\rho c_v \frac{\partial T}{\partial t} = \mathsf{k}\frac{\partial^2 T}{\partial x^2} + \underbrace{\rho q a e^{-\overline{\mathcal{E}}/\overline{R}/T}\left(1 - \frac{c_v(T-T_o)}{q}\right)}_{\text{reaction source term}}, \qquad (8.28)$$

The first two terms in Eq. (8.28) are nothing more than the classical heat equation. The non-classical term is an algebraic source term due to chemical reaction. Note when $T = T_o$, the reaction source term is $\rho q a \exp(-\overline{\mathcal{E}}/\overline{R}/T) > 0$, so at the initial state there is a tendency to increase the temperature. When $\lambda = 1$, so $T = T_o + q/c_v$, the reaction source term is zero, so there is no local heat release. This effectively accounts for reactant depletion.

Scaling the equation by ρc_v and employing the well known formula for thermal diffusivity $\alpha = \mathsf{k}/\rho/c_P \sim \mathsf{k}/\rho/c_v$ for the solid, we get

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + a \left(\frac{q}{c_v} - (T - T_o) \right) e^{-\overline{\mathcal{E}}/\overline{R}/T}, \tag{8.29}$$

$$T(-L, t) = T(L, t) = T_o, \qquad T(x, 0) = T_o. \tag{8.30}$$

From here on, we shall consider Eqs. (8.30) and cylindrical and spherical variants to be the full problem. We shall consider solutions to it in various limits. We will not return here to the original problem without the *ad hoc* assumption, but that would be a straightforward exercise.

8.1.3.2 More general coordinate systems

We note that Eq. (8.30) can be extended to general coordinate systems via

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T + a \left(\frac{q}{c_v} - (T - T_o) \right) e^{-\overline{\mathcal{E}}/\overline{R}/T}. \tag{8.31}$$

Appropriate initial and boundary conditions for the particular coordinate system would be necessary.

For one-dimensional solutions in planar, cylindrical, and spherical coordinates, one can summarize the formulations as

$$\frac{\partial T}{\partial t} = \alpha \frac{1}{x^m} \frac{\partial}{\partial x} \left(x^m \frac{\partial T}{\partial x} \right) + a \left(\frac{q}{c_v} - (T - T_o) \right) e^{-\overline{\mathcal{E}}/\overline{R}/T}. \tag{8.32}$$

Here, we have $m = 0$ for a planar coordinate system, $m = 1$ for cylindrical, and $m = 2$ for spherical. For cylindrical and spherical systems, the Dirichlet boundary condition at $x = -L$ would be replaced with a boundedness condition on T at $x = 0$.

8.2 Non-dimensionalization

Let us non-dimensionalize Eqs. (8.31). The scaling we will choose is not unique.

Let us define non-dimensional variables

$$T_* = \frac{c_v(T - T_o)}{q}, \qquad x_* = \frac{x}{L}, \qquad t_* = at. \tag{8.33}$$

With these choices, Eqs. (8.31) transform to

$$
\frac{qa}{c_v}\frac{\partial T_*}{\partial t_*} = \frac{q}{c_v}\alpha\frac{1}{L^2}x_*^{-m}\frac{\partial}{\partial x_*}\left(x_*^m\frac{\partial T_*}{\partial x_*}\right)
$$

$$
+a\left(\frac{q}{c_v}-\frac{q}{c_v}T_*\right)\exp\left(-\frac{\overline{\mathcal{E}}}{\overline{R}}\frac{1}{T_o+(q/c_v)T_*}\right), \tag{8.34}
$$

$$
\frac{\partial T_*}{\partial t_*} = \frac{\alpha}{aL^2}x_*^{-m}\frac{\partial}{\partial x_*}\left(x_*^m\frac{\partial T_*}{\partial x_*}\right) + (1-T_*)\exp\left(-\frac{\overline{\mathcal{E}}}{\overline{R}T_o}\frac{1}{\left(1+\left(\frac{q}{c_vT_o}\right)T_*\right)}\right). \tag{8.35}
$$

Now, both sides are dimensionless. Let us define the dimensionless parameters

$$
\mathfrak{D} = \frac{aL^2}{\alpha}, \qquad \Theta = \frac{\overline{\mathcal{E}}}{\overline{R}T_o}, \qquad Q = \frac{q}{c_vT_o}. \tag{8.36}
$$

Here, $\mathfrak{D}$ is a so-called Damköhler[4] number. If we recall a diffusion time scale τ_d is

$$
\tau_d = \frac{L^2}{\alpha}, \tag{8.37}
$$

and a first estimate (which will be shown to be crude) of the reaction time scale, τ_r is

$$
\tau_r = \frac{1}{a}. \tag{8.38}
$$

We see that the Damköhler number is the ratio of the thermal diffusion time to the reaction time (ignoring activation energy effects!):

$$
\mathfrak{D} = \frac{L^2/\alpha}{1/a} = \frac{\tau_d}{\tau_r} = \frac{\text{thermal diffusion time}}{\text{reaction time}}. \tag{8.39}
$$

We can think of Θ and Q as ratios as well with

$$
\Theta = \frac{\text{activation energy}}{\text{ambient energy}}, \qquad Q = \frac{\text{exothermic heat release}}{\text{ambient energy}}. \tag{8.40}
$$

The initial and boundary conditions scale to

$$
T_*(-1,t_*) = T_*(1,t_*) = 0, \qquad T_*(x_*,0) = 0, \qquad \text{if} \qquad m=0, \tag{8.41}
$$

$$
T_*(1,t_*) = 0, \qquad T_*(0,t_*) < \infty, \qquad T_*(x_*,0) = 0, \qquad \text{if} \qquad m=1,2. \tag{8.42}
$$

---

[4]Gerhard Damköhler, 1908-1944, German chemist.

8.2.1 Diffusion time discussion

As an aside, let us consider in more depth the thermal diffusion time. Consider the dimensional heat equation

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}, \tag{8.43}$$

with a complex representation of a sinusoidal initial condition:

$$T(x,0) = Ae^{i\hat{k}x}. \tag{8.44}$$

Here, A is a temperature amplitude, $\hat{k}$ is the wave number, and $i^2 = -1$. If one wants, one can insist we only worry about the real part of the solution, but that will not be important for this analysis. Note that since

$$Ae^{i\hat{k}x} = A\cos(\hat{k}x) + Ai\sin(\hat{k}x),$$

we can think of the initial condition as a signal with wavelength $\lambda = 2\pi/\hat{k}$. Note when the wave number $\hat{k}$ is large, the wavelength λ is small, and vice versa.

Let us assume a separation of variables solution of the form

$$T(x,t) = B(t)e^{i\hat{k}x}. \tag{8.45}$$

Thus,

$$\frac{\partial T}{\partial t} = \frac{dB}{dt}e^{i\hat{k}x}, \tag{8.46}$$

and

$$\frac{\partial T}{\partial x} = i\hat{k}Be^{i\hat{k}x}, \tag{8.47}$$

$$\frac{\partial^2 T}{\partial x^2} = -\hat{k}^2 Be^{i\hat{k}x}. \tag{8.48}$$

So, our partial differential equation reduces to

$$e^{i\hat{k}x}\frac{dB}{dt} = -\alpha\hat{k}^2 Be^{i\hat{k}x}, \tag{8.49}$$

$$\frac{dB}{dt} = -\alpha\hat{k}^2 B, \qquad B(0) = A, \tag{8.50}$$

$$B(t) = Ae^{-\alpha\hat{k}^2 t}. \tag{8.51}$$

Note that as $t \to \infty$, $B \to 0$ with diffusion time constant

$$\tau_d = \frac{1}{\alpha\hat{k}^2}.$$

So, a large thermal diffusivity α causes modes to relax quickly. But high wave number $\hat{k}$ also induces modes to relax quickly. Note also that in terms of wavelength of the initial disturbance,

$$\tau_d = \frac{1}{\alpha 4\pi^2}\lambda^2.$$

So, small wavelength disturbances induce fast relaxation.

Importantly, recall that an *arbitrary signal* will have a Fourier decomposition with an infinite number of modes, each with a different wave number. The preceding analysis shows that *each mode will decay with its own diffusion time constant.* Indeed some of the modes, even at the initial state, may have negligibly small amplitude. But many will not, and we cannot know *a priori* which ones will be large or small.

Lastly, we note that in a finite domain, we will find a discrete spectrum of wave numbers; in an infinite domain, we will find a continuous spectrum.

8.2.2   Final form

Let us now drop the $*$ notation and understand that all variables are dimensionless. So, our equations become

$$
\begin{aligned}
\frac{\partial T}{\partial t} &= \frac{1}{\mathfrak{D}}x^{-m}\frac{\partial}{\partial x}\left(x^m\frac{\partial T}{\partial x}\right) + (1-T)\exp\left(\frac{-\Theta}{1+QT}\right), \\
T(-1,t) &= T(1,t) = 0, \qquad T(x,0) = 0, \qquad \text{if} \qquad m = 0, \\
T(1,t) &= 0, \qquad T(0,t) < \infty, \qquad T(x,0) = 0, \qquad \text{if} \qquad m = 1,2.
\end{aligned}
$$

$$(8.52)$$

Note that the initial and boundary conditions are homogeneous. The only inhomogeneity lives in the exothermic reaction source term, which is non-linear due to the $\exp(-1/T)$ term. Also, it will prove to be the case that a symmetry boundary condition at $x = 0$ suffices, though our original formulation is more rigorous. Such equivalent boundary conditions are

$$T(1,t) = 0, \qquad \frac{\partial T}{\partial x}(0,t) = 0, \qquad T(x,0) = 0, \qquad m = 1,2,3. \qquad (8.53)$$

8.2.3   Integral form

As an aside, let us consider the evolution of total energy within the domain. To do so we integrate a differential volume element through the entire volume. We recall $dV \sim x^m\, dx$, for $m = 0,1,2$, (planar, cylindrical, spherical).

$$
x^m\frac{\partial T}{\partial t}dx = \frac{1}{\mathfrak{D}}x^m x^{-m}\frac{\partial}{\partial x}\left(x^m\frac{\partial T}{\partial x}\right)dx + x^m\,(1-T)\exp\left(\frac{-\Theta}{1+QT}\right)dx,
$$

$$(8.54)$$

$$
\int_0^1 x^m\frac{\partial T}{\partial t}dx = \int_0^1 \frac{1}{\mathfrak{D}}\frac{\partial}{\partial x}\left(x^m\frac{\partial T}{\partial x}\right)dx + \int_0^1 x^m\,(1-T)\exp\left(\frac{-\Theta}{1+QT}\right)dx,
$$

$$(8.55)$$

$$\underbrace{\frac{\partial}{\partial t}\int_0^1 x^m T dx}_{\text{thermal energy change}} = \underbrace{\frac{1}{\mathfrak{D}}\frac{\partial T}{\partial x}\bigg|_{x=1}}_{\text{boundary heat flux}} + \underbrace{\int_0^1 x^m (1-T)\exp\left(\frac{-\Theta}{1+QT}\right)dx}_{\text{internal conversion}}.$$

$$(8.56)$$

Note that the total thermal energy in our domain changes due to two reasons: 1) diffusive energy flux at the isothermal boundary, 2) internal conversion of chemical energy to thermal energy.

8.2.4 Infinite Damköhler limit

Note for $\mathfrak{D} \to \infty$ diffusion becomes unimportant in Eq. (8.52), and we recover a balance between unsteady effects and reaction:

$$\frac{dT}{dt} = (1-T)\exp\left(\frac{-\Theta}{1+QT}\right), \qquad T(0) = 0. \tag{8.57}$$

This is the problem we have already considered in thermal explosion theory, Sec. 1.2.1. We recall that thermal explosion theory predicts significant acceleration of reaction when

$$t \to \frac{e^{\Theta}}{Q\Theta}. \tag{8.58}$$

8.3 Steady solutions

Let us seek solutions to the planar $(m = 0)$ version of Eqs. (8.52) that are formally steady, so that $\partial/\partial t = 0$, and a balance between reaction and energy diffusion is attained. In that limit, Eqs.(8.52) reduce to the following two point boundary value problem:

$$0 = \frac{1}{\mathfrak{D}}\frac{d^2 T}{dx^2} + (1-T)\exp\left(\frac{-\Theta}{1+QT}\right), \tag{8.59}$$

$$0 = T(-1) = T(1). \tag{8.60}$$

This problem is difficult to solve analytically because of the strong non-linearity in the reaction source term.

8.3.1 High activation energy asymptotics

Motivated by our earlier success in getting approximate solutions to a similar problem in spatially homogeneous thermal explosion theory, let us take a similar approach here.

Let us seek low temperature solutions where the non-linearity may be weak. So, let us define a small parameter ϵ with $0 \leq \epsilon \ll 1$. And now let us assume a power series expansion of T of the form

$$T = \epsilon T_1 + \epsilon^2 T_2 + \ldots \tag{8.61}$$

Here, we assume $T_1(x) \sim \mathcal{O}(1)$, $T_2(x) \sim \mathcal{O}(1)$, …. We will focus attention on getting an approximate solution for $T_1(x)$.

With the assumption of Eq. (8.61), Eq. (8.59) expands to

$$\epsilon \frac{d^2 T_1}{dx^2} + \ldots = -\mathfrak{D}(1 - \epsilon T_1 - \ldots) \exp(-\Theta(1 - \epsilon Q T_1 + \ldots)). \tag{8.62}$$

Ignoring higher order terms and simplifying we get

$$\epsilon \frac{d^2 T_1}{dx^2} = -\mathfrak{D}(1 - \epsilon T_1) \exp(-\Theta) \exp(\epsilon \Theta Q T_1). \tag{8.63}$$

Now, let us once again take the high activation energy limit and insist that ϵ be defined such that

$$\epsilon \equiv \frac{1}{Q\Theta}. \tag{8.64}$$

This gives us

$$\frac{d^2 T_1}{dx^2} = -\frac{\mathfrak{D}}{\epsilon}(1 - \epsilon T_1) \exp(-\Theta) \exp(T_1). \tag{8.65}$$

We have gained an analytic advantage once again by moving the temperature into the numerator of the argument of the exponential.

Now, let us neglect ϵT_1 as small relative to 1 and define a new parameter δ such that

$$\delta \equiv \frac{\mathfrak{D}}{\epsilon} \exp(-\Theta) = \mathfrak{D}Q\Theta \exp(-\Theta). \tag{8.66}$$

Our governing equation system then reduces to

$$\frac{d^2 T_1}{dx^2} = -\delta e^{T_1}, \tag{8.67}$$

$$T_1(-1) = T_1(1) = 0. \tag{8.68}$$

It is still not clear how to solve this. It seems reasonable to assume that T_1 should have symmetry about $x = 0$. If so, we might also presume that the gradient of T_1 is zero at $x = 0$:

$$\left. \frac{dT_1}{dx} \right|_{x=0} = 0, \tag{8.69}$$

which induces $T_1(0)$ to take on an extreme value, say $T_1(0) = T_1^m$, where m could denote maximum or minimum. Certainly T_1^m is unknown at this point.

Let us explore the appropriate phase space solution. To aid in this, we can define q as

$$\mathsf{q} \equiv -\frac{dT_1}{dx}. \tag{8.70}$$

We included the minus sign so that q has a physical interpretation of heat flux. With this assumption, Eq. (8.67) can be written as two autonomous ordinary differential equations in two unknowns:

$$\frac{d\mathsf{q}}{dx} = \delta e^{T_1}, \qquad \mathsf{q}(0) = 0, \tag{8.71}$$

$$\frac{dT_1}{dx} = -\mathsf{q}, \qquad T_1(0) = T_1^m. \tag{8.72}$$

This is slightly unsatisfying because we do not know T_1^m. But we presume it exists, and is a constant. Let us see if the analysis can reveal it by pressing forward.

Let us scale Eq. (8.72) by Eq. (8.71) to get

$$\frac{dT_1}{d\mathsf{q}} = -\frac{\mathsf{q}}{\delta e^{T_1}}, \qquad T_1|_{\mathsf{q}=0} = T_1^m. \tag{8.73}$$

Now, Eq. (8.73) can be solved by separating variables. Doing so and solving we get

$$-\delta e^{T_1} dT_1 = \mathsf{q} d\mathsf{q}, \tag{8.74}$$

$$-\delta e^{T_1} = \frac{\mathsf{q}^2}{2} + C. \tag{8.75}$$

Applying the initial condition, we get

$$-\delta e^{T_1^m} = C, \tag{8.76}$$

$$\frac{\mathsf{q}^2}{2} = \delta(e^{T_1^m} - e^{T_1}), \tag{8.77}$$

$$\mathsf{q} = \sqrt{2\delta(e^{T_1^m} - e^{T_1})}. \tag{8.78}$$

The plus square root is taken here. This will correspond to $x \in [0, 1]$. The negative square root will correspond to $x \in [-1, 0]$.

We can now substitute Eq. (8.78) into Eq. (8.72) to get

$$\frac{dT_1}{dx} = -\sqrt{2\delta(e^{T_1^m} - e^{T_1})}. \tag{8.79}$$

Once again separate variables to get

$$\frac{dT_1}{\sqrt{2\delta(e^{T_1^m} - e^{T_1})}} = -dx. \tag{8.80}$$

Computer algebra reveals this can be integrated to form

$$-\frac{\sqrt{2}\tanh^{-1}\left(\sqrt{1-\frac{e^{T_1}}{e^{T_1^m}}}\right)}{e^{T_1^m/2}\sqrt{\delta}} = -x + C. \tag{8.81}$$

Now, when $x = 0$, we have $T_1 = T_1^m$. The inverse hyperbolic tangent has an argument of zero there, and it evaluates to zero. Thus, we must have $C = 0$, so

$$\frac{\sqrt{2}\tanh^{-1}\left(\sqrt{1-\frac{e^{T_1}}{e^{T_1^m}}}\right)}{e^{T_1^m/2}\sqrt{\delta}} = x, \tag{8.82}$$

$$\tanh^{-1}\left(\sqrt{1-\frac{e^{T_1}}{e^{T_1^m}}}\right) = e^{T_1^m/2}\sqrt{\frac{\delta}{2}}x. \tag{8.83}$$

Now, recall that

$$\tanh^{-1}\sqrt{1-\beta^2} = \operatorname{sech}^{-1}\beta,$$

so Eq. (8.83) becomes

$$\operatorname{sech}^{-1}\left(e^{\frac{T_1-T_1^m}{2}}\right) = e^{T_1^m/2}\sqrt{\frac{\delta}{2}}x, \tag{8.84}$$

$$e^{\frac{T_1-T_1^m}{2}} = \operatorname{sech}\left(e^{T_1^m/2}\sqrt{\frac{\delta}{2}}x\right), \tag{8.85}$$

$$e^{\frac{T_1}{2}} = e^{T_1^m/2}\operatorname{sech}\left(e^{T_1^m/2}\sqrt{\frac{\delta}{2}}x\right), \tag{8.86}$$

$$T_1 = 2\ln\left(e^{T_1^m/2}\operatorname{sech}\left(e^{T_1^m/2}\sqrt{\frac{\delta}{2}}x\right)\right). \tag{8.87}$$

So, we have an exact solution for $T_1(x)$. This is a nice achievement, but we are not sure it satisfies the boundary condition at $x = 1$, nor do we know the value of T_1^m. We must choose T_1^m such that $T_1(1) = 0$, which we have not yet enforced. So

$$0 = 2\ln\left(e^{T_1^m/2}\operatorname{sech}\left(e^{T_1^m/2}\sqrt{\frac{\delta}{2}}\right)\right). \tag{8.88}$$

Only when the argument of a logarithm is unity does it map to zero. So, we must demand that

$$e^{T_1^m/2}\operatorname{sech}\left(e^{T_1^m/2}\sqrt{\frac{\delta}{2}}\right) = 1, \tag{8.89}$$

$$e^{T_1^m/2}\sqrt{\frac{\delta}{2}} = \operatorname{sech}^{-1}\left(e^{-T_1^m/2}\right), \tag{8.90}$$
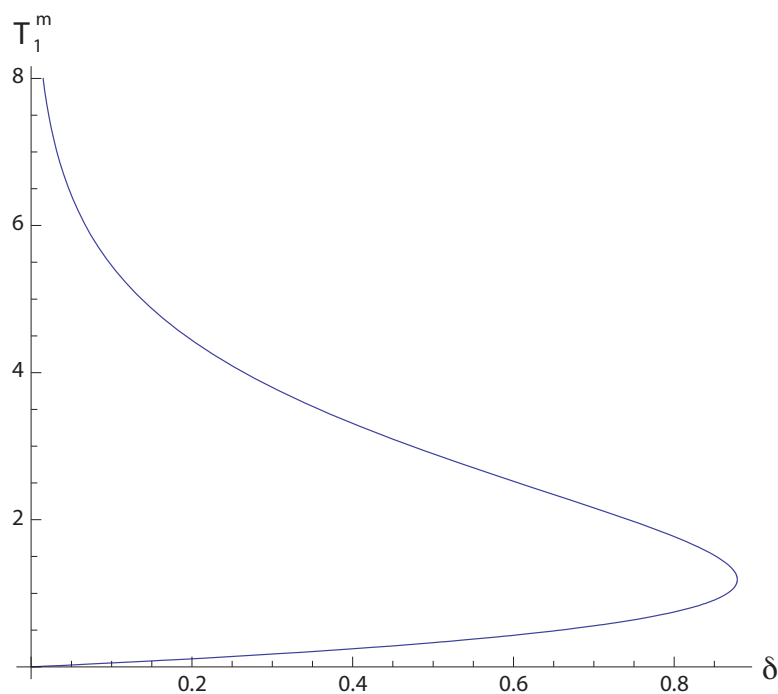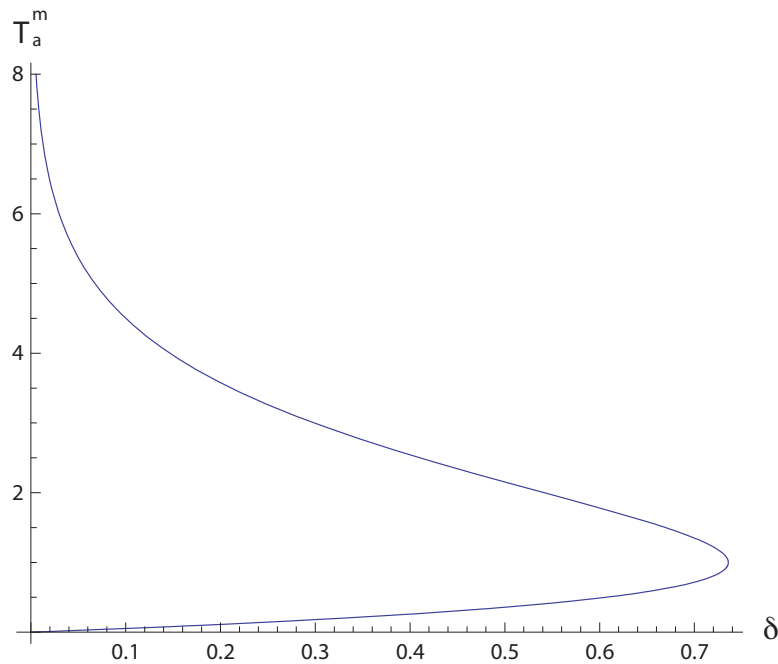
Figure 8.1: Plot of maximum temperature perturbation T_1^m versus reaction rate constant δ for steady reaction-diffusion in the high activation energy limit.

$$e^{T_1^m/2}\sqrt{\frac{\delta}{2}} = \cosh^{-1}\left(e^{T_1^m/2}\right), \tag{8.91}$$

$$\sqrt{\frac{\delta}{2}} = e^{-T_1^m/2}\cosh^{-1}\left(e^{T_1^m/2}\right). \tag{8.92}$$

Equation (8.92) gives a direct relationship between δ and T_1^m. Given T_1^m, we get δ explicitly. Thus, we can easily generate a plot; see Fig 8.1. The inverse cannot be achieved analytically, but can be done numerically via iterative techniques. We notice a *critical value* of δ, $\delta_c = 0.878458$. When $\delta = \delta_c = 0.878458$, we find $T_1^m = 1.118684$. For $\delta < \delta_c$, there are *two* admissible values of T_1^m. That is to say the solution is *non-unique* for $\delta < \delta_c$. Moreover, both solutions are physical. For $\delta = \delta_c$, there is a single solution. For $\delta > \delta_c$, there are no steady solutions.

Note also that since we have from Eq. (8.61) that $T \sim \epsilon T_1$ and from Eq. (8.64) that $\epsilon = 1/\Theta/Q$, we can say

$$T^m \sim \frac{T_1^m}{\Theta Q}. \tag{8.93}$$

Presumably re-introduction of neglected processes would aid in determining which solution is realized in nature. We shall see that transient stability analysis aids in selecting the correct solution when there are choices. We shall also see that re-introduction of reaction depletion into the model induces additional physical solutions, including those for $\delta > \delta_c$.
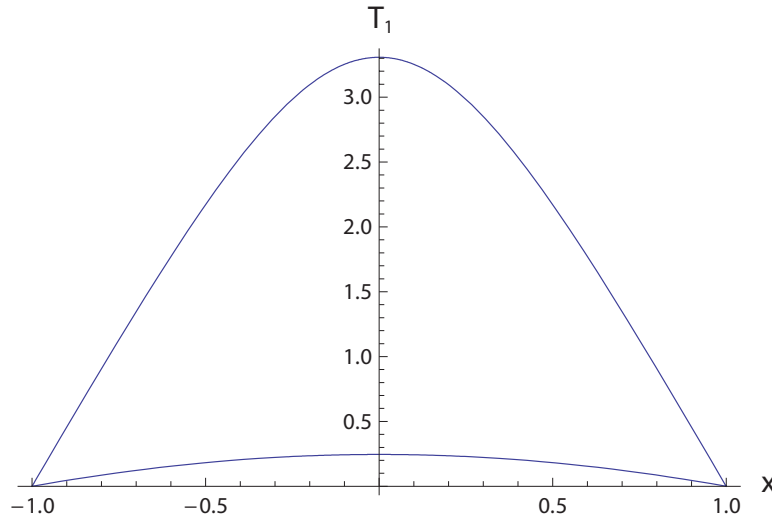
Figure 8.2: Plot of $T_1(x)$ for $\delta = 0.4$ showing the two admissible steady solutions.

For $\delta = 0.4 < \delta_c$ we get two solutions. Both are plotted in Fig 8.2. The high temperature solution has $T_1^m = 3.3079$, and the low temperature solution has $T_1^m = 0.24543$. At this point we are not sure if either solution is temporally stable to small perturbations. We shall later prove that the low temperature solution is stable, and the higher temperature solution is unstable. Certainly for $\delta > \delta_c$, there are no low temperature solutions. We will see that upon re-introduction of missing physics, there are stable high temperature solutions. *To prevent high temperature solutions, we need $\delta < \delta_c$.*

Now, recall from Eq. (8.66) that

$$\delta = \mathfrak{D} Q \Theta e^{-\Theta}. \tag{8.94}$$

Now, to prevent the high temperature solution, we demand

$$\delta = \mathfrak{D} Q \Theta e^{-\Theta} < 0.878458. \tag{8.95}$$

Let us bring back our dimensional parameters to examine this criteria:

$$\mathfrak{D} Q \Theta e^{-\Theta} \quad < \quad 0.878458, \tag{8.96}$$

$$\underbrace{\frac{L^2 a}{\alpha}}_{\mathfrak{D}} \underbrace{\frac{q}{c_v T_o}}_{Q} \underbrace{\frac{\overline{\mathcal{E}}}{\overline{R} T_o}}_{\Theta} \exp\left(\frac{-\overline{\mathcal{E}}}{\overline{R} T_o}\right) \quad < \quad 0.878458. \tag{8.97}$$

Thus, the factors that tend to prevent thermal explosion are

- High thermal diffusivity; this removes the thermal energy rapidly,

- Small length scales; the energy thus has less distance to diffuse,

- Slow reaction rate kinetics,

- High activation energy.

8.3.2 Method of weighted residuals

The method of the previous section was challenging. Let us approach the problem of calculating the temperature distribution with a powerful alternate method: the method of weighted residuals, using so-called Dirac[5] delta functions as weighting functions. We will first briefly review the Dirac delta function, then move on to solving the Frank-Kamenetskii problem with the method of weighted residuals.

The Dirac δ_D-*distribution* (or *generalized* function, or simply function), is defined by

$$\int_\alpha^\beta f(x)\delta_D(x-a)dx = \begin{cases} 0 & \text{if } a \notin [\alpha, \beta] \\ f(a) & \text{if } a \in [\alpha, \beta] \end{cases} \tag{8.98}$$

From this it follows by considering the special case in which $f(x) = 1$ that

$$\delta_D(x-a) = 0 \text{ if } x \neq a \tag{8.99}$$

$$\int_{-\infty}^{\infty} \delta_D(x-a)dx = 1. \tag{8.100}$$

Let us first return to Eq. (8.67), rearranged as

$$\frac{d^2T_1}{dx^2} + \delta e^{T_1} = 0, \tag{8.101}$$

$$T_1(-1) = T_1(1) = 0. \tag{8.102}$$

We shall approximate $T_1(x)$ by

$$T_1(x) = T_a(x) = \sum_{i=1}^{N} c_i f_i(x). \tag{8.103}$$

At this point, we do not know the so-called trial functions $f_i(x)$ nor the constants c_i.

8.3.2.1 One-term collocation solution

Let us choose $f_i(x)$ to be linearly independent functions which satisfy the boundary conditions. Moreover, let us consider the simplest of approximations for which $N = 1$. A simple function which satisfies the boundary conditions is a polynomial. The polynomial needs to be at least quadratic to be non-trivial. So, let us take

$$f_1(x) = 1 - x^2. \tag{8.104}$$

Note this gives $f_1(-1) = f_1(1) = 0$. So, our one-term approximate solution takes the form

$$T_a(x) = c_1(1 - x^2). \tag{8.105}$$

---

[5]Paul Adrien Maurice Dirac, 1902-1984, English physicist.

We still do not yet have a value for c_1. Let us choose c_1 so as to minimize a residual error of our approximation. The residual error of our approximation $r(x)$ will be

$$r(x) = \frac{d^2 T_a}{dx^2} + \delta e^{T_a(x)}, \tag{8.106}$$

$$= \frac{d^2}{dx^2} \left(c_1(1 - x^2) \right) + \delta \exp(c_1(1 - x^2)), \tag{8.107}$$

$$= -2c_1 + +\delta \exp(c_1(1 - x^2)). \tag{8.108}$$

If we could choose c_1 in such a way that $r(x)$ was exactly 0 for $x \in [-1, 1]$, we would be done. That will not happen. So, let us choose c_1 to drive a weighted domain-averaged residual to zero. That is, let us demand that

$$\int_{-1}^{1} \psi_1(x) r(x) \ dx = 0. \tag{8.109}$$

We have introduced here a weighting function $\psi_1(x)$. Many choices exist for the weighting function. If we choose $\psi_1(x) = f_1(x)$ our method is known as a *Galerkin*[6] method. Let us choose instead another common weighting, $\psi_1(x) = \delta_D(x)$. This method is known as a *collocation* method. We have chosen a single collocation point at $x = 0$. With this choice, Eq. (8.109) becomes

$$\int_{-1}^{1} \delta_D(x) \left(-2c_1 + \delta \exp(c_1(1 - x^2)) \right) \ dx = 0. \tag{8.110}$$

The evaluation of this integral is particularly simple due to the choice of the Dirac weighting. We simply evaluate the integrand at the collocation point $x = 0$ and get

$$-2c_1 + +\delta \exp(c_1) = 0. \tag{8.111}$$

Thus,

$$\delta = 2c_1 e^{-c_1}. \tag{8.112}$$

Note here δ is a physical parameter with no relation the Dirac delta function δ_D. Note that with our approximation $T_a = c_1(1 - x^2)$, that the maximum value of T_a is $T_a^m = c_1$. So, we can say

$$\delta = 2T_a^m e^{-T_a^m}. \tag{8.113}$$

We can plot T_a^m as a function of δ; see Fig 8.3. Note the predictions of Fig. 8.3 are remarkably similar to those of Fig. 8.1. For example, when $\delta = 0.4$, numerical solution of Eq. (8.113) yields two roots:

$$T_a^m = 0.259171, \qquad T_a^m = 2.54264. \tag{8.114}$$

---

[6]Boris Gigoryevich Galerkin, 1871-1945, Russian-Soviet engineer.

Figure 8.3: Plot of maximum temperature perturbation T_a^m versus reaction rate constant δ for steady reaction-diffusion using a one-term collocation method.

Thus, we get explicit approximations for the high and low temperature solutions for a one-term collocation approximation:

$$T_a(x) = 0.259171(1 - x^2), \tag{8.115}$$
$$T_a(x) = 2.54264(1 - x^2). \tag{8.116}$$

Plots of the one-term collocation approximation $T_a(x)$ for high and low temperature solutions are given in Fig 8.4.

We can easily find δ_c for this approximation. Note that differentiating Eq. (8.113) gives

$$\frac{d\delta}{dT_a^m} = 2e^{-T_a^m}(1 - T_a^m). \tag{8.117}$$

A critical point exists when $d\delta/dT_a^m = 0$. We find this exists when $T_a^m = 1$. So, $\delta_c = 2(1)e^{-1} = 0.735769$.

8.3.2.2 Two-term collocation solution

We can improve our accuracy by including more basis functions. Let us take $N = 2$. We have a wide variety of acceptable choices for basis function that 1) satisfy the boundary conditions, and 2) are linearly independent. Let us focus on polynomials. We can select the first as before with $f_1(x) = 1 - x^2$ as the lowest order non-trivial polynomial that satisfies
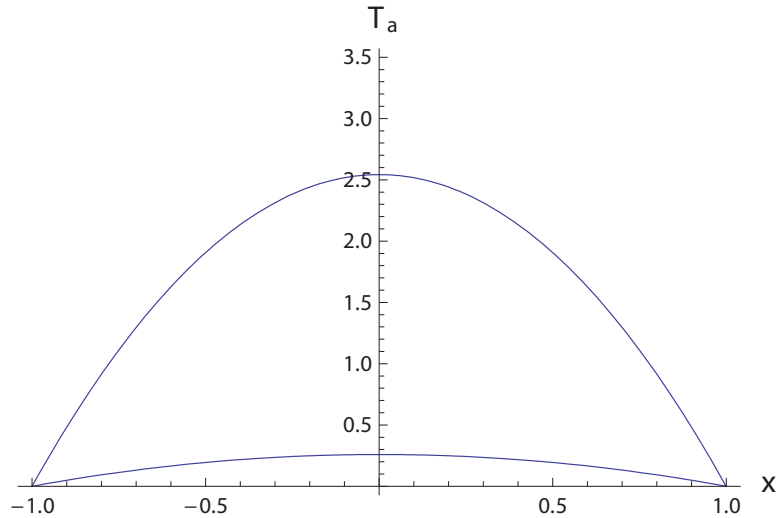
Figure 8.4: Plots of high and low temperature distributions $T_a(x)$ using a one-term colloca-tion method.

both boundary conditions. We could multiply this by an arbitrary constant, but that would not be of any particular use. Leaving out details, if we selected the second basis function as a cubic polynomial, we would find the coefficient on the cubic basis function to be $c_2 = 0$. That is a consequence of the oddness of the cubic basis function and the evenness of the solution we are simulating. So, it turns out the lowest order non-trivial basis function is a quartic polynomial, taken to be of the form

$$f_2(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4. \tag{8.118}$$

We can insist that $f_2(-1) = 0$ and $f_2(1) = 0$. This gives

$$a_0 + a_1 + a_2 + a_3 + a_4 = 0, \tag{8.119}$$
$$a_0 - a_1 + a_2 - a_3 + a_4 = 0. \tag{8.120}$$

We solve these for a_0 and a_1 to get $a_0 = -a_2 - a_4$, $a_1 = -a_3$. So, our approximation is

$$f_2(x) = (-a_2 - a_4) - a_3 x + a_2 x^2 + a_3 x^3 + a_4 x^4. \tag{8.121}$$

Motivated by the fact that a cubic approximation did not contribute to the solution, let us select $a_3 = 0$ so to get

$$f_2(x) = (-a_2 - a_4) + a_2 x^2 + a_4 x^4. \tag{8.122}$$

Let us now make the choice that $\int_{-1}^{1} f_1(x) f_2(x) \, dx = 0$. This guarantees an orthogonal basis, although these basis functions are not eigenfunctions of any relevant self-adjoint linear

operator for this problem. Often orthogonality of basis functions can lead to a more efficient capturing of the solution. This results in $a_4 = -7a_2/8$. Thus,

$$f_2(x) = a_2 \left(-\frac{1}{8} + x^2 - \frac{7}{8}x^4 \right). \tag{8.123}$$

Let us select $a_2 = -8$ so that

$$f_2(x) = 1 - 8x^2 + 7x^4 = (1 - x^2)(1 - 7x^2). \tag{8.124}$$

and

$$f_1(x) = 1 - x^2, \tag{8.125}$$
$$f_2(x) = (1 - x^2)(1 - 7x^2). \tag{8.126}$$

So, now we seek approximate solutions $T_A(x)$ of the form

$$T_A(x) = c_1(1 - x^2) + c_2(1 - x^2)(1 - 7x^2). \tag{8.127}$$

This leads to a residual $r(x)$ of

$$r(x) = \frac{d^2 T_A}{dx^2} + \delta e^{T_A(x)}, \tag{8.128}$$

$$= \frac{d^2}{dx^2} \left(c_1(1 - x^2) + c_2(1 - x^2)(1 - 7x^2) \right)$$
$$+ \delta \exp(c_1(1 - x^2) + c_2(1 - x^2)(1 - 7x^2)), \tag{8.129}$$

$$= -2c_1 + 56c_2 x^2 - 2c_2(1 - 7x^2) - 14c_2(1 - x^2)$$
$$+ \delta \exp(c_1(1 - x^2) + c_2(1 - x^2)(1 - 7x^2)). \tag{8.130}$$

Now, we drive two weighted residuals to zero:

$$\int_{-1}^{1} \psi_1(x) r(x) \, dx = 0, \tag{8.131}$$

$$\int_{-1}^{1} \psi_2(x) r(x) \, dx = 0. \tag{8.132}$$

Let us once again choose the weighting functions $\psi_i(x)$ to be Dirac delta functions so that we have a two-term collocation method. Let us choose unevenly distributed collocation points so as to generate independent equations taking $x = 0$ and $x = 1/2$. Symmetric choices would lead to a linearly dependent set of equations. Other unevenly distributed choices would work as well. So, we get

$$\int_{-1}^{1} \delta_D(x) r(x) \, dx = 0, \tag{8.133}$$

$$\int_{-1}^{1} \delta_D(x - 1/2) r(x) \, dx = 0. \tag{8.134}$$

or

$$r(0) = 0, \tag{8.135}$$
$$r(1/2) = 0. \tag{8.136}$$

Expanding, these equations are

$$-2c_1 - 16c_2 + \delta \exp(c_1 + c_2) = 0, \tag{8.137}$$
$$-2c_1 + 5c_2 + \delta \exp\left(\frac{3}{4}c_1 - \frac{9}{16}c_2\right) = 0. \tag{8.138}$$

For $\delta = 0.4$, we find a high temperature solution via numerical methods:

$$c_1 = 3.07054, \qquad c_2 = 0.683344, \tag{8.139}$$

and a low temperature solution as well

$$c_1 = 0.243622, \qquad c_2 = 0.00149141. \tag{8.140}$$

So, the high temperature distribution is

$$T_A(x) = 3.07054(1 - x^2) + 0.683344(1 - x^2)(1 - 7x^2). \tag{8.141}$$

The peak temperature of the high temperature distribution is $T_A^m = 3.75388$. This is an improvement over the one term approximation of $T_a^m = 2.54264$ and closer to the high temperature solution found via exact methods of $T_1^m = 3.3079$.

The low temperature distribution is

$$T_A(x) = 0.243622(1 - x^2) + 0.00149141(1 - x^2)(1 - 7x^2). \tag{8.142}$$

The peak temperature of the low temperature distribution is $T_A^m = 0.245113$. This in an improvement over the one term approximation of $T_a^m = 0.259171$ and compares very favorably to the low temperature solution found via exact methods of $T_1^m = 0.24543$.

Plots of the two-term collocation approximation $T_A(x)$ for high and low temperature solutions are given in Fig 8.5. While the low temperature solution is a very accurate representation, the high temperature solution exhibits a small negative portion near the boundary.

8.3.3   Steady solution with depletion

Let us return to the version of steady state reaction with depletion without resorting to the high activation energy limit, Eq.(8.60):

$$0 = \frac{1}{\mathfrak{D}}\frac{d^2 T}{dx^2} + (1 - T)\exp\left(\frac{-\Theta}{1 + QT}\right), \tag{8.143}$$
$$0 = T(-1) = T(1). \tag{8.144}$$
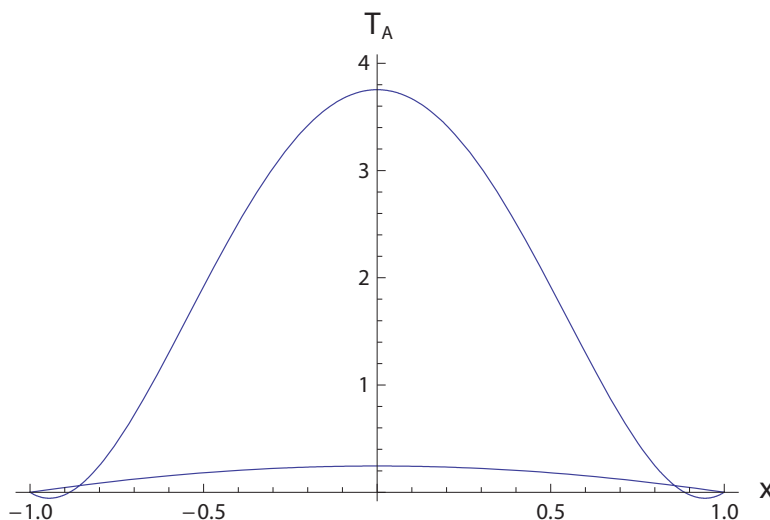
Figure 8.5: Plots of high and low temperature distributions $T_A(x)$ using a two-term collocation method.

Rearrange to get

$$\frac{d^2T}{dx^2} = -\mathfrak{D}(1-T)\exp\left(\frac{-\Theta}{1+QT}\right), \tag{8.145}$$

$$= -\mathfrak{D}\frac{Q\Theta\exp(-\Theta)}{Q\Theta\exp(-\Theta)}(1-T)\exp\left(\frac{-\Theta}{1+QT}\right). \tag{8.146}$$

Now, simply adapting our earlier definition of $\delta = \mathfrak{D}Q\Theta\exp(-\Theta)$, which we note does not imply we have taken any high activation energy limits, we get

$$\frac{d^2T}{dx^2} = -\delta\frac{\exp(\Theta)}{Q\Theta}(1-T)\exp\left(\frac{-\Theta}{1+QT}\right), \tag{8.147}$$

$$T(-1) = T(1) = 0. \tag{8.148}$$

Equations (8.147-8.148) can be solved by a numerical trial and error method where we demand that $dT/dx(x=0)=0$ and guess $T(0)$. We keep guessing $T(0)$ until we have satisfied the boundary conditions.

When we do this with $\delta = 0.4$, $\Theta = 15$, $Q = 1$ (so $\mathfrak{D} = \delta e^\Theta/Q/\Theta = 87173.8$ and $\epsilon = 1/\Theta/Q = 1/15$), we find *three* steady solutions. One is at low temperature with $T^m = 0.016$. This is essentially equal that predicted by our high activation energy limit estimate of $T^m \sim \epsilon T_1^m = 0.24542/15 = 0.016$. We find a second intermediate temperature solution with $T^m = 0.417$. This is a little higher than that predicted in the high activation limit of $T^m \sim \epsilon T_1^m = 3.3079/15 = 0.221$. And we find a high temperature solution with $T^m = 0.987$. There is no counterpart to this solution from the high activation energy limit analysis. Plots of $T(x)$ for high, low, and intermediate temperature solutions are given in Fig 8.6.
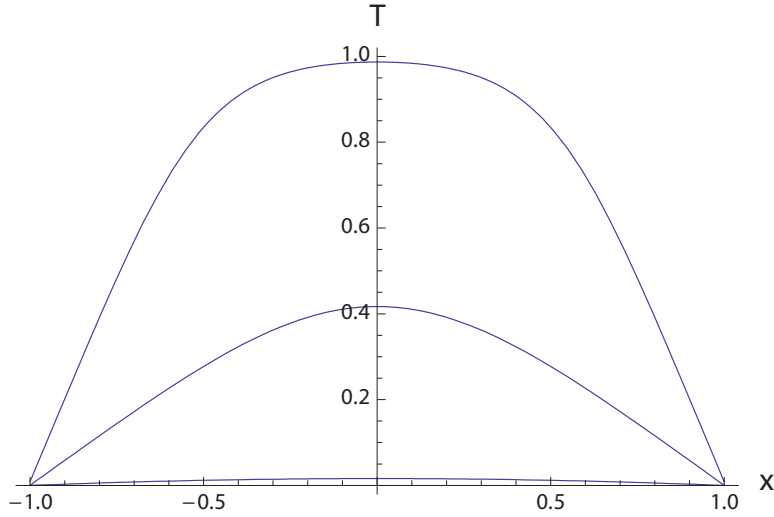
Figure 8.6: Plots of high, low, and intermediate temperature distributions $T(x)$ for $\delta = 0.4$, $Q = 1$, $\Theta = 15$.

We can use a one-term collocation approximation to estimate the relationship between δ and T^m. Let us estimate that

$$T_a(x) = c_1(1 - x^2).$$ (8.149)

With that choice, we get a residual of

$$r(x) = -2c_1 + \frac{\delta}{Q\Theta} \exp\left(\Theta - \frac{\Theta}{1 + c_1 Q(1 - x^2)}\right)(1 - c_1(1 - x^2)).$$ (8.150)

We choose a one term collocation method with $\psi_1(x) = \delta_D(x)$. Then, setting $\int_{-1}^{1} \psi_1(x)r(x)dx = 0$ gives

$$r(0) = -2c_1 + \frac{\delta}{Q\Theta} \exp\left(\Theta - \frac{\Theta}{1 + c_1 Q}\right)(1 - c_1) = 0.$$ (8.151)

We solve for δ and get

$$\delta = \frac{2c_1}{1 - c_1} \frac{Q\Theta}{e^\Theta} \exp\left(\frac{\Theta}{1 + c_1 Q}\right).$$ (8.152)

The maximum temperature of the approximation is given by $T_a^m = c_1$ and occurs at $x = 0$. A plot of T_a^m versus δ is given in Fig 8.7. For $\delta < \delta_{c1} \sim 0.2$, one low temperature solution exists. For $\delta_{c1} < \delta < \delta_{c2} \sim 0.84$, three solutions exist. For $\delta > \delta_{c2}$, one high temperature solution exists.
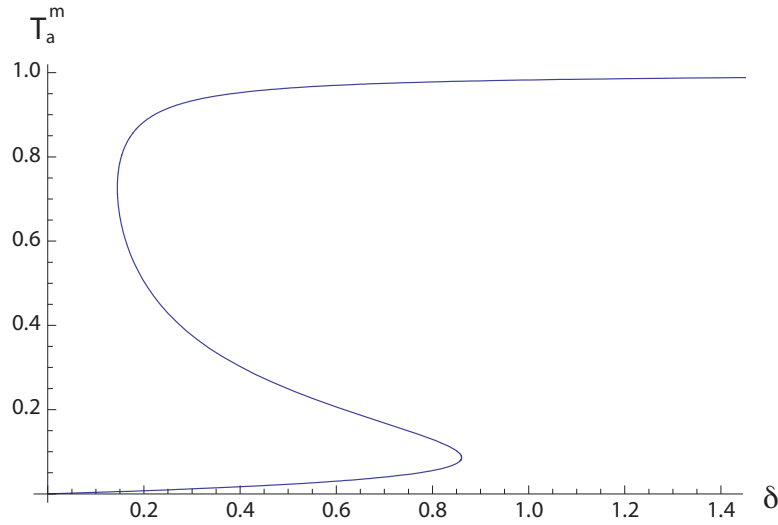
Figure 8.7: Plots of T_a^m versus δ, with $Q = 1$, $\Theta = 15$ from a one-term collocation approximate solution.

8.4 Unsteady solutions

Let us know study the effects of time-dependency on our combustion problem. Let us consider the planar, $m = 0$, version of Eqs. (8.52):

$$
\begin{aligned}
\frac{\partial T}{\partial t} &= \frac{1}{\mathfrak{D}} \frac{\partial^2 T}{\partial x^2} + (1 - T) \exp\left(\frac{-\Theta}{1 + QT}\right), \\
T(-1, t) &= T(1, t) = 0, \qquad T(x, 0) = 0.
\end{aligned} \tag{8.153}
$$

8.4.1 Linear stability

We will first consider small deviations from the steady solutions found earlier and see if those deviations grow or decay with time. This will allow us to make a definitive statement about the linear stability of those steady solutions.

8.4.1.1 Formulation

First, recall that we have independently determined three exact numerical steady solutions to the time-independent version of Eq. (8.153). Let us call any of these $T_e(x)$. Note that by construction $T_e(x)$ satisfies the boundary conditions on T.

Let us subject a steady solution to a small perturbation and consider that to be our initial condition for an unsteady calculation. Take then

$$
T(x, 0) = T_e(x) + \epsilon A(x), \qquad A(-1) = A(1) = 0, \tag{8.154}
$$

$$
A(x) = \mathcal{O}(1), \qquad 0 < \epsilon \ll 1. \tag{8.155}
$$

Here, $A(x)$ is some function which satisfies the same boundary conditions as $T(x,t)$.

Now, let us assume that

$$T(x,t) = T_e(x) + \epsilon T'(x,t). \tag{8.156}$$

with

$$T'(x,0) = A(x). \tag{8.157}$$

Here, T' is an $\mathcal{O}(1)$ quantity. We then substitute our Eq. (8.156) into Eq. (8.153) to get

$$
\frac{\partial}{\partial t}\left(T_e(x) + \epsilon T'(x,t)\right) = \frac{1}{\mathfrak{D}}\frac{\partial^2}{\partial x^2}\left(T_e(x) + \epsilon T'(x,t)\right)
$$
$$
+ (1 - T_e(x) - \epsilon T'(x,t)) \exp\left(\frac{-\Theta}{1 + QT_e(x) + Q\epsilon T'(x,t)}\right). \tag{8.158}
$$

From here on we will understand that T_e is $T_e(x)$ and T' is $T'(x,t)$. Now, consider the exponential term:

$$
\exp\left(\frac{-\Theta}{1 + QT_e + Q\epsilon T'}\right) = \exp\left(\frac{-\Theta}{1 + QT_e}\frac{1}{1 + \frac{Q}{1+QT_e}\epsilon T'}\right), \tag{8.159}
$$
$$
\sim \exp\left(\frac{-\Theta}{1 + QT_e}\left(1 - \frac{Q}{1 + QT_e}\epsilon T'\right)\right), \tag{8.160}
$$
$$
\sim \exp\left(\frac{-\Theta}{1 + QT_e}\right)\exp\left(\frac{\epsilon\Theta Q}{(1 + QT_e)^2}T'\right), \tag{8.161}
$$
$$
\sim \exp\left(\frac{-\Theta}{1 + QT_e}\right)\left(1 + \frac{\epsilon\Theta Q}{(1 + QT_e)^2}T'\right). \tag{8.162}
$$

So, our Eq. (8.158) can be rewritten as

$$
\frac{\partial}{\partial t}\left(T_e + \epsilon T'\right) = \frac{1}{\mathfrak{D}}\frac{\partial^2}{\partial x^2}\left(T_e + \epsilon T'\right)
$$
$$
+ (1 - T_e - \epsilon T')\exp\left(\frac{-\Theta}{1 + QT_e}\right)\left(1 + \frac{\epsilon\Theta Q}{(1 + QT_e)^2}T'\right),
$$
$$
= \frac{1}{\mathfrak{D}}\frac{\partial^2}{\partial x^2}\left(T_e + \epsilon T'\right)
$$
$$
+ \exp\left(\frac{-\Theta}{1 + QT_e}\right)(1 - T_e - \epsilon T')\left(1 + \frac{\epsilon\Theta Q}{(1 + QT_e)^2}T'\right),
$$
$$
= \frac{1}{\mathfrak{D}}\frac{\partial^2}{\partial x^2}\left(T_e + \epsilon T'\right)
$$
$$
+ \exp\left(\frac{-\Theta}{1 + QT_e}\right)\left((1 - T_e) + \epsilon T'\left(-1 + \frac{(1 - T_e)\Theta Q}{(1 + QT_e)^2}\right) + \mathcal{O}(\epsilon^2)\right)
$$

$$
= \frac{\epsilon}{\mathfrak{D}} \frac{\partial^2 T'}{\partial x^2} + \underbrace{\frac{1}{\mathfrak{D}} \frac{\partial^2 T_e}{\partial x^2} + \exp\left(\frac{-\Theta}{1 + QT_e}\right)(1 - T_e)}_{=0}
$$

$$
+ \exp\left(\frac{-\Theta}{1 + QT_e}\right)\left(\epsilon T'\left(-1 + \frac{(1 - T_e)\Theta Q}{(1 + QT_e)^2}\right) + \mathcal{O}(\epsilon^2)\right). \tag{8.163}
$$

Now, we recognize the bracketed term as zero because $T_e(x)$ is constructed to satisfy the steady state equation. We also recognize that $\partial T_e(x)/\partial t = 0$. So, our equation reduces to, neglecting $\mathcal{O}(\epsilon^2)$ terms, and canceling ϵ

$$
\frac{\partial T'}{\partial t} = \frac{1}{\mathfrak{D}} \frac{\partial^2 T'}{\partial x^2} + \exp\left(\frac{-\Theta}{1 + QT_e}\right)\left(-1 + \frac{(1 - T_e)\Theta Q}{(1 + QT_e)^2}\right)T'. \tag{8.164}
$$

Equation (8.164) is a *linear* partial differential equation for $T'(x, t)$. It is of the form

$$
\frac{\partial T'}{\partial t} = \frac{1}{\mathfrak{D}} \frac{\partial^2 T'}{\partial x^2} + B(x)T', \tag{8.165}
$$

with

$$
B(x) \equiv \exp\left(\frac{-\Theta}{1 + QT_e(x)}\right)\left(-1 + \frac{(1 - T_e(x))\Theta Q}{(1 + QT_e(x))^2}\right). \tag{8.166}
$$

8.4.1.2 Separation of variables

Let us use the standard technique of separation of variables to solve Eq. (8.165). We first assume that

$$
T'(x, t) = H(x)K(t). \tag{8.167}
$$

So, Eq. (8.165) becomes

$$
H(x)\frac{dK(t)}{dt} = = \frac{1}{\mathfrak{D}}K(t)\frac{d^2 H(x)}{dx^2} + B(x)H(x)K(t), \tag{8.168}
$$

$$
\frac{1}{K(t)}\frac{dK(t)}{dt} = \frac{1}{\mathfrak{D}}\frac{1}{H(x)}\frac{d^2 H(x)}{dx^2} + B(x) = -\lambda. \tag{8.169}
$$

Since the left side is a function of t and the right side is a function of x, the only way the two can be equal is if they are both the same constant. We will call that constant $-\lambda$.

Now, Eq. (8.169) really contains two equations, the first of which is

$$
\frac{dK(t)}{dt} + \lambda K(t) = 0. \tag{8.170}
$$

This has solution

$$
K(t) = C\exp(-\lambda t), \tag{8.171}
$$

where C is some arbitrary constant. Clearly if $\lambda > 0$, this solution is stable, with time constant of relaxation $\tau = 1/\lambda$.

The second differential equation contained within Eq. (8.169) is

$$\frac{1}{\mathfrak{D}}\frac{d^2 H(x)}{dx^2} + B(x)H(x) = -\lambda H(x), \tag{8.172}$$

$$\left(\frac{1}{\mathfrak{D}}\frac{d^2}{dx^2} + B(x)\right)H(x) = -\lambda H(x). \tag{8.173}$$

This is of the classical eigenvalue form for a linear operator $\mathcal{L}$; that is $\mathcal{L}(H(x)) = -\lambda H(x)$. We also must have

$$H(-1) = H(1) = 0, \tag{8.174}$$

to satisfy the spatially homogeneous boundary conditions on $T'(x,t)$.

This eigenvalue problem is difficult to solve because of the complicated nature of $B(x)$. Let us see how the solution would proceed in the limiting case of B as a constant. We will generalize later.

If B is a constant, we have

$$\frac{d^2 H}{dx^2} + (B + \lambda)\mathfrak{D}H = 0, \qquad H(-1) = H(1) = 0. \tag{8.175}$$

The following mapping simplifies the problem somewhat:

$$y = \frac{x+1}{2}. \tag{8.176}$$

This takes our domain of $x \in [-1, 1]$ to $y \in [0, 1]$. By the chain rule

$$\frac{dH}{dx} = \frac{dH}{dy}\frac{dy}{dx} = \frac{1}{2}\frac{dH}{dy}.$$

So

$$\frac{d^2 H}{dx^2} = \frac{1}{4}\frac{d^2 H}{dy^2}.$$

So, our eigenvalue problem transforms to

$$\frac{d^2 H}{dy^2} + 4\mathfrak{D}(B + \lambda)H = 0, \qquad H(0) = H(1) = 0. \tag{8.177}$$

This has solution

$$H(y) = C_1 \cos\left(\left(\sqrt{4\mathfrak{D}(B + \lambda)}\,\right)y\right) + C_2 \sin\left(\left(\sqrt{4\mathfrak{D}(B + \lambda)}\right)y\right). \tag{8.178}$$

At $y = 0$ we have then

$$H(0) = 0 = C_1(1) + C_2(0), \tag{8.179}$$

so $C_1 = 0$. Thus,

$$H(y) = C_2 \sin\left(\left(\sqrt{4\mathfrak{D}(B + \lambda)}\right) y\right). \tag{8.180}$$

At $y = 1$, we have the other boundary condition:

$$H(1) = 0 = C_2 \sin\left(\left(\sqrt{4\mathfrak{D}(B + \lambda)}\right)\right). \tag{8.181}$$

Since $C_2 \neq 0$ to avoid a trivial solution, we must require that

$$\sin\left(\left(\sqrt{4\mathfrak{D}(B + \lambda)}\right)\right) = 0. \tag{8.182}$$

For this to occur, the argument of the sin function must be an integer multiple of π:

$$\sqrt{4\mathfrak{D}(B + \lambda)} = n\pi, \qquad n = 1, 2, 3, \ldots \tag{8.183}$$

Thus,

$$\lambda = \frac{n^2\pi^2}{4\mathfrak{D}} - B. \tag{8.184}$$

We need $\lambda > 0$ for stability. For large n and $\mathfrak{D} > 0$, we have stability. Depending on the value of B, low n, which corresponds to low frequency modes, could be unstable.

8.4.1.3   Numerical eigenvalue solution

Let us return to the full problem where $B = B(x)$. Let us solve the eigenvalue problem via the method of finite differences. Let us take our domain $x \in [-1, 1]$ and discretize into N points with

$$\Delta x = \frac{2}{N - 1}, \qquad x_i = (i - 1)\Delta x - 1. \tag{8.185}$$

Note that when $i = 1$, $x_i = -1$, and when $i = N$, $x_i = 1$. Let us define $B(x_i) = B_i$ and $H(x_i) = H_i$.

We can rewrite Eq. (8.172) as

$$\frac{d^2 H(x)}{dx^2} + \mathfrak{D}(B(x) + \lambda)H(x) = 0, \qquad H(-1) = H(1) = 0. \tag{8.186}$$

Now, let us apply an appropriate equation at each node. At $i = 1$, we must satisfy the boundary condition so

$$H_1 = 0. \tag{8.187}$$

At $i = 2$, we discretize Eq. (8.186) with a second order central difference to obtain

$$\frac{H_1 - 2H_2 + H_3}{\Delta x^2} + \mathfrak{D}(B_2 + \lambda)H_2 = 0. \tag{8.188}$$

We get a similar equation at a general interior node i:

$$\frac{H_{i-1} - 2H_i + H_{i+1}}{\Delta x^2} + \mathfrak{D}(B_i + \lambda)H_i = 0. \tag{8.189}$$

At the $i = N - 1$ node, we have

$$\frac{H_{N-2} - 2H_{N-1} + H_N}{\Delta x^2} + \mathfrak{D}(B_{N-1} + \lambda)H_{N-1} = 0. \tag{8.190}$$

At the $i = N$ node, we have the boundary condition

$$H_N = 0. \tag{8.191}$$

These represent a linear tri-diagonal system of equations of the form

$$\underbrace{\begin{pmatrix} (-\frac{2}{\mathfrak{D}\Delta x^2} + B_2) & \frac{1}{\mathfrak{D}\Delta x^2} & 0 & 0 & \dots & 0 \\ \frac{1}{\mathfrak{D}\Delta x^2} & (-\frac{2}{\mathfrak{D}\Delta x^2} + B_3) & \frac{1}{\mathfrak{D}\Delta x^2} & 0 & \dots & 0 \\ 0 & \frac{1}{\mathfrak{D}\Delta x^2} & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \dots & \dots & \dots \end{pmatrix}}_{=\mathbf{L}} \underbrace{\begin{pmatrix} H_2 \\ H_3 \\ \vdots \\ \vdots \\ \vdots \end{pmatrix}}_{=\mathbf{h}} = -\lambda \begin{pmatrix} H_2 \\ H_3 \\ \vdots \\ \vdots \\ \vdots \end{pmatrix} \tag{8.192}$$

This is of the classical linear algebraic eigenvalue form $\mathbf{L} \cdot \mathbf{h} = -\lambda\mathbf{h}$. All one need do is discretize and find the eigenvalues of the matrix $\mathbf{L}$. These will be good approximations to the eigenvalues of the differential operator $\mathcal{L}$. The eigenvectors of $\mathbf{L}$ will be good approximations of the eigenfunctions of $\mathcal{L}$. To get a better approximation, one need only reduce Δx.

Note because the matrix $\mathbf{L}$ is symmetric, the eigenvalues are guaranteed real, and the eigenvectors are guaranteed orthogonal. This is actually a consequence of the original problem being in Sturm-Liouville form, which is guaranteed to be self-adjoint with real eigenvalues and orthogonal eigenfunctions.

8.4.1.3.1   Low temperature transients   For our case of $\delta = 0.4$, $Q = 1$, $\Theta = 15$ (so $\mathfrak{D} = 87173.8$), we can calculate the stability of the low temperature solution. Choosing $N = 101$ points to discretize the domain, we find a set of eigenvalues. They are all positive, so the solution is stable. The first few are

$$\lambda = 0.0000232705, 0.000108289, 0.000249682, 0.000447414, \dots . \tag{8.193}$$

The first few eigenvalues can be approximated by inert theory with $B(x) = 0$, see Eq. (8.184):

$$\lambda \sim \frac{n^2\pi^2}{4\mathfrak{D}} = 0.0000283044, 0.000113218, 0.00025474, 0.00045287, \dots . \tag{8.194}$$

The first eigenvalue is associated with the longest time scale $\tau = 1/0.0000232705 = 42972.9$ and a low frequency mode, whose shape is given by the associated eigenvector, plotted in Fig. 8.8. This represents the fundamental mode. Shown also in Fig. 8.8 are the first and second harmonic modes.
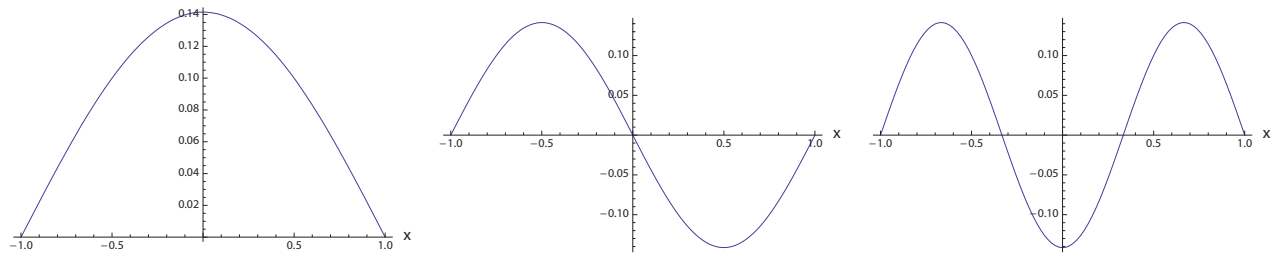
Figure 8.8: Plots of fundamental, first, and second harmonic modes of eigenfunctions versus x, with $\delta = 0.4$, $Q = 1$, $\Theta = 15$, low temperature steady solution $T_e(x)$.

8.4.1.3.2 Intermediate temperature transients For the intermediate temperature solution with $T^m = 0.417$, we find the first few eigenvalues to be

$$\lambda = -0.0000383311, 0.0000668221, 0.000209943, \ldots \tag{8.195}$$

Except for the first, all the eigenvalues are positive. The first eigenvalue of $\lambda = -0.0000383311$ is associated with an *unstable* fundamental mode. All the harmonic modes are stable. We plot the first three modes in Fig. 8.9.
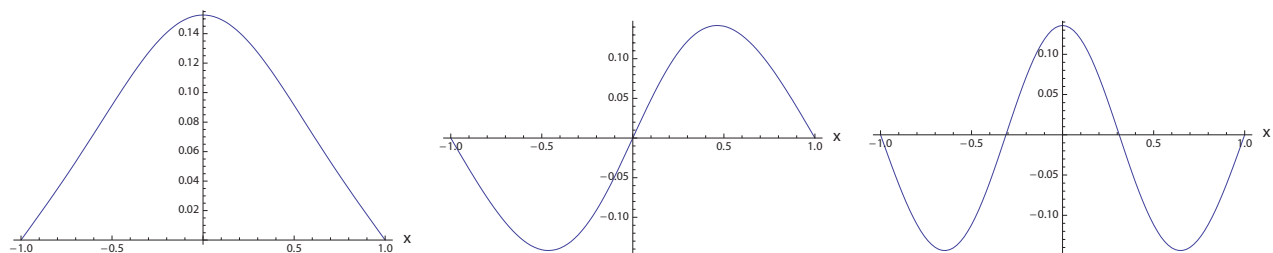
Figure 8.9: Plot of fundamental, first, and second harmonic modes of eigenfunctions versus x, with $\delta = 0.4$, $Q = 1$, $\Theta = 15$, intermediate temperature steady solution $T_e(x)$.

8.4.1.3.3 High temperature transients For the high temperature solution with $T^m = 0.987$, we find the first few eigenvalues to be

$$\lambda = 0.000146419, 0.00014954, 0.000517724, \ldots \tag{8.196}$$

All the eigenvalues are positive, so all modes are stable. We plot the first three modes in Fig. 8.10..

8.4.2 Full transient solution

We can get a full transient solution to Eqs. (8.153) with numerical methods. We omit details of such numerical methods, which can be found in standard texts.
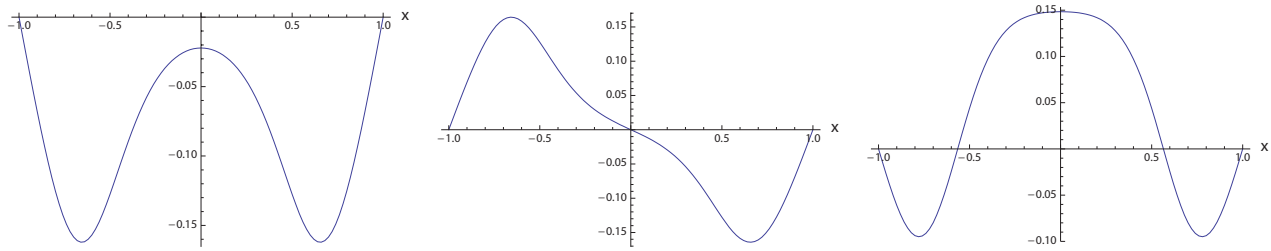
Figure 8.10: Plot of fundamental, first, and second harmonic modes of eigenfunctions versus x, with $\delta = 0.4$, $Q = 1$, $\Theta = 15$, high temperature steady solution $T_e(x)$.
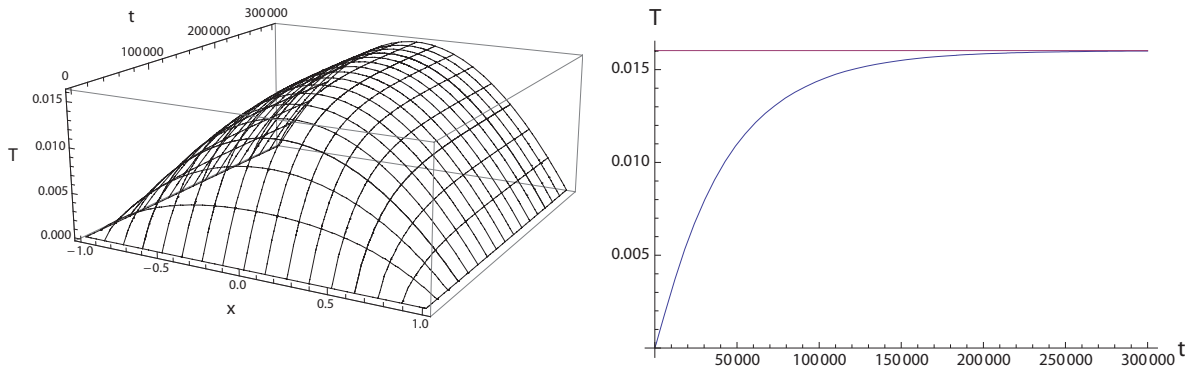
Figure 8.11: Plot of $T(x, t)$ and plot of $T(0, t)$ along with the long time exact low temperature centerline solution, $T_e(0)$, with $\delta = 0.4$, $Q = 1$, $\Theta = 15$.

8.4.2.1   Low temperature solution

For our case of $\delta = 0.4$, $Q = 1$, $\Theta = 15$ (so $\mathfrak{D} = 87173.8$), we show a plot of the full transient solution in Fig. 8.11. Also seen in Fig. 8.11 is that the centerline temperature $T(0, t)$ relaxes to the long time value predicted by the low temperature steady solution:

$$\lim_{t \to \infty} T(0, t) = 0.016. \tag{8.197}$$

8.4.2.2   High temperature solution

We next select a value of $\delta = 1.2 > \delta_c$. This should induce transition to a high temperature solution. We maintain $\Theta = 15$, $Q = 1$. We get $\mathfrak{D} = \delta e^{\Theta}/\Theta/Q = 261521$. The full transient solution is shown in Fig. 8.12 Also shown in Fig. 8.12 is the centerline temperature $T(0, t)$. We see it relaxes to the long time value predicted by the high temperature steady solution:

$$\lim_{t \to \infty} T(0, t) = 0.9999185. \tag{8.198}$$
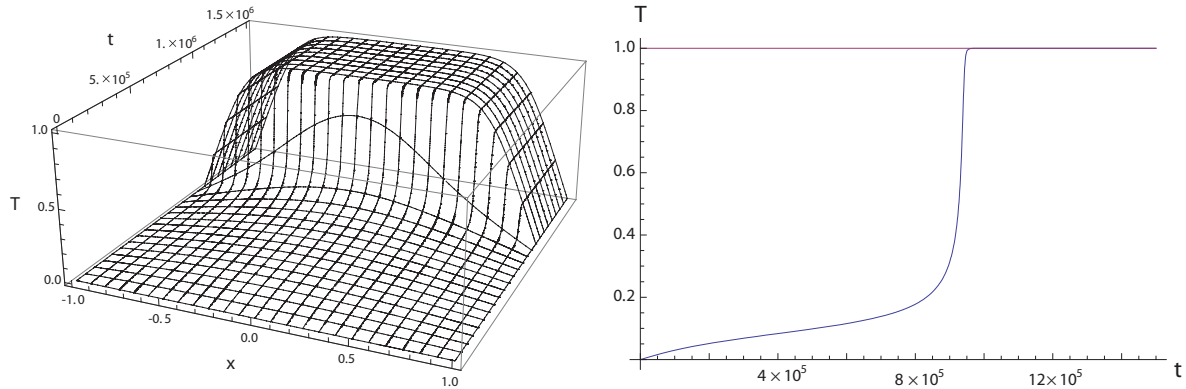
Figure 8.12: Plot of $T(x,t)$ and plot of $T(0,t)$ along with the long time exact low temperature centerline solution, $T_e(0)$, with $\delta = 1.2$, $Q = 1$, $\Theta = 15$.

It is clearly seen that there is a rapid acceleration of the reaction for $t \sim 10^6$. This compares with the prediction of the induction time from the infinite Damköhler number, $\mathfrak{D} \to \infty$, thermal explosion theory of explosion to occur when

$$t \to \frac{e^{\Theta}}{Q\Theta} = \frac{e^{15}}{(1)(15)} = 2.17934 \times 10^5. \tag{8.199}$$

The estimate under-predicts the value by a factor of five. This is likely due to 1) cooling of the domain due to the low temperature boundaries at $x = \pm 1$, and 2) effects of finite activation energy.

Chapter 9

Laminar flames: reaction-advection-diffusion

> There is no more open door by which you can enter into the study of natural philosophy than by considering the physical phenomena of a candle.

Michael Faraday (1791-1867), *The Chemical History of a Candle*, Griffin and Bohn, London, 1861.

————————————-

Here, we will consider premixed one-dimensional steady laminar flames. Background is available in many sources.[1][2][3] This topic is broad, but we will restrict attention to the simplest cases. We will consider a simple reversible kinetics model

$$A \rightleftharpoons B, \tag{9.1}$$

where A and B have identical molecular masses, $M_A = M_B = M$, and are both calorically perfect ideal gases with the same specific heats, $c_{PA} = c_{PB} = c_P$. Because we are modelling the system as premixed, we consider species A to be composed of molecules which have their own fuel and oxidizer. This is not common in hydrocarbon kinetics, but is more so in the realm of explosives. More common in gas phase kinetics are situations in which cold fuel and cold oxidizer react together to form hot products. In such a situation, one can also consider non-premixed flames in which streams of fuel first must mix with streams of oxidizer before significant reaction can commence. Such flames will not be considered in this chapter.

We shall see that the introduction of advection introduces some unusual mathematical difficulties in properly modelling cold unreacting flow. This will be overcome in a way which is æsthetically unappealing, but nevertheless useful: we shall introduce an ignition temperature T_{ig} in our reaction kinetics law to suppress all reaction for $T < T_{ig}$. This will serve to render the cold boundary to be a true mathematical equilibrium point of the

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[1]Buckmaster, J. D., and Ludford, G. S. S., 2008, *Theory of Laminar Flames*, Cambridge, Cambridge.
[2]Williams, F. A., 1985, *Combustion Theory*, Benjamin-Cummings, Menlo Park, California.
[3]Law, C. K., 2006, *Combustion Physics*, Cambridge, Cambridge.

model; this is not a traditional chemical equilibrium, but it is an equilibrium in the formal mathematical sense nonetheless.

9.1   Governing Equations

9.1.1   Evolution equations

We will first consider conservation and evolution equations which are independent of any specific material.

9.1.1.1   Conservative form

Let us commence with the one-dimensional versions of Eqs. (6.1-6.3) and (6.5):

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}\left(\rho u\right) = 0, \tag{9.2}$$

$$\frac{\partial}{\partial t}\left(\rho u\right) + \frac{\partial}{\partial x}\left(\rho u^2 + P - \tau\right) = 0, \tag{9.3}$$

$$\frac{\partial}{\partial t}\left(\rho\left(e + \frac{1}{2}u^2\right)\right) + \frac{\partial}{\partial x}\left(\rho u\left(e + \frac{1}{2}u^2\right) + j^q + (P - \tau)u\right) = 0, \tag{9.4}$$

$$\frac{\partial}{\partial t}(\rho Y_B) + \frac{\partial}{\partial x}\left(\rho u Y_B + j_B^m\right) = M\dot{\omega}_B. \tag{9.5}$$

9.1.1.2   Non-conservative form

Using standard reductions similar to those made to achieve Eqs. (6.34),(6.37),(6.42), (6.54), the non-conservative form of the governing equations, Eqs. (9.2-9.5) is

$$\frac{\partial \rho}{\partial t} + u\frac{\partial \rho}{\partial x} + \rho\frac{\partial u}{\partial x} = 0, \tag{9.6}$$

$$\rho\frac{\partial u}{\partial t} + \rho u\frac{\partial u}{\partial x} + \frac{\partial P}{\partial x} - \frac{\partial \tau}{\partial x} = 0, \tag{9.7}$$

$$\rho\frac{\partial e}{\partial t} + \rho u\frac{\partial e}{\partial x} + \frac{\partial j^q}{\partial x} + P\frac{\partial u}{\partial x} - \tau\frac{\partial u}{\partial x} = 0, \tag{9.8}$$

$$\rho\frac{\partial Y_B}{\partial t} + \rho u\frac{\partial Y_B}{\partial x} + \frac{\partial j_B^m}{\partial x} = M\dot{\omega}_B. \tag{9.9}$$

Equations (9.6-9.9) can be written more compactly using the material derivative, $d/dt = \partial/\partial t + u\partial/\partial x$:

$$\frac{d\rho}{dt} + \rho\frac{\partial u}{\partial x} = 0, \tag{9.10}$$

$$\rho\frac{du}{dt} + \frac{\partial P}{\partial x} - \frac{\partial \tau}{\partial x} = 0, \tag{9.11}$$

$$\rho\frac{de}{dt} + \frac{\partial j^q}{\partial x} + P\frac{\partial u}{\partial x} - \tau\frac{\partial u}{\partial x} = 0, \tag{9.12}$$

$$\rho\frac{dY_B}{dt} + \frac{\partial j_B^m}{\partial x} = M\dot{\omega}_B. \tag{9.13}$$

9.1.1.3 Formulation using enthalpy

It will be more useful to formulate the equations using enthalpy. Use the definition of enthalpy Eq. (3.78), $h = e + Pv = e + P/\rho$, to get an expression for dh:

$$dh = de - \frac{P}{\rho^2}d\rho + \frac{1}{\rho}dP, \tag{9.14}$$

$$\frac{dh}{dt} = \frac{de}{dt} - \frac{P}{\rho^2}\frac{d\rho}{dt} + \frac{1}{\rho}\frac{dP}{dt}, \tag{9.15}$$

$$\frac{de}{dt} - \frac{P}{\rho^2}\frac{d\rho}{dt} = \frac{dh}{dt} - \frac{1}{\rho}\frac{dP}{dt}, \tag{9.16}$$

$$\rho\frac{de}{dt} - \frac{P}{\rho}\frac{d\rho}{dt} = \rho\frac{dh}{dt} - \frac{dP}{dt}. \tag{9.17}$$

Now, using the mass equation, Eq. (9.10) to eliminate $P\partial u/\partial x$ in the energy equation, Eq. (9.12), the energy equation can be rewritten as

$$\rho\frac{de}{dt} + \frac{\partial j^q}{\partial x} - \frac{P}{\rho}\frac{d\rho}{dt} - \tau\frac{\partial u}{\partial x} = 0, \tag{9.18}$$

Next use Eq. (9.17) to simplify Eq. (9.18):

$$\rho\frac{dh}{dt} + \frac{\partial j^q}{\partial x} - \frac{dP}{dt} - \tau\frac{\partial u}{\partial x} = 0. \tag{9.19}$$

9.1.1.4 Low Mach number limit

In the limit of low Mach number, one can do a formal asymptotic expansion with the reciprocal of the Mach number squared as a perturbation parameter. All variables take the form $\psi = \psi_o + \mathsf{M}^2\psi_1 + \ldots$, where ψ is a general variable, and M is the Mach number, not to be confused with the molecular mass M. In this limit, the linear momentum equation can be shown to reduce at leading order to $\partial P_o/\partial x = 0$, giving rise to $P_o = P_o(t)$.

We shall ultimately be concerned only with time-independent flows where $P = P_o$. We adopt the constant pressure assumption now. Also in the low Mach number limit, it can be shown that viscous work is negligible, so $\tau\partial u/\partial x \sim 0$. Our evolution equations, Eqs. (9.10),(9.19),(9.13), then in the low Mach number, constant pressure limit are

$$\frac{\partial\rho}{\partial t} + u\frac{\partial\rho}{\partial x} + \rho\frac{\partial u}{\partial x} = 0, \tag{9.20}$$

$$\rho\frac{\partial h}{\partial t} + \rho u\frac{\partial h}{\partial x} + \frac{\partial j^q}{\partial x} = 0, \tag{9.21}$$

$$\rho\frac{\partial Y_B}{\partial t} + \rho u\frac{\partial Y_B}{\partial x} + \frac{\partial j_B^m}{\partial x} = M\dot{\omega}_B. \tag{9.22}$$

Note that we have effectively removed the momentum equation. It would re-appear in a non-trivial way were we to formulate the equations at the next order.

Equations (9.20-9.22) take on the conservative form

$$\frac{\partial\rho}{\partial t} + \frac{\partial}{\partial x}(\rho u) = 0, \tag{9.23}$$

$$\frac{\partial}{\partial t}(\rho h) + \frac{\partial}{\partial x}(\rho u h + j^q) = 0, \tag{9.24}$$

$$\frac{\partial}{\partial t}(\rho Y_B) + \frac{\partial}{\partial x}(\rho u Y_B + j_B^m) = M\dot{\omega}_B. \tag{9.25}$$

9.1.2   Constitutive models

Equations (9.20-9.22) are supplemented by simple constitutive models:

$$P_o = \rho R T, \tag{9.26}$$

$$h = c_P(T - T_o) - Y_B q, \tag{9.27}$$

$$j_B^m = -\rho\mathcal{D}\frac{\partial Y_B}{\partial x}, \tag{9.28}$$

$$j^q = -\mathsf{k}\frac{\partial T}{\partial x} + \rho\mathcal{D}q\frac{\partial Y_B}{\partial x}, \tag{9.29}$$

$$\dot{\omega}_B = aT^\beta e^{-\mathcal{E}/(RT)}\underbrace{\frac{\rho}{M}(1-Y_B)}_{=\bar{\rho}_A}\left(1 - \frac{1}{K_c}\underbrace{\left(\frac{Y_B}{1-Y_B}\right)}_{=\bar{\rho}_B/\bar{\rho}_A}\right)H(T - T_{ig}), \tag{9.30}$$

$$K_c = e^{q/(RT)}. \tag{9.31}$$

Thus, we have nine equations for the nine unknowns, ρ, u, h, T, j^q, Y_B, j_B^m, $\dot{\omega}_B$, K_c.

Many of these are obvious. Some are not. First, we note the new factor $H(T - T_{ig})$ in our kinetics law, Eq. (9.30). Here, H is a Heaviside unit step function. For $T < T_{ig}$ it takes a value of zero. For $T \geq T_{ig}$, it takes a value of unity:

$$H(T - T_{ig}) = \begin{cases} 0, & T < T_{ig}, \\ 1, & T \geq T_{ig}. \end{cases} \tag{9.32}$$

Next, let us see how to get Eq. (9.28) from the more general Eq. (6.81). We first take the thermal diffusion coefficient to be zero, $D_i^T = 0$. We also note since $M_A = M_B = M$

that $y_k = Y_k$; that is mole fractions are the same as mass fractions. So, Eq. (6.81) simplifies considerably to

$$j_i^m = \rho \sum_{k=1, k \neq i}^{N} D_{ik} \frac{\partial Y_k}{\partial x}. \tag{9.33}$$

Next we take $D_{ik} = \mathcal{D}$ and write for each of the two diffusive mass fluxes that

$$j_A^m = \rho \mathcal{D} \frac{\partial Y_B}{\partial x}, \tag{9.34}$$

$$j_B^m = \rho \mathcal{D} \frac{\partial Y_A}{\partial x}. \tag{9.35}$$

Since $Y_A + Y_B = 1$, we have also

$$j_A^m = -\rho \mathcal{D} \frac{\partial Y_A}{\partial x}, \tag{9.36}$$

$$j_B^m = -\rho \mathcal{D} \frac{\partial Y_B}{\partial x}. \tag{9.37}$$

Note that $j_A^m + j_B^m = 0$, as required by Eq. (6.6).

Under the same assumptions, Eq. (6.80) reduces to

$$j^q = -\mathsf{k} \frac{\partial T}{\partial x} + j_A^m h_A + j_B^m h_B, \tag{9.38}$$

$$= -\mathsf{k} \frac{\partial T}{\partial x} + j_A^m (h_{A,T_o} + c_P(T - T_o)) + j_B^m (h_{B,T_o} + c_P(T - T_o)), \tag{9.39}$$

$$= -\mathsf{k} \frac{\partial T}{\partial x} + j_A^m h_{A,T_o} + j_B^m h_{B,T_o} + \underbrace{(j_A^m + j_B^m)}_{=0} c_P(T - T_o), \tag{9.40}$$

$$= -\mathsf{k} \frac{\partial T}{\partial x} - j_B^m h_{A,T_o} + j_B^m h_{B,T_o}, \tag{9.41}$$

$$= -\mathsf{k} \frac{\partial T}{\partial x} - j_B^m \underbrace{(h_{A,T_o} - h_{B,T_o})}_{=q}, \tag{9.42}$$

$$j^q = -\mathsf{k} \frac{\partial T}{\partial x} - j_B^m q, \tag{9.43}$$

$$j^q = -\mathsf{k} \frac{\partial T}{\partial x} + \rho \mathcal{D} q \frac{\partial Y_B}{\partial x}. \tag{9.44}$$

Here, we have defined a heat release per unit mass, q, as

$$q = h_{A,T_o} - h_{B,T_o}. \tag{9.45}$$

For the equilibrium constant K_c, we specialize Eq. (4.270), recalling $\nu_A + \nu_B = 1 - 1 = 0$ for our simple reaction kinetics, and get

$$K_c = \exp\left(\frac{-\Delta G^o}{\overline{R} T}\right), \tag{9.46}$$

$$= \exp\left(\frac{-(\overline{g}_B^o - \overline{g}_A^o)}{\overline{R}T}\right), \tag{9.47}$$

$$= \exp\left(\frac{g_A^o - g_B^o}{RT}\right), \tag{9.48}$$

$$= \exp\left(\frac{h_A^o - Ts_A^o - (h_B^o - Ts_B^o)}{RT}\right), \tag{9.49}$$

$$= \exp\left(\frac{h_A^o - h_B^o}{RT}\right)\exp\left(\frac{s_B^o - s_A^o}{R}\right), \tag{9.50}$$

$$= \exp\left(\frac{h_{A,T_o}^o - h_{B,T_o}^o}{RT}\right)\exp\left(\frac{s_{B,T_o}^o - s_{A,T_o}^o}{R}\right). \tag{9.51}$$

Here, because of constant specific heats for A and B, many terms have canceled. Let us take now $s_{B,T_o}^o = s_{A,T_o}^o$ and our definition of the heat release, Eq. (9.45), to get

$$K_c = \exp\left(\frac{q}{RT}\right). \tag{9.52}$$

9.1.3   Alternate forms

Further analysis of the evolution equations combined with the constitutive equations can yield forms which give physical insight.

9.1.3.1   Species equation

If we combine our species evolution equation, Eq. (9.22) with the constitutive law, Eq. (9.28), we get

$$\rho\frac{\partial Y_B}{\partial t} + \rho u\frac{\partial Y_B}{\partial x} - \frac{\partial}{\partial x}\left(\rho\mathcal{D}\frac{\partial Y_B}{\partial x}\right) = M\dot{\omega}_B. \tag{9.53}$$

Note that for flows with no advection ($u = 0$), constant density ($\rho =$ constant), and no reaction ($\dot{\omega}_B = 0$), this reduces to the classical "heat" equation from mathematical physics $\partial Y_B/\partial t = \mathcal{D}(\partial^2 Y_B/\partial x^2)$.

9.1.3.2   Energy equation

Consider the energy equation, Eq. (9.21), using Eqs. (9.27,9.29) to eliminate h and j^q:

$$\rho\frac{\partial}{\partial t}\underbrace{(c_P(T - T_o) - Y_B q)}_{=h} + \rho u\frac{\partial}{\partial x}\underbrace{(c_P(T - T_o) - Y_B q)}_{=h} + \frac{\partial}{\partial x}\underbrace{\left(-\mathsf{k}\frac{\partial T}{\partial x} + \rho\mathcal{D}q\frac{\partial Y_B}{\partial x}\right)}_{=j^q} = 0,$$

$$\tag{9.54}$$

$$\rho\frac{\partial}{\partial t}\left(T - Y_B\frac{q}{c_P}\right) + \rho u\frac{\partial}{\partial x}\left(T - Y_B\frac{q}{c_P}\right) - \frac{\partial}{\partial x}\left(\frac{\mathsf{k}}{c_P}\frac{\partial T}{\partial x} - \rho\mathcal{D}\frac{\partial Y_B}{\partial x}\frac{q}{c_P}\right) = 0,$$

$$(9.55)$$

$$\rho\frac{\partial T}{\partial t} + \rho u\frac{\partial T}{\partial x} - \frac{\mathsf{k}}{c_P}\frac{\partial^2 T}{\partial x^2} - \frac{q}{c_P}\underbrace{\left(\rho\frac{\partial Y_B}{\partial t} + \rho u\frac{\partial Y_B}{\partial x} - \frac{\partial}{\partial x}\left(\rho\mathcal{D}\frac{\partial Y_B}{\partial x}\right)\right)}_{=M\dot{\omega}_B} = 0,$$

$$(9.56)$$

We notice that the terms involving Y_B simplify via Eq. (9.53) to yield an equation for temperature evolution

$$\rho\frac{\partial T}{\partial t} + \rho u\frac{\partial T}{\partial x} - \frac{\mathsf{k}}{c_P}\frac{\partial^2 T}{\partial x^2} - \frac{q}{c_P}M\dot{\omega}_B = 0, \qquad (9.57)$$

$$\frac{\partial T}{\partial t} + u\frac{\partial T}{\partial x} = \underbrace{\frac{\mathsf{k}}{\rho c_P}}_{=\alpha}\frac{\partial^2 T}{\partial x^2} + \frac{q}{\rho c_P}M\dot{\omega}_B. \qquad (9.58)$$

We note, see p. 273, that thermal diffusivity α is

$$\alpha = \frac{\mathsf{k}}{\rho c_P}. \qquad (9.59)$$

We note here that this definition, convenient and in the combustion literature, is slightly non-traditional as it involves a variable property ρ. So, the reduced energy equation is

$$\frac{\partial T}{\partial t} + u\frac{\partial T}{\partial x} = \alpha\frac{\partial^2 T}{\partial x^2} + \frac{q}{\rho c_P}M\dot{\omega}_B. \qquad (9.60)$$

Equation (9.60) is closely related to the more general Eq. (6.103). Note that for exothermic reaction, $q > 0$ accompanied with production of product B, $\dot{\omega}_B > 0$, induces a temperature rise of a material particle. The temperature change is modulated by energy diffusion. In the inert zero advection limit, we recover the ordinary heat equation $\partial T/\partial t = \alpha(\partial^2 T/\partial x^2)$.

9.1.3.3 Shvab-Zel'dovich form

Let us now adopt the assumption that mass and energy diffuse at the same rate. This is not difficult to believe as both are molecular collision phenomena in gas flames. Such an assumption will allow us to write the energy equation in the Shvab-Zel'dovich form such as studied in a more general sense in Sec. 6.5. We note the dimensionless ratio of energy diffusivity α to mass diffusivity $\mathcal{D}$ is known as the Lewis[4] number, Le:

$$Le = \frac{\alpha}{\mathcal{D}}. \qquad (9.61)$$

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[4]Warren Kendall Lewis, 1882-1975, American chemical engineer.

If we insist that mass and energy diffuse at the same rate, we have $Le = 1$, which gives

$$\mathcal{D} = \alpha = \frac{\mathsf{k}}{\rho c_P}. \tag{9.62}$$

With this assumption, the energy equation, Eq. (9.55), takes the form

$$\rho\frac{\partial}{\partial t}\left(T - Y_B\frac{q}{c_P}\right) + \rho u\frac{\partial}{\partial x}\left(T - Y_B\frac{q}{c_P}\right) - \frac{\partial}{\partial x}\left(\frac{\mathsf{k}}{c_P}\frac{\partial T}{\partial x} - \frac{\mathsf{k}}{c_P}\frac{\partial Y_B}{\partial x}\frac{q}{c_P}\right) = 0, \tag{9.63}$$

$$\rho\frac{\partial}{\partial t}\left(T - Y_B\frac{q}{c_P}\right) + \rho u\frac{\partial}{\partial x}\left(T - Y_B\frac{q}{c_P}\right) - \frac{\mathsf{k}}{c_P}\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x}\left(T - Y_B\frac{q}{c_P}\right)\right) = 0, \tag{9.64}$$

$$\frac{\partial}{\partial t}\left(T - Y_B\frac{q}{c_P}\right) + u\frac{\partial}{\partial x}\left(T - Y_B\frac{q}{c_P}\right) - \frac{\mathsf{k}}{\rho c_P}\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x}\left(T - Y_B\frac{q}{c_P}\right)\right) = 0. \tag{9.65}$$

We rewrite in terms of the material derivative

$$\frac{d}{dt}\left(T - Y_B\frac{q}{c_P}\right) = \frac{\mathsf{k}}{\rho c_P}\frac{\partial^2}{\partial x^2}\left(T - Y_B\frac{q}{c_P}\right). \tag{9.66}$$

Equation (9.66) holds that for a material fluid particle, the quantity $T - Y_B q/c_P$ changes only in response to local spatial gradients. Now, if we consider an initial value problem in which T and Y_B are initially spatially uniform and there are no gradients of either T or Y_B at $x \to \pm\infty$, then there will no tendency for *any* material particle to have its value of $T - Y_B q/c_P$ change. Let us assume that at $t = 0$, we have $T = T_o$ and no product, so $Y_B = 0$. Then, we can conclude that the following relation holds for all space and time:

$$T - Y_B\frac{q}{c_P} = T_o. \tag{9.67}$$

Solving for Y_B, we get

$$Y_B = \frac{c_P(T - T_o)}{q}. \tag{9.68}$$

For this chapter, we are mainly interested in steady waves. We can imagine that our steady waves are the long time limit of a situation just described which was initially spatially uniform. Compare Eq. (9.68) to our related *ad hoc* assumption for reactive solids, Eq. (8.26). They are essentially equivalent, especially when one recalls that λ plays the same role as Y_B and for the reactive solid $c_P \sim c_v$.

We can use Eq. (9.68) to eliminate Y_B in the species equation, Eq. (9.53) to get a single equation for temperature evolution. First adopt the equal diffusion assumption, Eq. (9.62), in Eq. (9.53):

$$\rho\frac{\partial Y_B}{\partial t} + \rho u\frac{\partial Y_B}{\partial x} - \frac{\partial}{\partial x}\left(\frac{\mathsf{k}}{c_P}\frac{\partial Y_B}{\partial x}\right) = M\dot{\omega}_B. \tag{9.69}$$

Next use Eq. (9.68) to eliminate Y_B:

$$\rho\frac{\partial}{\partial t}\left(\frac{c_P(T-T_o)}{q}\right) + \rho u\frac{\partial}{\partial x}\left(\frac{c_P(T-T_o)}{q}\right) - \frac{\partial}{\partial x}\left(\frac{\mathsf{k}}{c_P}\frac{\partial}{\partial x}\left(\frac{c_P(T-T_o)}{q}\right)\right) = M\dot{\omega}_B.$$

$$(9.70)$$

Simplifying, we get

$$\rho c_P\left(\frac{\partial T}{\partial t} + u\frac{\partial T}{\partial x}\right) - \mathsf{k}\frac{\partial^2 T}{\partial x^2} = qM\dot{\omega}_B. \tag{9.71}$$

Now, let us use Eq. (9.30) to eliminate $\dot{\omega}_B$:

$$\rho c_P\left(\frac{\partial T}{\partial t} + u\frac{\partial T}{\partial x}\right) - \mathsf{k}\frac{\partial^2 T}{\partial x^2}$$
$$= \rho q a T^\beta e^{-\mathcal{E}/(RT)}(1-Y_B)\left(1 - \frac{1}{K_c}\frac{Y_B}{1-Y_B}\right)H(T-T_{ig}). \tag{9.72}$$

Now, use Eq. (9.52) to eliminate K_c and Eq. (9.68) to eliminate Y_B so to get

$$\rho c_P\left(\frac{\partial T}{\partial t} + u\frac{\partial T}{\partial x}\right) - \mathsf{k}\frac{\partial^2 T}{\partial x^2}$$
$$= \rho q a T^\beta e^{-\mathcal{E}/(RT)}\left(1 - \frac{c_P(T-T_o)}{q}\right)\left(1 - e^{-q/(RT)}\frac{\frac{c_P(T-T_o)}{q}}{1 - \frac{c_P(T-T_o)}{q}}\right)H(T-T_{ig}). \tag{9.73}$$

Equation (9.73) is remarkably similar to our earlier Eq. (8.28) for temperature evolution in a heat conducting reactive solid. The differences are as follows:

- We use c_P instead of c_v,

- We have included advection,

- We have accounted for finite β,

- We have accounted for reversible reaction.

- We have imposed and ignition temperature.

9.1.4 Equilibrium conditions

We can gain further insights by examining when Eq. (9.73) is in equilibrium. There is one potential equilibria, the state of chemical equilibrium where $K_c = Y_B/(1-Y_B) = Y_B/Y_A$. This occurs when

$$1 - e^{-q/(RT)}\frac{\frac{c_P(T-T_o)}{q}}{1 - \frac{c_P(T-T_o)}{q}} = 0. \tag{9.74}$$

Parameter	Value	Units
Fundamental Dimensional		
T_o	300	K
c_P	1000	$J/kg/K$
R	287	$J/kg/K$
q	1.5×10^6	J/kg
$\mathcal{E}$	1.722×10^5	J/kg
α_o	10^{-5}	m^2/s
a	10^5	$1/s$
u_o	1.4142	m/s
P_o	10^5	Pa
T_{ig}	600	K
Secondary Dimensional		
ρ_o	1.1614	kg/m^3
k	0.0116114	$J/m/s$
Fundamental Dimensionless		
γ	1.4025	
Q	5	
Θ	2	
$\mathfrak{D}$	2	
T_{IG}	0.2	

Table 9.1: Numerical values of parameters for simple laminar flame calculation.

This is a transcendental equation for T. Let us examine how the equilibrium T varies for some sample parameters. For this and later calculations, we give a set of parameters in Table 9.1. Let us consider how the equilibrium temperature varies as q is varied from near zero to its maximum value of Table 9.1. The chemical equilibrium flame temperature and product mass fraction are plotted as functions of q in Figure 9.1. For $q = 0$, the equilibrium
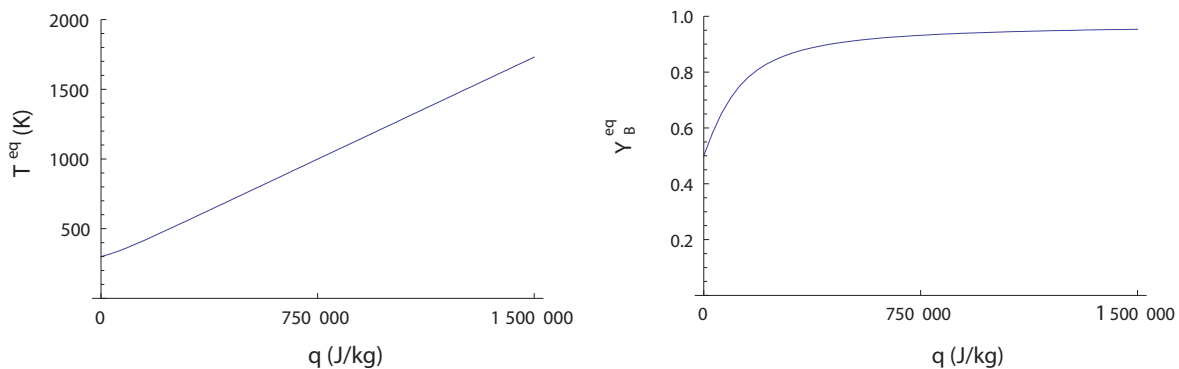
Figure 9.1: Variation of chemical equilibrium temperature and product mass fraction with heat release.

temperature is the ambient temperature. As q increases, the equilibrium temperature increases monotonically. When $q = 0$, the equilibrium mass fraction is $Y_B = 0.5$; that is, there is no tendency for either products or reactants. As q increases, the tendency for increased product mass fraction increases, and $Y_B \to 1$.

There is also the state of complete reaction when $Y_B = 1$, which corresponds to

$$1 - \frac{c_P(T - T_o)}{q} = 0, \tag{9.75}$$

$$T = T_o + \frac{q}{c_P}. \tag{9.76}$$

Numerically, at our maximum value of $q = 1.5 \times 10^6 \ J/kg$, we get complete reaction when $T = 1800 \ K$. Note this state is not an equilibrium state unless $K_c \to \infty$. As $x \to \infty$, we expect a state of chemical equilibrium and a corresponding high temperature. At some intermediate point, the temperature will have its value at ignition, T_{ig}. We will ultimately transform our domain so the ignition temperature is realized at $x = 0$, which we can associate with a burner surface. We say that the flame is thus anchored to the burner. Without such a prescribed anchor, our equations are such that any translation in x will yield an invariant solution, so the origin of x is arbitrary.

9.2 Steady burner-stabilized flames

Let us consider an important problem in laminar flame theory: that of a burner-stabilized flame. We shall consider a doubly-infinite domain, $x \in (-\infty, \infty)$. We will assume that as

$x \to -\infty$, we have a fresh unburned stream of reactant A, $Y_A = 1$, $Y_B = 0$, with known velocity u_o, density ρ_o and temperature T_o. The values of ρ_o and T_o will be consistent with a state equation so that the pressure has a value of P_o.

9.2.1 Formulation

Let us consider our governing equations in the steady wave frame where there is no variation with t: $\partial/\partial t = 0$. This, coupled with our other reductions, yields the system

$$\frac{d}{dx}(\rho u) = 0, \tag{9.77}$$

$$\rho u c_P \frac{dT}{dx} - \mathsf{k}\frac{d^2T}{dx^2} = \rho q a T^\beta e^{-\mathcal{E}/(RT)}\left(1 - \frac{c_P(T - T_o)}{q}\right)$$
$$\times \left(1 - e^{-q/(RT)}\frac{\frac{c_P(T-T_o)}{q}}{1 - \frac{c_P(T-T_o)}{q}}\right) H(T - T_{ig}), \tag{9.78}$$

$$P_o = \rho RT. \tag{9.79}$$

Now, we have three equations for the three remaining unknowns, ρ, u, T.

For a burner-stabilized flame, we assume at $x \to -\infty$ that we know the velocity, u_o, the temperature, T_o, and the density, ρ_o. We can integrate the mass equation to get

$$\rho u = \rho_o u_o. \tag{9.80}$$

We then rewrite the remaining differential equation as

$$\rho_o u_o c_P \frac{dT}{dx} - \mathsf{k}\frac{d^2T}{dx^2} = \frac{P_o}{R}q a T^{\beta-1} e^{-\mathcal{E}/(RT)}\left(1 - \frac{c_P(T - T_o)}{q}\right)$$
$$\times \left(1 - e^{-q/(RT)}\frac{\frac{c_P(T-T_o)}{q}}{1 - \frac{c_P(T-T_o)}{q}}\right) H(T - T_{ig}). \tag{9.81}$$

Our boundary conditions for this second order differential equation are

$$\frac{dT}{dx} \to 0, \quad x \to \pm\infty. \tag{9.82}$$

We will ultimately need to integrate this equation numerically, and this poses some difficulty because the boundary conditions are applied at $\pm\infty$. We can overcome this in the following way. Note that our equations are invariant under a translation in x. We will choose some large value of x to commence numerical integration. We shall initially assume this is near the chemical equilibrium point. We shall integrate backwards in x. We shall note the value of x where $T = T_{ig}$. Beyond that point, the reaction rate is zero, and we can obtain an exact solution for T. We will then translate all our results so that the ignition temperature is realized at $x = 0$.

Let us scale temperature so that

$$T = T_o \left(1 + \frac{q}{c_P T_o} T_* \right). \tag{9.83}$$

Inverting, we see that

$$T_* = \frac{c_P (T - T_o)}{q}. \tag{9.84}$$

We get a dimensionless ignition temperature T_{IG} of

$$T_{IG} = \frac{c_P (T_{ig} - T_o)}{q}. \tag{9.85}$$

Let us also define a dimensionless heat release Q as

$$Q = \frac{q}{c_P T_o}. \tag{9.86}$$

Thus

$$\frac{T}{T_o} = 1 + Q T_*. \tag{9.87}$$

Note that $T_* = 1$ corresponds to our complete reaction point where $Y_B = 1$. Let us also restrict ourselves, for convenience, to the case where $\beta = 0$. With these scalings, and with

$$\Theta = \frac{\mathcal{E}}{R T_o}, \tag{9.88}$$

our differential equations become

$$\rho_o u_o c_P T_o Q \frac{dT_*}{dx} - k T_o Q \frac{d^2 T_*}{dx^2} = \frac{P_o}{R} qa \exp\left(\frac{-\Theta}{1 + Q T_*} \right) \left(\frac{1 - T_*}{T_o (1 + Q T_*)} \right)$$
$$\times \left(1 - \exp\left(-\frac{\frac{\gamma}{\gamma - 1} Q}{1 + Q T_*} \right) \frac{T_*}{1 - T_*} \right) H(T_* - T_{IG}) \tag{9.89}$$

$$\frac{dT_*}{dx} \to 0, \quad x \to \pm\infty. \tag{9.90}$$

Let us now scale both sides by $\rho_o u_o c_P T_o$ to get

$$Q \frac{dT_*}{dx} - \frac{k}{\rho_o c_P} \frac{1}{u_o} Q \frac{d^2 T_*}{dx^2} = \underbrace{\frac{P_o}{\rho_o R T_o}}_{=1} \underbrace{\frac{q}{c_P T_o}}_{=Q} \frac{a}{u_o} \exp\left(\frac{-\Theta}{1 + Q T_*} \right) \left(\frac{1 - T_*}{1 + Q T_*} \right)$$
$$\times \left(1 - \exp\left(-\frac{\frac{\gamma}{\gamma - 1} Q}{1 + Q T_*} \right) \frac{T_*}{1 - T_*} \right) H(T_* - T_{IG}). \tag{9.91}$$

Realizing that $P_o = \rho_o R T_o$, the ambient thermal diffusivity, $\alpha_o = \mathsf{k}/(\rho_o c_P)$ and canceling Q, we get

$$
\frac{dT_*}{dx} - \alpha_o \frac{1}{u_o} \frac{d^2 T_*}{dx^2} = \frac{a}{u_o} \exp\left(\frac{-\Theta}{1 + Q T_*}\right)\left(\frac{1 - T_*}{1 + Q T_*}\right)
$$
$$
\times \left(1 - \exp\left(-\frac{\frac{\gamma}{\gamma - 1} Q}{1 + Q T_*} \frac{T_*}{1 - T_*}\right)\right) H(T_* - T_{IG}). \qquad (9.92)
$$

Now, let us scale x by a characteristic length, $L = u_o/a$. This length scale is dictated by a balance between reaction and advection. When the reaction is fast, a is large, and the length scale is reduced. When the incoming velocity is fast, u_o is large, and the length scale is increased.

$$
x_* = \frac{x}{L} = \frac{ax}{u_o}. \qquad (9.93)
$$

With this choice of length scale, Eq. (9.92) becomes

$$
\frac{dT_*}{dx_*} - \alpha_o \frac{a}{u_o^2} \frac{d^2 T_*}{dx_*^2} = \exp\left(\frac{-\Theta}{1 + Q T_*}\right)\left(\frac{1 - T_*}{1 + Q T_*}\right)
$$
$$
\times \left(1 - \exp\left(-\frac{\frac{\gamma}{\gamma - 1} Q}{1 + Q T_*} \frac{T_*}{1 - T_*}\right)\right) H(T_* - T_{IG}). \qquad (9.94)
$$

Now, similar to Eq. (8.36), we take the Damköhler number $\mathfrak{D}$ to be

$$
\mathfrak{D} = \frac{aL^2}{\alpha_o} = \frac{u_o^2}{a\alpha_o}. \qquad (9.95)
$$

In contrast to Eq. (8.36) the Damköhler number here includes the effects of advection. With this choice, Eq. (9.94) becomes

$$
\frac{dT_*}{dx_*} - \frac{1}{\mathfrak{D}} \frac{d^2 T_*}{dx_*^2} = \exp\left(\frac{-\Theta}{1 + Q T_*}\right)\left(\frac{1 - T_*}{1 + Q T_*}\right)
$$
$$
\times \left(1 - \exp\left(-\frac{\frac{\gamma}{\gamma - 1} Q}{1 + Q T_*} \frac{T_*}{1 - T_*}\right)\right) H(T_* - T_{IG}). \qquad (9.96)
$$

Lastly, let us dispose with the $*$ notation and understand that all variables are dimensionless. Our differential equation and boundary conditions become

$$
\frac{dT}{dx} - \frac{1}{\mathfrak{D}} \frac{d^2 T}{dx^2} = \exp\left(\frac{-\Theta}{1 + Q T}\right)\left(\frac{1 - T}{1 + Q T}\right)
$$
$$
\times \left(1 - \exp\left(-\frac{\frac{\gamma}{\gamma - 1} Q}{1 + Q T} \frac{T}{1 - T}\right)\right) H(T - T_{IG}), \qquad (9.97)
$$

$$
\left.\frac{dT}{dx}\right|_{x \to \pm\infty} \to 0. \qquad (9.98)
$$

Equation (9.97) is remarkably similar to our Frank-Kamenetskii problem embodied in Eq. (8.59). The major differences are reflected in that Eq. (9.97) accounts for

- advection,

- variable density,

- reversible reaction,

- doubly-infinite spatial domain.

9.2.2 Solution procedure

There are some unusual challenges in the numerical solution of the equations for laminar flames. Formally we are solving a two-point boundary value problem on a doubly-infinite domain. The literature is not always coherent on solutions methods or the interpretations of results. At the heart of the issue is the cold boundary difficulty. We have patched this problem via the use of an ignition temperature built into a Heaviside[5] function; see Eq. (9.30). We shall see that this patch has advantages and disadvantages. Here, we will not dwell on nuances, but will present a result which is mathematically sound and offer interpretations. Our result will use standard techniques of non-linear analysis from dynamic systems theory. We will pose the problem as a coupled system of first order non-linear differential equations, find their equilibria, use local linear analysis to ascertain the stability of the chemical equilibrium fixed point, and use numerical integration to calculate the non-linear laminar flame structure.

9.2.2.1 Model linear system

Before commencing with the difficult Eq. (9.97), let us consider a related linear model system, given here:

$$3\frac{dT}{dx} - \frac{d^2T}{dx^2} = 4(1-T)H(T-T_{IG}), \qquad \left.\frac{dT}{dx}\right|_{x\to\pm\infty} \to 0. \qquad (9.99)$$

The forcing is removed when either $T = 1$ or $T < T_{IG}$.

Defining $\mathsf{q} \equiv -dT/dx$, we rewrite our model equation as a linear system of first order equations:

$$\frac{d\mathsf{q}}{d\mathsf{x}} = 3\mathsf{q} + 4(1-T)H(T-T_{IG}), \qquad \mathsf{q}(\infty) = 0, \qquad (9.100)$$

$$\frac{dT}{dx} = -\mathsf{q}, \qquad \mathsf{q}(-\infty) = 0. \qquad (9.101)$$

---

[5]Oliver Heaviside, 1850-1925, English engineer.

The system has an equilibrium point at $q = 0$ and $T = 1$. The system is also in equilibrium when $q = 0$ and $T < T_{IG}$, but we will not focus on this. Taking $T' = T - 1$, the system near the equilibrium point is

$$\frac{d}{dx}\begin{pmatrix} q \\ T' \end{pmatrix} = \begin{pmatrix} 3 & -4 \\ -1 & 0 \end{pmatrix}\begin{pmatrix} q \\ T' \end{pmatrix}. \tag{9.102}$$

The local Jacobian matrix has two eigenvalues $\lambda = 4$ and $\lambda = -1$. Thus, the equilibrium is a saddle.

Considering the solution away from the equilibrium point, but still for $T > T_{IG}$, and returning from T' to T, the solution takes the form

$$\begin{pmatrix} q \\ T \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} + \frac{1}{5}e^{-x}\begin{pmatrix} C_1 + 4C_2 \\ C_1 + 4C_2 \end{pmatrix} + \frac{1}{5}e^{4x}\begin{pmatrix} 4C_1 - 4C_2 \\ -C_1 + C_2 \end{pmatrix}. \tag{9.103}$$

We imagine as $x \to \infty$ that T approaches unity from below. We wish this equilibrium to be achieved. Thus, we must suppress the unstable $\lambda = 4$ mode; this is achieved by requiring $C_1 = C_2$. This yields

$$\begin{pmatrix} q \\ T \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} + \frac{1}{5}e^{-x}\begin{pmatrix} 5C_1 \\ 5C_1 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} + C_1 e^{-x}\begin{pmatrix} 1 \\ 1 \end{pmatrix}. \tag{9.104}$$

We can force $T(x_{IG}) = T_{IG}$ by taking $C_1 = -(1 - T_{IG})e^{x_{IG}}$. The solution for $x > x_{IG}$ is

$$T = 1 - (1 - T_{IG})e^{-(x-x_{IG})}, \tag{9.105}$$
$$q = -(1 - T_{IG})e^{-(x-x_{IG})}. \tag{9.106}$$

At the interface $x = x_{IG}$, we have $T(x_{IG}) = T_{IG}$ and $q(x_{IG}) = -(1 - T_{IG})$.

For $x < x_{IG}$, our system reduces to

$$3\frac{dT}{dx} - \frac{d^2T}{dx^2} = 0, \qquad T(x_{IG}) = T_{IG}, \qquad \left.\frac{dT}{dx}\right|_{x\to-\infty} = 0. \tag{9.107}$$

Solutions in this region take the form

$$T = T_{IG}e^{3(x-x_{IG})} + C\left(1 - e^{3(x-x_{IG})}\right), \tag{9.108}$$
$$q = -3T_{IG}e^{3(x-x_{IG})} + 3Ce^{3(x-x_{IG})}. \tag{9.109}$$

All of them have the property that $q \to 0$ as $x \to -\infty$. One is faced with the question of how to choose the constant C. Let us choose it to match the energy flux predicted at $x = x_{IG}$. At the interface $x = x_{IG}$ we get $T = T_{IG}$ and $q = -3T_{IG} + 3C$. Matching values of q at the interface, we get

$$-(1 - T_{IG}) = -3T_{IG} + 3C. \tag{9.110}$$

Solving for C, we get

$$C = \frac{4T_{IG} - 1}{3}. \tag{9.111}$$

So, we find for $x < x_{IG}$ that

$$T = T_{IG}e^{3(x-x_{IG})} + \left(\frac{4T_{IG} - 1}{3}\right)\left(1 - e^{3(x-x_{IG})}\right), \tag{9.112}$$

$$\mathsf{q} = -3T_{IG}e^{3(x-x_{IG})} + (4T_{IG} - 1)\,e^{3(x-x_{IG})}. \tag{9.113}$$

9.2.2.2 System of first order equations

Let us apply this technique to the full non-linear Eq. (9.97). First, again define the non-dimensional Fourier heat flux q as

$$\mathsf{q} = -\frac{dT}{dx}. \tag{9.114}$$

Note this is a mathematical convenience. It is not the full diffusive energy flux as it makes no account for mass diffusion affects. However, it is physically intuitive. With this definition, we can rewrite Eq. (9.114) along with Eq. (9.97) as

$$\frac{d\mathsf{q}}{dx} = \mathfrak{D}\mathsf{q} + \mathfrak{D}\exp\left(\frac{-\Theta}{1 + QT}\right)\left(\frac{1 - T}{1 + QT}\right)$$
$$\times \left(1 - \exp\left(-\frac{\frac{\gamma}{\gamma-1}Q}{1 + QT}\right)\frac{T}{1 - T}\right)H(T - T_{IG}), \tag{9.115}$$

$$\frac{dT}{dx} = -\mathsf{q}. \tag{9.116}$$

We have two boundary conditions for this problem:

$$\mathsf{q}(\pm\infty) = 0. \tag{9.117}$$

We are also going to fix our coordinate system so that $T = T_{IG}$ at $x = x_{IG} \equiv 0$. We will require continuity of T and dT/dx at $x = x_{IG} = 0$.

   Our non-linear system has the form

$$\frac{d}{dx}\begin{pmatrix} \mathsf{q} \\ T \end{pmatrix} = \begin{pmatrix} f(\mathsf{q}, T) \\ g(\mathsf{q}, T) \end{pmatrix}. \tag{9.118}$$

9.2.2.3 Equilibrium

Our equilibrium condition is $f(\mathsf{q}, T) = 0$, $g(\mathsf{q}, T) = 0$. By inspection, equilibrium is found when

$$\mathsf{q} = 0, \tag{9.119}$$

$$1 - \exp\left(-\frac{\frac{\gamma}{\gamma-1}Q}{1 + QT}\right)\frac{T}{1 - T} = 0 \quad \text{or} \quad T < T_{IG}. \tag{9.120}$$

We will focus most attention on the isolated equilibrium point which corresponds to traditional chemical equilibrium. We have considered the dimensional version of the same equilibrium condition for T in an earlier section. The solution is found via solving a transcendental equation for T.

9.2.2.4 Linear analysis near equilibrium

Linear analysis near the equilibrium point can be achieved by first examining the eigenvalues of the Jacobian matrix $\mathbf{J}$:

$$\mathbf{J} = \left. \begin{pmatrix} \frac{\partial f}{\partial \mathsf{q}} & \frac{\partial f}{\partial T} \\ \frac{\partial g}{\partial \mathsf{q}} & \frac{\partial g}{\partial T} \end{pmatrix} \right|_{eq} = \begin{pmatrix} \mathfrak{D} & \frac{\partial f}{\partial T}\big|_{eq} \\ -1 & 0 \end{pmatrix}. \tag{9.121}$$

This Jacobian has eigenvalues of

$$\lambda = \frac{\mathfrak{D}}{2} \left(1 \pm \sqrt{1 - \frac{4}{\mathfrak{D}^2} \frac{\partial f}{\partial T}\bigg|_{eq}} \right). \tag{9.122}$$

For $\mathfrak{D} \gg \sqrt{\partial f / \partial T}$, the eigenvalues are approximated well by

$$\lambda_1 \sim \mathfrak{D}, \qquad \lambda_2 \sim \frac{1}{\mathfrak{D}} \frac{\partial f}{\partial T}\bigg|_{eq}. \tag{9.123}$$

This gives rise to a stiffness ratio, valid in the limit of $\mathfrak{D} \gg \sqrt{\partial f / \partial T}$, of

$$\left| \frac{\lambda_1}{\lambda_2} \right| \sim \frac{\mathfrak{D}^2}{\left| \frac{\partial f}{\partial T} \right|}. \tag{9.124}$$

We adopt the parameters of Table 9.1. With these, we find the dimensionless chemical equilibrium temperature at

$$T^{eq} = 0.953. \tag{9.125}$$

This corresponds to a dimensional value of 1730.24 K. Our parameters induce a dimensional length scale of $u_o/a = 1.4142 \times 10^{-5}$ m. This is smaller than actual flames, which actually have much larger values of $\mathfrak{D}$. So as to de-stiffen the system, we have selected a smaller than normal value for $\mathfrak{D}$. For these values, we get a Jacobian matrix of

$$\mathbf{J} = \begin{pmatrix} 2 & -0.287 \\ -1 & 0 \end{pmatrix}. \tag{9.126}$$

We get eigenvalues near the equilibrium point of

$$\lambda = 2.134, \quad \lambda = -0.134. \tag{9.127}$$

The equilibrium is a saddle point. Note the negative value of $\partial f / \partial T$ at equilibrium gives rise to the saddle character of the equilibrium. The actual stiffness ratio is $|2.134/(-0.134)| = 15.9$. This is well predicted by our simple formula which gives $|2^2/(-0.287)| = 13.9$.

In principle, we could also analyze the set of equilibrium points along the cold boundary, where $\mathsf{q} = 0$ and $T < T_{IG}$. Near such points, linearization techniques fail because of the nature of the Heaviside function. We would have to perform a more robust analysis. As an alternative, we shall simply visually examine the results of calculations and infer the stability of this set of fixed points.

9.2.2.5 Laminar flame structure

9.2.2.5.1 $T_{IG} = 0.2.$ Let us get a numerical solution by integrating backwards in space from the equilibrium point. Here, we will use the parameters of Table 9.1, in particular to contrast with a later calculation, the somewhat elevated ignition temperature of $T_{IG} = 0.2$. We shall commence the solution near the isolated equilibrium point corresponding to chemical equilibrium. We could be very careful and choose the initial condition to lie just off the saddle along the eigenvector associated with the negative eigenvalue. It will work just as well to choose a point on the correct side of the equilibrium. Let us approximate $x \to \infty$ by x_B, require $\mathsf{q}(x_B) = 0$, $T(x_B) = T^{eq} - \epsilon$, where $0 < \epsilon \ll 1$. That is, we perturb the temperature to be just less than its equilibrium value. We integrate from the large positive $x = x_B$ back towards $x = -\infty$. When we find $T = T_{IG}$, we record the value of x. We translate the plots so that the ignition point is reached at $x = 0$ and give results.

Predictions of $T(x)$ and $\mathsf{q}(x)$ are shown in in Figure 9.2. We see the temperature has
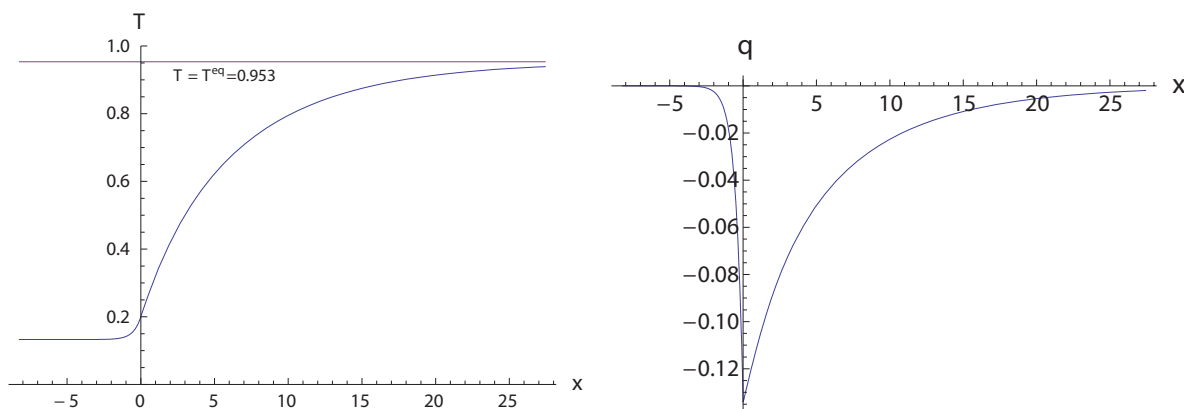
Figure 9.2: Dimensionless temperature and heat flux as a function of position for a burner-stabilized premixed laminar flame, $T_{IG} = 0.2$.

$T(0) = 0.2 = T_{IG}$. As $x \to \infty$, the temperature approaches its equilibrium value. For $x < 0$, the temperature continues to fall until it comes to a final value of $T \sim 0.132$. Note that this value cannot be imposed by the boundary conditions, since we enforce no other condition on T except to anchor it at the ignition temperature at $x = 0$. The heat flux $\mathsf{q}(x)$

is always negative. And it clearly relaxes to zero as $x \to \pm\infty$. This indicates that energy released in combustion makes its way back into the fresh mixture, triggering combustion of the fresh material. This is the essence of the laminar diffusion flame. Predictions of $\rho(x) \sim 1/(1 + QT(x))$ and $u(x) \sim 1 + QT(x)$ are shown in in Figure 9.3. We are somewhat
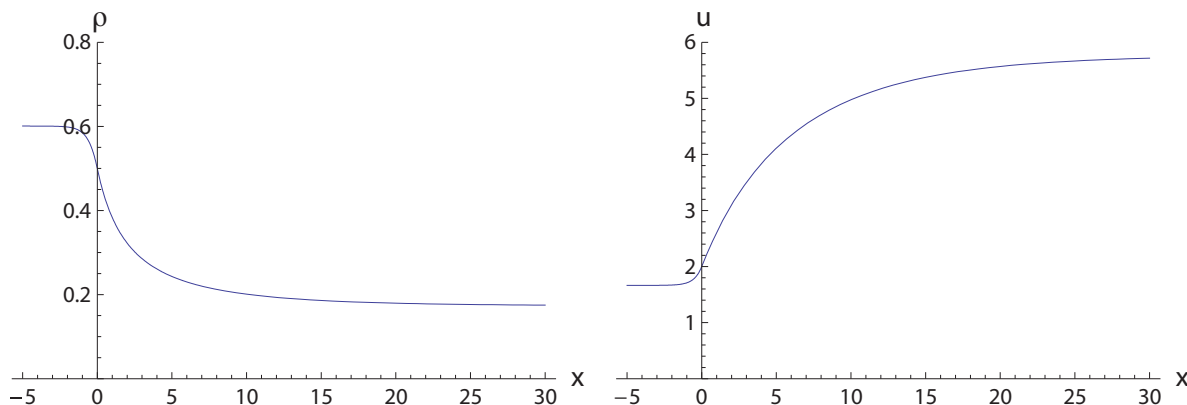
Figure 9.3:   Dimensionless density ρ and fluid particle velocity u as functions of distance for a burner-stabilized premixed laminar flame, $T_{IG} = 0.2$.

troubled because $\rho(x)$ nowhere takes on dimensionless value of unity, despite it being scaled by ρ_o. Had we anchored the flame at an ignition temperature very close to zero, we in fact would have seen ρ approach unity at the anchor point of the flame. We chose an elevated ignition temperature so as to display the actual idiosyncrasies of the model. Even for a flame anchored, in dimensional variables, at $T_{ig} \sim T_o$, we would find a significant decay of density in the cold region of the flow for $x < x_{ig}$. Similar to ρ, we are somewhat troubled that the dimensionless velocity does not take a value near unity. Once again, had we set $T_{ig} \sim T_o$, we would have found the u at $x = x_{ig}$ would have taken a value very near unity. But it also would modulate significantly in the cold region $x < x_{ig}$. We also would have discovered that had $T_{ig} \sim T_o$ that the temperature in the cold region would drop significantly below T_o, which is a curious result. Alternatively, we could iterate on the parameter T_{ig} until we found a value for which $\lim_{x \to -\infty} T \to 0$. For such a value, we would also find u and ρ to approach unity as $x \to -\infty$.

We can better understand the flame structure by considering the (T, q) phase plane as shown in Fig. 9.4. Here, green denotes equilibria. We see the isolated equilibrium point at $(T, \mathsf{q}) = (0.953, 0)$. And we see a continuous one-dimensional set of equilibria for $\{(T, \mathsf{q}) | \mathsf{q} = 0, T \in (-\infty, T_{IG}]\}$. Blue lines are trajectories in the phase space. The arrows have been associated with movement in the $-x$ direction. This is because this is the direction in which it is easiest to construct the flame structure.

We know from dynamic systems theory that special trajectories, known as heteroclinic, are those that connect one equilibrium point to another. These usually have special meaning. The heteroclinic orbit shown here in the thick blue line is that of the actual flame structure. It
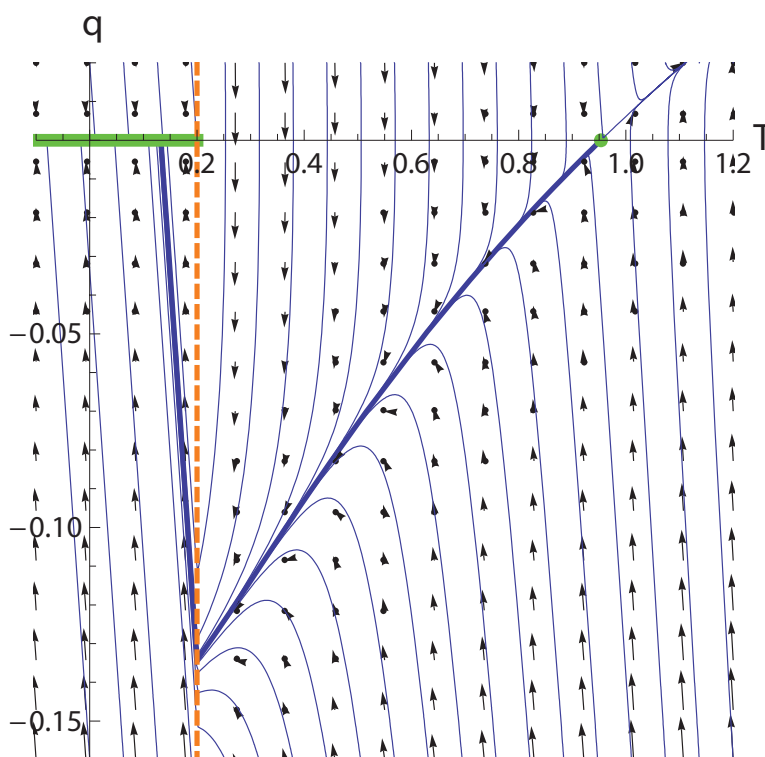
Figure 9.4: (T, q) phase plane for a burner-stabilized premixed laminar flame, $T_{IG} = 0.2$.

connects the saddle at $(T, q) = (0.953, 0)$ to a stable point on the one-dimensional continuum of equilibria at $(T, q) = (0.132, 0)$. It originates on the eigenvector associated with the negative eigenvalue at the equilibrium point. Moreover, it appears that the heteroclinic trajectory is an *attracting* trajectory, as points that begin on nearby trajectories seem to be drawn into the heteroclinic trajectory.

The orange dashed line represents our chosen ignition temperature, $T_{IG} = 0.2$. Had we selected a different ignition temperature, the heteroclinic trajectory originating from the saddle would be the same for $T > T_{IG}$. However it would have turned at a different location and relaxed to a different cold equilibrium on the one-dimensional continuum of equilibria.

Had we attempted to construct our solution by integrating forward in x, our task would have been more difficult. We would likely have chosen the initial temperature to be just greater than T_{IG}. But we would have to had guessed the initial value of q. And because of the saddle nature of the equilibrium point, a guess on either side of the correct value would cause the solution to diverge as x became large. It would be possible to construct a trial and error procedure to hone the initial guess so that on one side of a critical value, the solution diverged to ∞, while on the other it diverged to $-\infty$. Our procedure, however, has the clear advantage, as no guessing is required.

As an aside, we note there is one additional heteroclinic orbit admitted mathematically; however, its physical relevance is far from clear. It seems there is another attracting trajec-

tory for $T > 0.953$. This trajectory is associated with the same eigenvector as the physical trajectory. Along this trajectory, T increases beyond unity, at which point the mass fraction becomes greater than unity, and is thus non-physical. Mathematically this trajectory continues until it reaches an equilibrium at $(T, \mathsf{q}) \to (\infty, 0)$. These dynamics can be revealed using the mapping of the Poincaré sphere; see Fig. 9.5. Details can be found in some dynamic
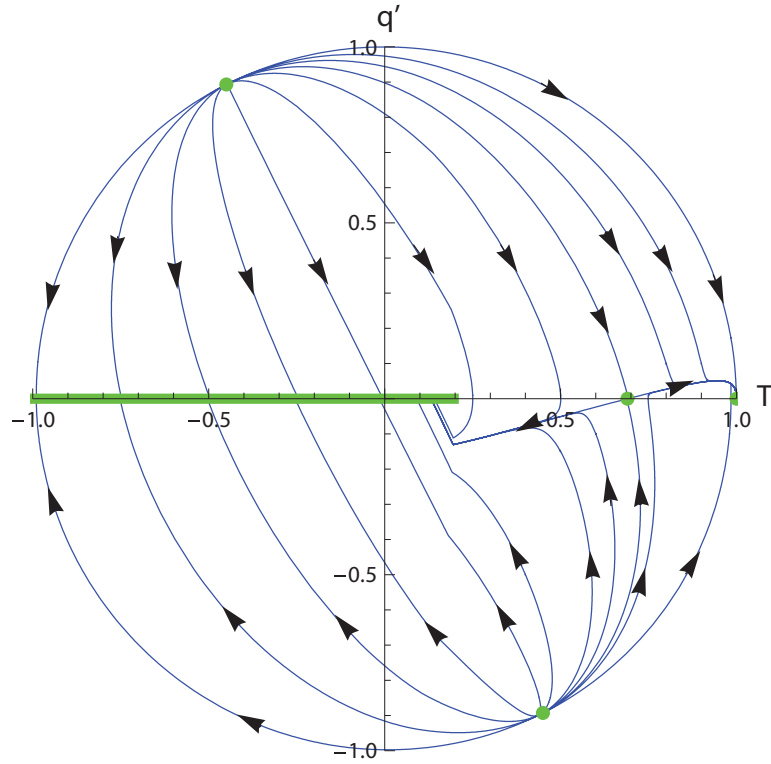
Figure 9.5:   Projection of trajectories on Poincaré sphere onto the (T', q') phase plane for a burner-stabilized premixed laminar flame, $T_{IG} = 0.2$.

systems texts.[6] In short the mapping from $(T, \mathsf{q}) \to (T', \mathsf{q}')$ via

$$T' = \frac{T}{\sqrt{1 + T^2 + \mathsf{q}^2}}, \tag{9.128}$$

$$\mathsf{q}' = \frac{\mathsf{q}}{\sqrt{1 + T^2 + \mathsf{q}^2}}, \tag{9.129}$$

is introduced. Often a third variable in the mapping is introduced $Z = 1/\sqrt{1 + T^2 + \mathsf{q}^2}$. This induces $T'^2 + \mathsf{q}'^2 + Z^2 = 1$, the equation of a sphere, known as the Poincaré sphere. As it is not clear that physical relevance can be found for this, we leave out most of the mathematical details and briefly describe the results. This mapping takes points at infinity in physical space onto the unit circle.

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[6]Perko, L., 2001, *Differential Equations and Dynamical Systems*, Third Edition, Springer, New York.

Equilibria are marked in green. Trajectories are in blue. While the plot is somewhat incomplete, we notice in Fig. 9.5 that the saddle is evident around $(T', \mathsf{q}') \sim (0.7, 0)$. We also see new equilibria on the unit circle, which corresponds to points at infinity in the original space. One of these new equilibria is at $(T', \mathsf{q}') = (1, 0)$. It is a sink. The other two, one in the second quadrant, the other in the fourth, are sources. The heteroclinic trajectories which connect to the saddle from the sources in the second and fourth quadrants form the boundaries for the basins of attraction. To the left of this boundary, trajectories are attracted to the continuous set of equilibria. To the right, they are attracted to the point $(1, 0)$.

9.2.2.5.2 $T_{IG} = 0.076$. We can modulate the flame structure by altering the ignition temperature. In particular, it is possible to iterate on the ignition temperature in such a way that as $x \to -\infty$, $T \to 0$, $\rho \to 1$, and $u \to 1$. Thus, the cold flow region takes on its ambient value. This has some æsthetic appeal. It is however unsatisfying in that one would like to think that an ignition temperature, if it truly existed, would be a physical property of the system, and not just a parameter to adjust to meet some other criterion. That duly noted, we present flame structures using all the parameters of Table 9.1 except we take $T_{ig} = 414\ K$, so that $T_{IG} = 0.076$.

Predictions of $T(x)$ and $\mathsf{q}(x)$ are shown in in Figure 9.6. We see the temperature has
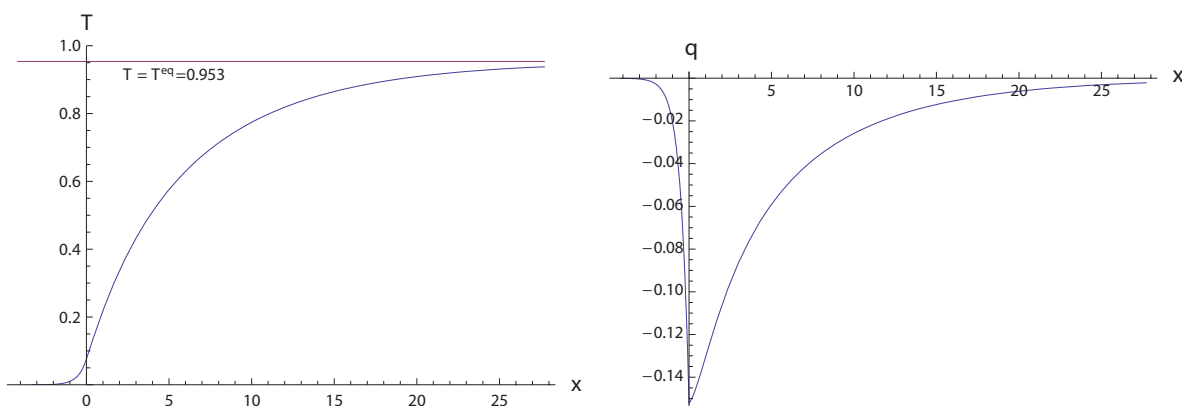
Figure 9.6: Dimensionless temperature and heat flux as a function of position for a burner-stabilized premixed laminar flame, $T_{IG} = 0.076$.

$T(0) = 0.076 = T_{IG}$. As $x \to \infty$, the temperature approaches its chemical equilibrium value. For $x < 0$, the temperature continues to fall until it comes to a final value of $T \sim 0$. Thus, in dimensional terms, the temperature has arrived at T_o in the cold region.

Predictions of $\rho(x) \sim 1/(1 + QT(x))$ and $u(x)$ are shown in in Figure 9.7. We see that this special value of T_{IG} has allowed the dimensionless density to take on a value of unity as $x \to -\infty$. In contrast to our earlier result, for this special value of T_{IG}, we have been able to allow $u = 1$ as $x \to -\infty$. We can better understand the flame structure by considering
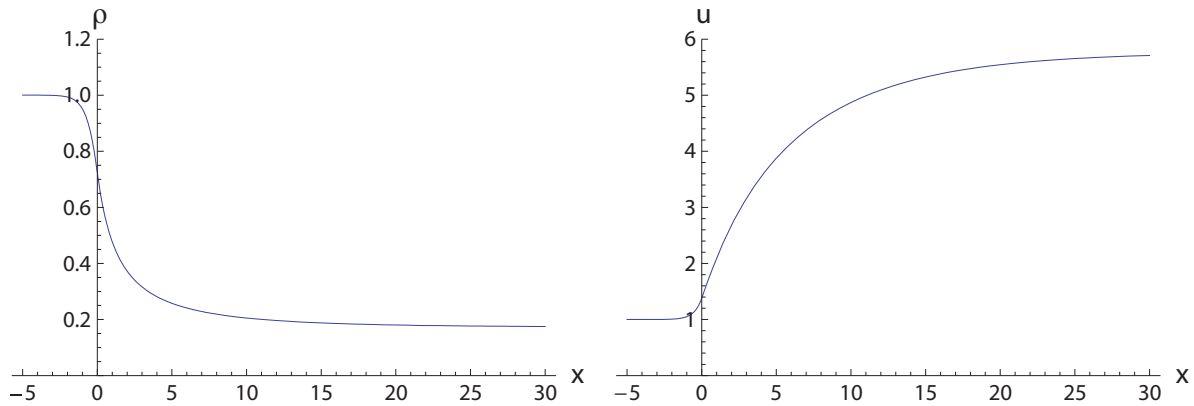
Figure 9.7:   Dimensionless density ρ and fluid particle velocity u as functions of distance for a burner-stabilized premixed laminar flame, $T_{IG} = 0.076$.

the (T, q) phase plane as shown in Fig. 9.8. Figure 9.8 is essentially the same as Figure 9.4 except the ignition point has been moved.
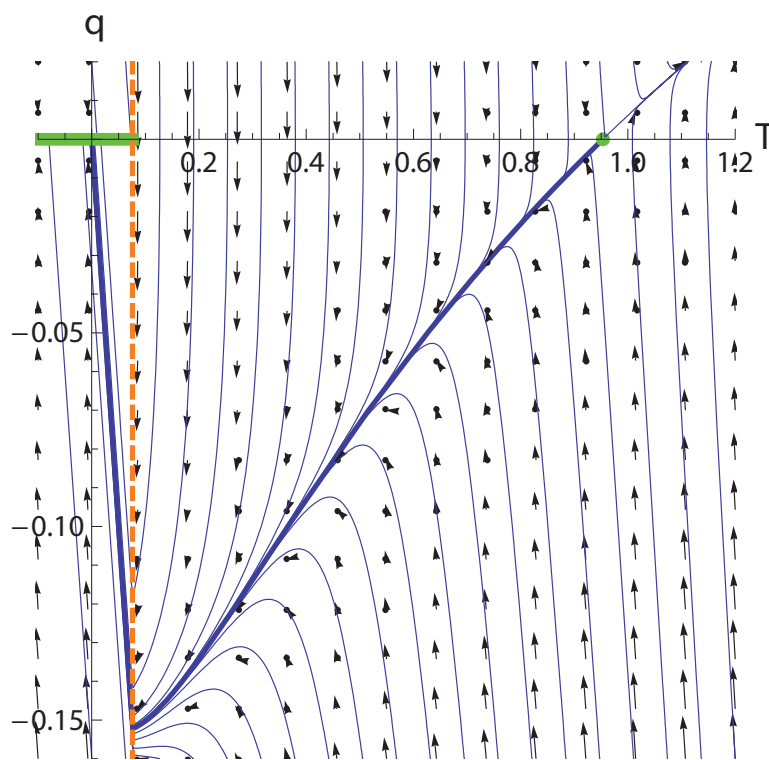
Figure 9.8: (T,q) phase plane for a burner-stabilized premixed laminar flame, $T_{IG} = 0.076$.

9.2.3   Detailed H_2-O_2-N_2 kinetics

We give brief results for a premixed laminar flame in a mixture of calorically imperfect ideal gases which obey mass action kinetics with Arrhenius reaction rates. Multi-component diffusion is modelled as is thermal diffusion. We consider the kinetics model of Table 1.2. The solution method is described in detail in a series of reports from Reaction Design, Inc.[7][8][9][10]

The methods employed in the solution here are slightly different. In short, a large, but finite domain defined. Then, the ordinary differential equations describing the flame structure are discretized. This leads to a large system of non-linear algebraic equations. These are solved by iterative methods, seeded with an appropriate initial guess. The temperature is pinned at T_o at one end of the domain, which is a slightly different boundary condition than we employed previously. At an intermediate value of x, $x = x_f$, the temperature is pinned at $T = T_f$. Full details are in the report.

For $T_o = 298 \ K$, $P_o = 1.01325 \times 10^5 \ Pa$, and a stoichiometric unreacted mixture of $2H_2 + O_2 + 3.76 \ N_2$, along with a very small amount of minor species, we give plots of $Y_i(x)$ in Fig. 9.9. There is, on a log-log scale, an incubation period spanning a few orders of
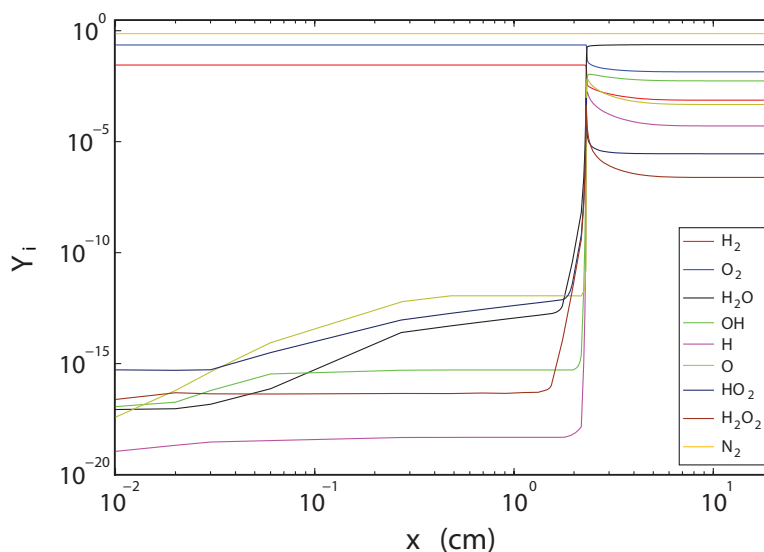
Figure 9.9: Mass fractions as a function of distance in a premixed laminar flame with detailed H_2-O_2-N_2 kinetics.

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[7]Kee, R. J., et al., 2000, "Premix: A Fortran Program for Modeling Steady, Laminar, One Dimensional Premixed Flames," from the Chemkin Collection, Release 3.6, Reaction Design, San Diego, CA.

[8]Kee, R. J., et al., 2000, "Chemkin: A Software Package for the Analysis of Gas-Phase Chemical and Plasma Kinetics," from the Chemkin Collection, Release 3.6, Reaction Design, San Diego, CA.

[9]R. J. Kee, et al., 2000, "The Chemkin Thermodynamic Data Base," part of the Chemkin Collection Release 3.6, Reaction Design, San Diego, CA.

[10]Kee, R. J., Dixon-Lewis, G., Warnatz, J., Coltrin, M. E., and Miller, J. A., 1998, "A Fortran Computer Code Package for the Evaluation of Gas-Phase Multicomponent Transport Properties," Sandia National Laboratory, Report SAND86-8246, Livermore, CA.

magnitude of length. Just past $x = 2 \ cm$, a vigorous reaction commences, and all species relax to a final equilibrium. Temperature, density, and fluid particle velocity as functions of distance are shown in Fig. 9.10.
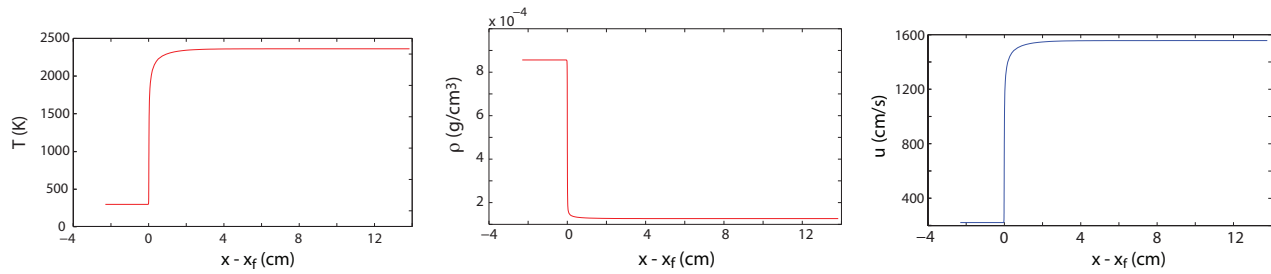
Figure 9.10: Temperature, density, and fluid particle velocity as functions of distance in a premixed laminar flame with detailed H_2-O_2-N_2 kinetics.

Chapter 10

Simple detonations: reaction-advection

Plato says, my friend, that society cannot be saved until either the Professors of Greek take to making gunpowder, or else the makers of gunpowder become Professors of Greek.

Undershaft to Cusins in George Bernard Shaw's, 1856-1950, *Major Barbara*, Act III, § iv.

Let us consider aspects of the foundations of detonation theory. Detonation is defined as a shock-induced combustion process. Most major features of detonations are well modelled by considering only the mechanisms of advection and reaction. Diffusion, which we will neglect here, plays a more subtle role. Its inclusion is not critical to the main physics; however, among other things it is potentially important in determining stability boundaries, as well as in correctly capturing multi-dimensional instabilities. The definitive text is that of Fickett and Davis.[1] The present chapter is strongly influenced by this monograph.

10.1 Reactive Euler equations

10.1.1 One-step irreversible kinetics

Let us focus here on one-dimensional planar solutions in which all diffusion processes are neglected. This is known as a reactive Euler[2] model. We shall also here only be concerned with simple one-step irreversible kinetics in which

$$A \to B. \tag{10.1}$$

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[1]Fickett, W., and Davis, W. C., 1979, *Detonation*, U. California, Berkeley.
[2]Leonhard Euler, 1707-1783, Swiss mathematician.

We will adopt the assumption that A and B are materials with identical properties; thus,

$$M_A = M_B = M, \qquad c_{PA} = c_{PB} = c_P, \tag{10.2}$$

but A is endowed with chemical energy which is released as it forms B. So here, we have $N = 2$ species and $J = 1$ reaction. The number of elements will not be important for this analysis. Extension to multi-step kinetics is straightforward, but involves a sufficient number of details to obscure many of the key elements of the analysis. At this point, we will leave the state equations relatively general, but we will soon extend them to simple ideal, calorically perfect relations. Since we have only a single reaction, our reaction rate vector r_j, is a scalar, which we will call r. Our stoichiometric matrix ν_{ij} is of dimension 2×1 and is

$$\nu_{ij} = \begin{pmatrix} -1 \\ 1 \end{pmatrix}. \tag{10.3}$$

Here, the first entry is associated with A, and the second with B. Thus, our species production rate vector, from $\dot{\omega}_i = \sum_{j=1}^{J} \nu_{ij} r_j$, reduces to

$$\begin{pmatrix} \dot{\omega}_A \\ \dot{\omega}_B \end{pmatrix} = \begin{pmatrix} -1 \\ 1 \end{pmatrix} (r) = \begin{pmatrix} -r \\ r \end{pmatrix}. \tag{10.4}$$

Now, the right side of Eq. (6.5) takes the form

$$M_i \dot{\omega}_i. \tag{10.5}$$

Let us focus on the products and see how this form expands.

$$
\begin{aligned}
M_B \dot{\omega}_B &= M_B r, & (10.6) \\
&= M_B k \overline{\rho}_A, & (10.7) \\
&= M_A k \overline{\rho}_A, & (10.8) \\
&= M_A k \left(\frac{\rho Y_A}{M_A} \right), & (10.9) \\
&= \rho k Y_A, & (10.10) \\
&= \rho k (1 - Y_B). & (10.11)
\end{aligned}
$$

For a reaction which commences with all A, let us define the reaction progress variable λ as $\lambda = Y_B = 1 - Y_A$. And let us define r for this problem, such that

$$\mathsf{r} = k(1 - Y_B) = k(1 - \lambda). \tag{10.12}$$

Expanding further, we could say

$$\mathsf{r} = aT^\beta \exp\left(-\frac{\overline{\mathcal{E}}}{\overline{R}T} \right) (1 - \lambda) = aT^\beta \exp\left(-\frac{\mathcal{E}}{RT} \right) (1 - \lambda), \tag{10.13}$$

but we will delay introduction of temperature T. Here, we have defined $\mathcal{E} = \overline{\mathcal{E}}/M$. Note that the units of r for this problem will be $1/s$, whereas the units for r must be $mole/cm^3/s$, and that

$$r = \frac{\rho}{M_B}\mathsf{r}. \tag{10.14}$$

The use of two different forms of the reaction rate, r and r is unfortunate. One is nearly universal in the physical chemistry literature, r; the other is nearly universal in the one-step detonation chemistry community, r. It is important that the two be distinguished.

10.1.2 Sound speed and thermicity

Let us specialize the definition of frozen sound speed, Eq. (3.320), for our one-step chemistry:

$$c = v\sqrt{\frac{P + \left.\frac{\partial e}{\partial v}\right|_{P,\lambda}}{\left.\frac{\partial e}{\partial P}\right|_{v,\lambda}}}. \tag{10.15}$$

This gives, using $v = 1/\rho$,

$$\rho^2 c^2 = \frac{P + \left.\frac{\partial e}{\partial v}\right|_{P,\lambda}}{\left.\frac{\partial e}{\partial P}\right|_{v,\lambda}} \tag{10.16}$$

Let us, as is common in the detonation literature, define the *thermicity* σ via the relation

$$\rho c^2 \sigma = -\frac{\left.\frac{\partial e}{\partial \lambda}\right|_{P,v}}{\left.\frac{\partial e}{\partial P}\right|_{v,\lambda}}. \tag{10.17}$$

We now specialize our general mathematical relation, Eq. (3.59), to get

$$\left.\frac{\partial P}{\partial e}\right|_{v,\lambda} \left.\frac{\partial e}{\partial \lambda}\right|_{p,v} \left.\frac{\partial \lambda}{\partial P}\right|_{v,e} = -1, \tag{10.18}$$

so that one gets

$$-\frac{\left.\frac{\partial e}{\partial \lambda}\right|_{P,v}}{\left.\frac{\partial e}{\partial P}\right|_{v,\lambda}} = \left.\frac{\partial P}{\partial \lambda}\right|_{v,e}. \tag{10.19}$$

Thus, using Eq. (10.19), we can rewrite Eq. (10.17) as

$$\rho c^2 \sigma = \left.\frac{\partial P}{\partial \lambda}\right|_{v,e}, \tag{10.20}$$

$$\sigma = \frac{1}{\rho c^2} \left.\frac{\partial P}{\partial \lambda}\right|_{v,e}. \tag{10.21}$$

For our one step reaction, we see that as the reaction moves forward, i.e. as λ increases, that σ is a measure of how much the pressure increases, since $\rho > 0$, $c^2 > 0$.

Parameter	Value	Units
γ	1.4	
M	20.91	$kg/kmole$
R	397.58	$J/kg/K$
P_o	1.01325×10^5	Pa
T_o	298	K
ρ_o	0.85521	kg/m^3
v_o	1.1693	m^3/kg
q	1.89566×10^6	J/kg
$\mathcal{E}$	8.29352×10^6	J/kg
a	5×10^9	$1/s$
β	0	

Table 10.1: Numerical values of parameters which roughly model H_2-air detonation.

10.1.3 Parameters for H_2-air

Let us postulate some parameters which loosely match results of the detailed kinetics calculation of Powers and Paolucci [3] for for H_2-air detonations. Rough estimates which allow one-step kinetics models with calorically perfect ideal gas assumptions to approximate the results of detailed kinetics models with calorically imperfect ideal gas mixtures are given in Table 10.1.

10.1.4 Conservative form

Let us first consider a three-dimensional conservative form of the governing equations in the inviscid limit:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \tag{10.22}$$

$$\frac{\partial}{\partial t}(\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u}\mathbf{u} + P\mathbf{I}) = \mathbf{0}, \tag{10.23}$$

$$\frac{\partial}{\partial t}\left(\rho\left(e + \frac{1}{2}\mathbf{u}\cdot\mathbf{u}\right)\right) + \nabla \cdot \left(\rho\mathbf{u}\left(e + \frac{1}{2}\mathbf{u}\cdot\mathbf{u} + \frac{P}{\rho}\right)\right) = 0, \tag{10.24}$$

$$\frac{\partial}{\partial t}(\rho\lambda) + \nabla \cdot (\rho\mathbf{u}\lambda) = \rho\mathsf{r}, \tag{10.25}$$

$$e = e(P, \rho, \lambda), \tag{10.26}$$

$$\mathsf{r} = \mathsf{r}(P, \rho, \lambda). \tag{10.27}$$

For mass conservation, Eq. (10.22) is identical to the earlier Eq. (6.1). For linear momentum conservation, Eq. (10.23) is Eq. (6.2) with the viscous stress, $\boldsymbol{\tau} = \mathbf{0}$. For energy

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[3] Powers, J. M., and Paolucci, S., 2005, "Accurate Spatial Resolution Estimates for Reactive Supersonic Flow with Detailed Chemistry," *AIAA Journal*, 43(5): 1088-1099.

conservation, Eq. (10.24) is Eq. (6.3) with viscous stress $\boldsymbol{\tau} = \mathbf{0}$, and diffusive energy transport $\mathbf{j}^q = \mathbf{0}$. For species evolution, Eq. (10.27) is Eq. (6.5) with diffusive mass flux $\mathbf{j}_i^m = 0$. Equations (10.22-10.27) form eight equations in the eight unknowns, ρ, $\mathbf{u}$, P, e, λ, r. Note that $\mathbf{u}$ has three unknowns, and Eq. (10.23) gives three equations. Note also that we assume the functional forms of e and r are given.

The conservative form of the equations is the most useful and one of the more fundamental forms. It is the form which arises from the even more fundamental integral form, which admits discontinuities. We shall take advantage of this in later forming shock jump equations. The disadvantage of the conservative form is that it is unwieldy and masks simpler causal relations.

10.1.5 Non-conservative form

We can reveal some of the physics described by Eqs. (10.22-10.24) by writing them in what is known as a non-conservative form.

10.1.5.1 Mass

We can use the product rule to expand Eq. (10.22) as

$$\underbrace{\frac{\partial \rho}{\partial t} + \mathbf{u} \cdot \nabla \rho}_{=d\rho/dt} + \rho \nabla \cdot \mathbf{u} = 0. \tag{10.28}$$

We recall the well known *material derivative*, also known as the derivative following a material particle, the total derivative, or the substantial derivative:

$$\frac{d}{dt} \equiv \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla.$$

Using the material derivative, we can rewrite the mass equation as

$$\frac{d\rho}{dt} + \rho \nabla \cdot \mathbf{u} = 0. \tag{10.29}$$

Often, Newton's notation for derivatives, the dot, is used to denote the material derivative. We can also recall the definition of the divergence operator, div, to be used in place of $\nabla\cdot$, so that the mass equation can be written compactly as

$$\dot{\rho} + \rho \operatorname{div} \mathbf{u} = 0. \tag{10.30}$$

The density of a material particle changes in response to the divergence of the velocity field, which can be correlated with the rate of volume expansion of the material region.

10.1.5.2   Linear momenta

We can use the product rule to expand the linear momenta equations, Eq. (10.23), as

$$\rho\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u}\frac{\partial \rho}{\partial t} + \mathbf{u}(\nabla \cdot (\rho\mathbf{u})) + \rho\mathbf{u} \cdot \nabla\mathbf{u} + \nabla P = 0, \tag{10.31}$$

$$\rho\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u}\underbrace{\left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho\mathbf{u})\right)}_{=0} + \rho\mathbf{u} \cdot \nabla\mathbf{u} + \nabla P = 0, \tag{10.32}$$

$$\rho\underbrace{\left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla\mathbf{u}\right)}_{=d\mathbf{u}/dt} + \nabla P = 0, \tag{10.33}$$

$$\rho\frac{d\mathbf{u}}{dt} + \nabla P = 0. \tag{10.34}$$

Or in terms of our simplified notation with $v = 1/\rho$, we have

$$\dot{\mathbf{u}} + v \text{ grad } P = 0. \tag{10.35}$$

The fluid particle accelerates in response to a pressure gradient.

10.1.5.3   Energy

We can apply the product rule to the energy equation, Eq. (10.24) to get

$$\rho\frac{\partial}{\partial t}\left(e + \frac{1}{2}\mathbf{u} \cdot \mathbf{u}\right) + \left(e + \frac{1}{2}\mathbf{u} \cdot \mathbf{u}\right)\frac{\partial \rho}{\partial t} + \left(e + \frac{1}{2}\mathbf{u} \cdot \mathbf{u}\right)\nabla \cdot (\rho\mathbf{u})$$
$$+\rho\mathbf{u} \cdot \nabla\left(e + \frac{1}{2}\mathbf{u} \cdot \mathbf{u}\right) + \nabla \cdot (P\mathbf{u}) = 0, \tag{10.36}$$

$$\rho\frac{\partial}{\partial t}\left(e + \frac{1}{2}\mathbf{u} \cdot \mathbf{u}\right) + \left(e + \frac{1}{2}\mathbf{u} \cdot \mathbf{u}\right)\underbrace{\left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho\mathbf{u})\right)}_{=0}$$
$$+\rho\mathbf{u} \cdot \nabla\left(e + \frac{1}{2}\mathbf{u} \cdot \mathbf{u}\right) + \nabla \cdot (P\mathbf{u}) = 0, \tag{10.37}$$

$$\rho\frac{\partial}{\partial t}\left(e + \frac{1}{2}\mathbf{u} \cdot \mathbf{u}\right) + \rho\mathbf{u} \cdot \nabla\left(e + \frac{1}{2}\mathbf{u} \cdot \mathbf{u}\right) + \nabla \cdot (P\mathbf{u}) = 0. \tag{10.38}$$

This is simpler, but there is more that can be done by taking advantage of the linear momenta equations. Let us continue working with the product rule once more along with some simple rearrangements

$$\rho\frac{\partial e}{\partial t} + \rho\mathbf{u} \cdot \nabla e + \rho\frac{\partial}{\partial t}\left(\frac{1}{2}\mathbf{u} \cdot \mathbf{u}\right) + \rho\mathbf{u} \cdot \nabla\left(\frac{1}{2}\mathbf{u} \cdot \mathbf{u}\right) + \nabla \cdot (P\mathbf{u}) = 0, \tag{10.39}$$

$$\rho\frac{\partial e}{\partial t} + \rho\mathbf{u}\cdot\nabla e + \rho\mathbf{u}\cdot\frac{\partial\mathbf{u}}{\partial t} + \rho\mathbf{u}\cdot(\mathbf{u}\cdot\nabla)\mathbf{u} + \mathbf{u}\cdot\nabla P + P\nabla\cdot\mathbf{u} = 0, \qquad (10.40)$$

$$\underbrace{\rho\frac{\partial e}{\partial t} + \rho\mathbf{u}\cdot\nabla e}_{=\rho\ de/dt} + \mathbf{u}\cdot\underbrace{\left(\rho\frac{\partial\mathbf{u}}{\partial t} + \rho(\mathbf{u}\cdot\nabla)\mathbf{u} + \nabla P\right)}_{=\mathbf{0}} + P\nabla\cdot\mathbf{u} = 0, \qquad (10.41)$$

$$\rho\frac{de}{dt} + P\nabla\cdot\mathbf{u} = 0. \qquad (10.42)$$

Now, from Eq. (10.29), we have $\nabla\cdot\mathbf{u} = -(1/\rho)d\rho/dt$. Eliminating the divergence of the velocity field from Eq. (10.42), we get

$$\rho\frac{de}{dt} - \frac{P}{\rho}\frac{d\rho}{dt} = 0, \qquad (10.43)$$

$$\frac{de}{dt} - \frac{P}{\rho^2}\frac{d\rho}{dt} = 0. \qquad (10.44)$$

Recalling that $\rho = 1/v$, so $d\rho/dt = -(1/v^2)dv/dt = -\rho^2 dv/dt$, our energy equation becomes

$$\frac{de}{dt} + P\frac{dv}{dt} = 0. \qquad (10.45)$$

Or in terms of our dot notation, we get

$$\dot{e} + P\dot{v} = 0. \qquad (10.46)$$

The internal energy of a fluid particle changes in response to the work done by the pressure force.

10.1.5.4   Reaction

Using the product rule on Eq. (10.27) we get

$$\rho\frac{\partial\lambda}{\partial t} + \lambda\frac{\partial\rho}{\partial t} + \rho\mathbf{u}\nabla\lambda + \lambda\nabla\cdot(\rho\mathbf{u}) = \rho r, \qquad (10.47)$$

$$\rho\underbrace{\left(\frac{\partial\lambda}{\partial t} + \mathbf{u}\cdot\nabla\lambda\right)}_{=d\lambda/dt} + \lambda\underbrace{\left(\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\mathbf{u})\right)}_{=0} = \rho r, \qquad (10.48)$$

$$\frac{d\lambda}{dt} = r, \qquad (10.49)$$

$$\dot{\lambda} = r. \qquad (10.50)$$

The mass fraction of a fluid particles product species changes according to the forward reaction rate.

10.1.5.5   Summary

In summary, our non-conservative equations are

$$\dot{\rho} + \rho \operatorname{div} \mathbf{u} = 0, \tag{10.51}$$

$$\dot{\mathbf{u}} + v \operatorname{grad} P = 0, \tag{10.52}$$

$$\dot{e} + P\dot{v} = 0, \tag{10.53}$$

$$\dot{\lambda} = \mathsf{r}, \tag{10.54}$$

$$e = e(P, \rho, \lambda), \tag{10.55}$$

$$\mathsf{r} = \mathsf{r}(P, \rho, \lambda), \tag{10.56}$$

$$\rho = \frac{1}{v}. \tag{10.57}$$

10.1.6   One-dimensional form

Here, we consider the equations to be restricted to one-dimensional planar geometries.

10.1.6.1   Conservative form

In the one-dimensional planar limit, Eqs. (10.22-10.27) reduce to

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho u) = 0, \tag{10.58}$$

$$\frac{\partial}{\partial t}(\rho u) + \frac{\partial}{\partial x}\left(\rho u^2 + P\right) = 0, \tag{10.59}$$

$$\frac{\partial}{\partial t}\left(\rho\left(e + \frac{1}{2}u^2\right)\right) + \frac{\partial}{\partial x}\left(\rho u\left(e + \frac{1}{2}u^2 + \frac{P}{\rho}\right)\right) = 0, \tag{10.60}$$

$$\frac{\partial}{\partial t}(\rho\lambda) + \frac{\partial}{\partial x}(\rho u\lambda) = \rho\mathsf{r}, \tag{10.61}$$

$$e = e(P, \rho, \lambda), \tag{10.62}$$

$$\mathsf{r} = \mathsf{r}(P, \rho, \lambda). \tag{10.63}$$

10.1.6.2   Non-conservative form

The non-conservative Eqs. (10.51-10.57) reduce to the following in the one-dimensional planar limit:

$$\dot{\rho} + \rho\,\frac{\partial u}{\partial x} = 0, \tag{10.64}$$

$$\dot{u} + v\,\frac{\partial P}{\partial x} = 0, \tag{10.65}$$

$$\dot{e} + P\dot{v} = 0, \tag{10.66}$$

$$\dot{\lambda} = \mathsf{r}, \tag{10.67}$$

$$e = e(P, \rho, \lambda), \tag{10.68}$$

$$r = r(P, \rho, \lambda), \tag{10.69}$$

$$\rho = \frac{1}{v}. \tag{10.70}$$

Equations (10.64-10.70) can be expanded using the definition of the material derivative:

$$\left(\frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} \right) + \rho \frac{\partial u}{\partial x} = 0, \tag{10.71}$$

$$\left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} \right) + v \frac{\partial P}{\partial x} = 0, \tag{10.72}$$

$$\left(\frac{\partial e}{\partial t} + u \frac{\partial e}{\partial x} \right) + P \left(\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} \right) = 0, \tag{10.73}$$

$$\left(\frac{\partial \lambda}{\partial t} + u \frac{\partial \lambda}{\partial x} \right) = r, \tag{10.74}$$

$$e = e(P, \rho, \lambda), \tag{10.75}$$

$$r = r(P, \rho, \lambda), \tag{10.76}$$

$$\rho = \frac{1}{v}. \tag{10.77}$$

10.1.6.3 Reduction of energy equation

Let us use standard results from calculus of many variables to expand the caloric equation of state, Eq. (10.75):

$$de = \left. \frac{\partial e}{\partial P} \right|_{v,\lambda} dP + \left. \frac{\partial e}{\partial v} \right|_{P,\lambda} dv + \left. \frac{\partial e}{\partial \lambda} \right|_{P,v} d\lambda. \tag{10.78}$$

Taking the time derivative gives

$$\dot{e} = \left. \frac{\partial e}{\partial P} \right|_{v,\lambda} \dot{P} + \left. \frac{\partial e}{\partial v} \right|_{P,\lambda} \dot{v} + \left. \frac{\partial e}{\partial \lambda} \right|_{P,v} \dot{\lambda}. \tag{10.79}$$

Note this is simply a time derivative of the caloric state equation; it says nothing about energy conservation. Next let us use Eq. (10.79) to eliminate $\dot{e}$ in the first law of thermodynamics, Eq. (10.66) to get

$$\underbrace{\left. \frac{\partial e}{\partial P} \right|_{v,\lambda} \dot{P} + \left. \frac{\partial e}{\partial v} \right|_{P,\lambda} \dot{v} + \left. \frac{\partial e}{\partial \lambda} \right|_{P,v} \dot{\lambda}}_{=\dot{e}} + P\dot{v} = 0, \tag{10.80}$$

$$\dot{P} + \underbrace{\left(\frac{P + \left. \frac{\partial e}{\partial v} \right|_{P,\lambda}}{\left. \frac{\partial e}{\partial P} \right|_{v,\lambda}} \right)}_{=\rho^2 c^2} \dot{v} + \underbrace{\frac{\left. \frac{\partial e}{\partial \lambda} \right|_{P,v}}{\left. \frac{\partial e}{\partial P} \right|_{v,\lambda}}}_{=-\rho c^2 \sigma} \dot{\lambda} = 0, \tag{10.81}$$

$$\dot{P} + \rho^2 c^2 \dot{v} - \rho c^2 \sigma \dot{\lambda} = 0, \tag{10.82}$$

$$\dot{P} = -\rho^2 c^2 \dot{v} + \rho c^2 \sigma \dot{\lambda}, \tag{10.83}$$

$$\dot{P} = \rho c^2 \left(\sigma \mathsf{r} - \rho \dot{v} \right). \tag{10.84}$$

Now, since $\dot{v} = -(1/\rho^2)\dot{\rho}$, we get

$$\dot{P} = c^2 \dot{\rho} + \rho c^2 \sigma \mathsf{r}. \tag{10.85}$$

Note that if either $\mathsf{r} = 0$ or $\sigma = 0$, the pressure changes will be restricted to those from classical isentropic thermo-acoustics: $\dot{P} = c^2 \dot{\rho}$. If $\sigma \mathsf{r} > 0$, reaction induces positive pressure changes. If $\sigma \mathsf{r} < 0$, reaction induces negative pressure changes. Moreover, note that Eq. (10.85) is not restricted to calorically perfect ideal gases. It is valid for general state equations.

10.1.7   Characteristic form

Let us obtain a standard form known as *characteristic form* for the one-dimensional unsteady equations. We follow the procedure described by Whitham (1927-).[4] For this form let us use Eq. (10.85) and generalized forms for sound speed c and thermicity σ to recast our governing equations, Eq. (10.71-10.77) as

$$\frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} + \rho \frac{\partial u}{\partial x} = 0, \tag{10.86}$$

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + \frac{1}{\rho} \frac{\partial P}{\partial x} = 0, \tag{10.87}$$

$$\frac{\partial P}{\partial t} + u \frac{\partial P}{\partial x} - c^2 \left(\frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} \right) = \rho c^2 \sigma \mathsf{r}, \tag{10.88}$$

$$\frac{\partial \lambda}{\partial t} + u \frac{\partial \lambda}{\partial x} = \mathsf{r}, \tag{10.89}$$

$$c^2 = c^2(P, \rho), \tag{10.90}$$

$$\mathsf{r} = \mathsf{r}(P, \rho, \lambda), \tag{10.91}$$

$$\sigma = \sigma(P, \rho, \lambda). \tag{10.92}$$

Let us write the differential equations in matrix form:

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ -c^2 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{\partial \rho}{\partial t} \\ \frac{\partial u}{\partial t} \\ \frac{\partial P}{\partial t} \\ \frac{\partial \lambda}{\partial t} \end{pmatrix} + \begin{pmatrix} u & \rho & 0 & 0 \\ 0 & u & \frac{1}{\rho} & 0 \\ -c^2 u & 0 & u & 0 \\ 0 & 0 & 0 & u \end{pmatrix} \begin{pmatrix} \frac{\partial \rho}{\partial x} \\ \frac{\partial u}{\partial x} \\ \frac{\partial P}{\partial x} \\ \frac{\partial \lambda}{\partial x} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \rho c^2 \sigma \mathsf{r} \\ \mathsf{r} \end{pmatrix}. \tag{10.93}$$

These take the general form

$$A_{ij} \frac{\partial w_j}{\partial t} + B_{ij} \frac{\partial w_j}{\partial x} = C_i. \tag{10.94}$$

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[4]Whitham, G. B., 1974, *Linear and Nonlinear Waves*, Wiley, New York.

Let us attempt to cast this the left hand side of this system in the form $\partial w_j/\partial t + \mu \partial w_j/\partial x$. Here, μ is a scalar which has the units of velocity. To do so, we shall seek vectors ℓ_i such that

$$\ell_i A_{ij} \frac{\partial w_j}{\partial t} + \ell_i B_{ij} \frac{\partial w_j}{\partial x} = \ell_i C_i = m_j \left(\frac{\partial w_j}{\partial t} + \mu \frac{\partial w_j}{\partial x} \right). \tag{10.95}$$

For ℓ_i to have the desired properties, we will insist that

$$\ell_i A_{ij} = m_j, \tag{10.96}$$
$$\ell_i B_{ij} = \mu m_j. \tag{10.97}$$

Using Eq. (10.96) to eliminate m_j in Eq. (10.97), we get

$$\ell_i B_{ij} = \mu \ell_i A_{ij}, \tag{10.98}$$
$$0 = \ell_i (\mu A_{ij} - B_{ij}). \tag{10.99}$$

Equation (10.99) has the trivial solution $\ell_i = 0$. For a non-trivial solution, standard linear algebra tells us that we must enforce the condition that the determinant of the coefficient matrix be zero:

$$|\mu A_{ij} - B_{ij}| = 0. \tag{10.100}$$

Specializing Eq. (10.100) for Eq. (10.93), we find

$$\begin{vmatrix} \mu - u & -\rho & 0 & 0 \\ 0 & \mu - u & -\frac{1}{\rho} & 0 \\ -c^2(\mu - u) & 0 & \mu - u & 0 \\ 0 & 0 & 0 & \mu - u \end{vmatrix} = 0. \tag{10.101}$$

Let us employ standard co-factor expansion operations to reduce the determinant:

$$(\mu - u) \begin{vmatrix} \mu - u & -\rho & 0 \\ 0 & \mu - u & -\frac{1}{\rho} \\ -c^2(\mu - u) & 0 & \mu - u \end{vmatrix} = 0, \tag{10.102}$$

$$(\mu - u) \left((\mu - u) \left((\mu - u)^2 \right) + \rho \left(\frac{-c^2(\mu - u)}{\rho} \right) \right) = 0, \tag{10.103}$$

$$(\mu - u)^2 \left((\mu - u)^2 - c^2 \right) = 0. \tag{10.104}$$

There are four roots to this equation; two are repeated:

$$\mu = u, \tag{10.105}$$
$$\mu = u, \tag{10.106}$$
$$\mu = u + c, \tag{10.107}$$
$$\mu = u - c. \tag{10.108}$$

Let us find the eigenvector ℓ_i associated with the eigenvalues $\mu = u \pm c$. So, Eq. (10.99) reduces to

$$
(\ell_1 \quad \ell_2 \quad \ell_3 \quad \ell_4)
\begin{pmatrix}
(u \pm c) - u & -\rho & 0 & 0 \\
0 & (u \pm c) - u & -\frac{1}{\rho} & 0 \\
-c^2((u \pm c) - u) & 0 & (u \pm c) - u & 0 \\
0 & 0 & 0 & (u \pm c) - u
\end{pmatrix}
= (0 \quad 0 \quad 0 \quad 0).
$$

$$(10.109)$$

Simplifying,

$$
(\ell_1 \quad \ell_2 \quad \ell_3 \quad \ell_4)
\begin{pmatrix}
\pm c & -\rho & 0 & 0 \\
0 & \pm c & -\frac{1}{\rho} & 0 \\
\mp c^3 & 0 & \pm c & 0 \\
0 & 0 & 0 & \pm c
\end{pmatrix}
= (0 \quad 0 \quad 0 \quad 0). \qquad (10.110)
$$

We thus find four equations, with linear dependencies:

$$
\pm c\ell_1 \mp c^3 \ell_3 = 0, \qquad (10.111)
$$
$$
-\rho\ell_1 \pm c\ell_2 = 0, \qquad (10.112)
$$
$$
-\frac{1}{\rho}\ell_2 \pm c\ell_3 = 0, \qquad (10.113)
$$
$$
\pm c\ell_4 = 0. \qquad (10.114)
$$

Now, $c \neq 0$, so Eq. (10.114) insists that

$$
\ell_4 = 0. \qquad (10.115)
$$

We expect a linear dependency, which implies that we are free to set at least one of the remaining ℓ_i to an arbitrary value. Let us see if we can get a solution with $\ell_3 = 1$. With that Eqs. (10.111-10.113) reduce to

$$
\pm c\ell_1 \mp c^3 = 0, \qquad (10.116)
$$
$$
-\rho\ell_1 \pm c\ell_2 = 0, \qquad (10.117)
$$
$$
-\frac{1}{\rho}\ell_2 \pm c = 0. \qquad (10.118)
$$

Solving Eq. (10.116) gives

$$
\ell_1 = c^2. \qquad (10.119)
$$

Then, Eq. (10.117) becomes $-\rho c^2 \pm c\ell_2 = 0$. Solving gives

$$
\ell_2 = \pm\rho c. \qquad (10.120)
$$

This is redundant with solving Eq. (10.118), which also gives $\ell_2 = \pm\rho c$. So, we have for $\mu = u \pm c$ that

$$\ell_i = (\; c^2 \quad \pm\rho c \quad 1 \quad 0 \;).\tag{10.121}$$

So, Eq. (10.93) becomes after multiplication by ℓ_i from Eq. (10.121):

$$(\; c^2 \quad \pm\rho c \quad 1 \quad 0 \;)\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ -c^2 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} \frac{\partial\rho}{\partial t} \\ \frac{\partial u}{\partial t} \\ \frac{\partial P}{\partial t} \\ \frac{\partial\lambda}{\partial t} \end{pmatrix} + (\; c^2 \quad \pm\rho c \quad 1 \quad 0 \;)\begin{pmatrix} u & \rho & 0 & 0 \\ 0 & u & \frac{1}{\rho} & 0 \\ -c^2 u & 0 & u & 0 \\ 0 & 0 & 0 & u \end{pmatrix}\begin{pmatrix} \frac{\partial\rho}{\partial x} \\ \frac{\partial u}{\partial x} \\ \frac{\partial P}{\partial x} \\ \frac{\partial\lambda}{\partial x} \end{pmatrix}$$
$$= (\; c^2 \quad \pm\rho c \quad 1 \quad 0 \;)\begin{pmatrix} 0 \\ 0 \\ \rho c^2 \sigma\mathsf{r} \\ \mathsf{r} \end{pmatrix}\tag{10.122}$$

Carrying out the vector-matrix multiplication operations, we get

$$(\; 0 \quad \pm\rho c \quad 1 \quad 0 \;)\begin{pmatrix} \frac{\partial\rho}{\partial t} \\ \frac{\partial u}{\partial t} \\ \frac{\partial P}{\partial t} \\ \frac{\partial\lambda}{\partial t} \end{pmatrix} + (\; 0 \quad \pm\rho c(u \pm c) \quad u \pm c \quad 0 \;)\begin{pmatrix} \frac{\partial\rho}{\partial x} \\ \frac{\partial u}{\partial x} \\ \frac{\partial P}{\partial x} \\ \frac{\partial\lambda}{\partial x} \end{pmatrix}$$
$$= (\; c^2 \quad \pm\rho c \quad 1 \quad 0 \;)\begin{pmatrix} 0 \\ 0 \\ \rho c^2 \sigma\mathsf{r} \\ \mathsf{r} \end{pmatrix}.\tag{10.123}$$

Simplifying,

$$\pm\rho c\left(\frac{\partial u}{\partial t} + (u \pm c)\frac{\partial u}{\partial x}\right) + \left(\frac{\partial P}{\partial t} + (u \pm c)\frac{\partial P}{\partial x}\right) = \rho c^2 \sigma\mathsf{r}.\tag{10.124}$$

Now, let us confine our attention to lines in $x - t$ space on which

$$\frac{dx}{dt} = u \pm c.\tag{10.125}$$

On such lines, Eq. (10.124) can be written as

$$\pm\rho c\left(\frac{\partial u}{\partial t} + \frac{dx}{dt}\frac{\partial u}{\partial x}\right) + \left(\frac{\partial P}{\partial t} + \frac{dx}{dt}\frac{\partial P}{\partial x}\right) = \rho c^2 \sigma\mathsf{r}.\tag{10.126}$$

Consider now a variable, say u, which is really $u(x,t)$. From calculus of many variables, we have

$$du = \frac{\partial u}{\partial t}dt + \frac{\partial u}{\partial x}dx, \tag{10.127}$$

$$\frac{du}{dt} = \frac{\partial u}{\partial t} + \frac{dx}{dt}\frac{\partial u}{\partial x}. \tag{10.128}$$

If we insist $dx/dt = u \pm c$, let us call the derivative $du/dt_\pm$, so that Eq. (10.126) becomes

$$\pm\rho c\frac{du}{dt_\pm} + \frac{dP}{dt_\pm} = \rho c^2 \sigma\mathsf{r}. \tag{10.129}$$

In the inert limit, after additional analysis, Eq. (10.129) reduces to the form $d\psi/dt_\pm = 0$, which shows that ψ is maintained as a constant on lines where $dx/dt = u \pm c$. Thus, one can say that a signal is propagated in $x - t$ space at speed $u \pm c$. So, we see from the characteristic analysis how the thermodynamic property c has the added significance of influencing the speed at which signals propagate.

Let us now find ℓ_i for $\mu = u$. For this root, we find

$$(\ell_1 \quad \ell_2 \quad \ell_3 \quad \ell_4) \begin{pmatrix} 0 & -\rho & 0 & 0 \\ 0 & 0 & -\frac{1}{\rho} & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} = (0 \quad 0 \quad 0 \quad 0). \tag{10.130}$$

It can be seen by inspection that two independent solutions ℓ_i satisfy Eq. (10.130):

$$\ell_i = (0 \quad 0 \quad 1 \quad 0), \tag{10.131}$$

$$\ell_i = (0 \quad 0 \quad 0 \quad 1). \tag{10.132}$$

These two eigenvectors induce the characteristic form which was already obvious from the initial form of the energy and species equations:

$$\frac{\partial P}{\partial t} + u\frac{\partial P}{\partial x} - c^2\left(\frac{\partial\rho}{\partial t} + u\frac{\partial\rho}{\partial x}\right) = \rho c^2 \sigma\mathsf{r}, \tag{10.133}$$

$$\frac{\partial\lambda}{\partial t} + u\frac{\partial\lambda}{\partial x} = \mathsf{r}. \tag{10.134}$$

On lines where $dx/dt = u$, that is to say on material particle pathlines, these reduce to $\dot{P} - c^2\dot{\rho} = \rho c^2 \sigma\mathsf{r}$ and $\dot{\lambda} = \mathsf{r}$.

Because we all of the eigenvalues μ are real, and because we were able to find a set of four linearly independent right eigenvectors ℓ_i so as to transform our four partial differential equations into characteristic form, we can say that our system is *strictly hyperbolic*. Thus, it

- is well posed for initial value problems given that initial data is provided on a non-characteristic curve, and

- admits discontinuous solutions described by a set of Rankine-Hugoniot jump conditions which arise from a more primitive form of the governing equations.

In summary we can write our equations in characteristic form as

$$\frac{dP}{dt_+} + \rho c \frac{du}{dt_+} = \rho c^2 \sigma \mathsf{r}, \qquad \text{on} \qquad \frac{dx}{dt} = u + c, \tag{10.135}$$

$$\frac{dP}{dt_-} - \rho c \frac{du}{dt_-} = \rho c^2 \sigma \mathsf{r}, \qquad \text{on} \qquad \frac{dx}{dt} = u - c, \tag{10.136}$$

$$\frac{dP}{dt} - c^2 \frac{d\rho}{dt} = \rho c^2 \sigma \mathsf{r}, \qquad \text{on} \qquad \frac{dx}{dt} = u, \tag{10.137}$$

$$\frac{d\lambda}{dt} = \mathsf{r} \qquad \text{on} \qquad \frac{dx}{dt} = u. \tag{10.138}$$

10.1.8 Rankine-Hugoniot jump conditions

As described by LeVeque[5] the proper way to arrive at what are known as Rankine[6]-Hugoniot[7] jump equations describing discontinuities is to use a more primitive form of the conservation laws, expressed in terms of integrals of conservative form quantities balanced by fluxes and source terms of those quantities. If $\mathbf{q}$ is a set of conservative form variables, and $\mathbf{f}(\mathbf{q})$ is the flux of $\mathbf{q}$ (e.g. for mass conservation, ρ is a conserved variable and ρu is the flux), and $\mathbf{s}(\mathbf{q})$ is the internal source term, then the primitive form of the conservation form law can be written as

$$\frac{d}{dt} \int_{x_1}^{x_2} \mathbf{q}(x,t)dx = \mathbf{f}(\mathbf{q}(x_1,t)) - \mathbf{f}(\mathbf{q}(x_2,t)) + \int_{x_1}^{x_2} \mathbf{s}(\mathbf{q}(x,t))dx. \tag{10.139}$$

Here, we have considered flow into and out of a one-dimensional box for $x \in [x_1, x_2]$. For our reactive Euler equations we have

$$\mathbf{q} = \begin{pmatrix} \rho \\ \rho u \\ \rho \left(e + \frac{1}{2}u^2\right) \\ \rho\lambda \end{pmatrix}, \qquad \mathbf{f}(\mathbf{q}) = \begin{pmatrix} \rho u \\ \rho u^2 + P \\ \rho u \left(e + \frac{1}{2}u^2 + \frac{P}{\rho}\right) \\ \rho u\lambda \end{pmatrix}, \qquad \mathbf{s}(\mathbf{q}) = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \rho\mathsf{r} \end{pmatrix}. \tag{10.140}$$

If we assume there is a discontinuity in the region $x \in [x_1, x_2]$ propagating at speed U, we can find the Cauchy[8] principal value of the integral by splitting it into the form

$$\frac{d}{dt} \int_{x_1}^{x_1+Ut^-} \mathbf{q}(x,t)dx + \frac{d}{dt} \int_{x_1+Ut^+}^{x_2} \mathbf{q}(x,t)dx$$

$$= \mathbf{f}(\mathbf{q}(x_1,t)) - \mathbf{f}(\mathbf{q}(x_2,t)) + \int_{x_1}^{x_2} \mathbf{s}(\mathbf{q}(x,t))dx. \tag{10.141}$$

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[5]LeVeque, R. J., 1992, *Numerical Methods for Conservation Laws*, Birkhäuser, Basel.
[6]William John Macquorn Rankine, 1820-1872, Scottish engineer.
[7]Pierre Henri Hugoniot, 1851-1887, French mathematician.
[8]Augustin-Louis Cauchy, 1789-1857, French mechanician.

Here, $x_1 + Ut^-$ lies just before the discontinuity and $x_1 + Ut^+$ lies just past the discontinuity. Using Leibniz's rule, we get

$$\mathbf{q}(x_1 + Ut^-, t)U - 0 + \int_{x_1}^{x_1+Ut^-} \frac{\partial \mathbf{q}}{\partial t} dx + 0 - \mathbf{q}(x_1 + Ut^+, t)U + \int_{x_1+Ut^+}^{x_2} \frac{\partial \mathbf{q}}{\partial t} dx \quad (10.142)$$

$$= \mathbf{f}(\mathbf{q}(x_1, t)) - \mathbf{f}(\mathbf{q}(x_2, t)) + \int_{x_1}^{x_2} \mathbf{s}(\mathbf{q}(x, t)) dx.$$

Now, if we assume that $x_2 - x_1 \to 0$ and that on either side of the discontinuity the volume of integration is sufficiently small so that the time and space variation of $\mathbf{q}$ is negligibly small, we get

$$\mathbf{q}(x_1)U - \mathbf{q}(x_2)U = \mathbf{f}(\mathbf{q}(x_1)) - \mathbf{f}(\mathbf{q}(x_2)), \quad (10.143)$$
$$U\left(\mathbf{q}(x_1) - \mathbf{q}(x_2)\right) = \mathbf{f}(\mathbf{q}(x_1)) - \mathbf{f}(\mathbf{q}(x_2)). \quad (10.144)$$

Note that the contribution of the source term $\mathbf{s}$ is negligible as $x_2 - x_1 \to 0$. Defining next the notation for a jump as

$$[\![\mathbf{q}(x)]\!] \equiv \mathbf{q}(x_2) - \mathbf{q}(x_1), \quad (10.145)$$

the jump conditions are rewritten as

$$U [\![\mathbf{q}(x)]\!] = [\![\mathbf{f}(\mathbf{q}(x))]\!]. \quad (10.146)$$

If $U = 0$, as is the case when we transform to the frame where the wave is at rest, we simply recover

$$\mathbf{0} = \mathbf{f}(\mathbf{q}(x_1)) - \mathbf{f}(\mathbf{q}(x_2)), \quad (10.147)$$
$$\mathbf{f}(\mathbf{q}(x_1)) = \mathbf{f}(\mathbf{q}(x_2)), \quad (10.148)$$
$$[\![\mathbf{f}(\mathbf{q}(x))]\!] = \mathbf{0}. \quad (10.149)$$

That is, the fluxes on either side of the discontinuity are equal. We also get a more general result for $U \neq 0$, which is the well-known

$$U = \frac{\mathbf{f}(\mathbf{q}(x_2)) - \mathbf{f}(\mathbf{q}(x_1))}{\mathbf{q}(x_2) - \mathbf{q}(x_1)} = \frac{[\![\mathbf{f}(\mathbf{q}(x))]\!]}{[\![\mathbf{q}(x)]\!]}. \quad (10.150)$$

The general Rankine-Hugoniot equation then for the one-dimensional reactive Euler equations across a non-stationary jump is given by

$$U \begin{pmatrix} \rho_2 - \rho_1 \\ \rho_2 u_2 - \rho_1 u_1 \\ \rho_2 \left(e_2 + \frac{1}{2} u_2^2\right) - \rho_1 \left(e_1 + \frac{1}{2} u_1^2\right) \\ \rho_2 \lambda_2 - \rho_1 \lambda_1 \end{pmatrix} = \begin{pmatrix} \rho_2 u_2 - \rho_1 u_1 \\ \rho_2 u_2^2 + P_2 - \rho_1 u_1^2 - P_1 \\ \rho_2 u_2 \left(e_2 + \frac{1}{2} u_2^2 + \frac{P_2}{\rho_2}\right) - \rho_1 u_1 \left(e_1 + \frac{1}{2} u_1^2 + \frac{P_1}{\rho_1}\right) \\ \rho_2 u_2 \lambda_2 - \rho_2 u_1 \lambda_1 \end{pmatrix}.$$
$$(10.151)$$

Note that if there is no discontinuity, Eq. (10.139) reduces to our partial differential equations which are the reactive Euler equations. We can rewrite Eq. (10.139) as

$$\left(\frac{d}{dt} \int_{x_1}^{x_2} \mathbf{q}(x,t)dx \right) + (\mathbf{f}(\mathbf{q}(x_2,t)) - \mathbf{f}(\mathbf{q}(x_1,t))) = \int_{x_1}^{x_2} \mathbf{s}(\mathbf{q}(x,t))dx, \quad (10.152)$$

Now, if we assume *continuity* of all fluxes and variables, we can use Taylor series expansion and Leibniz's rule to say

$$\left(\int_{x_1}^{x_2} \frac{\partial}{\partial t}\mathbf{q}(x,t)dx \right) + \left(\left(\mathbf{f}(\mathbf{q}(x_1,t)) + \frac{\partial \mathbf{f}}{\partial x}(x_2 - x_1) + \dots \right) - \mathbf{f}(\mathbf{q}(x_1,t)) \right) = \int_{x_1}^{x_2} \mathbf{s}(\mathbf{q}(x,t))dx,$$

$$\text{let } x_2 \to x_1$$

$$\left(\int_{x_1}^{x_2} \frac{\partial}{\partial t}\mathbf{q}(x,t)dx \right) + \left(\frac{\partial \mathbf{f}}{\partial x}(x_2 - x_1) \right) = \int_{x_1}^{x_2} \mathbf{s}(\mathbf{q}(x,t))dx,$$

$$\left(\int_{x_1}^{x_2} \frac{\partial}{\partial t}\mathbf{q}(x,t)dx \right) + \int_{x_1}^{x_2} \frac{\partial \mathbf{f}}{\partial x}dx = \int_{x_1}^{x_2} \mathbf{s}(\mathbf{q}(x,t))dx.$$

$$(10.153)$$

Combining all terms under a single integral, we get

$$\int_{x_1}^{x_2} \left(\frac{\partial \mathbf{q}}{\partial t} + \frac{\partial \mathbf{f}}{\partial x} - \mathbf{s} \right) dx = 0. \quad (10.154)$$

Now, this integral must be zero for an arbitrary x_1 and x_2, so the integrand itself must be zero, and we get our partial differential equation:

$$\frac{\partial \mathbf{q}}{\partial t} + \frac{\partial \mathbf{f}}{\partial x} - \mathbf{s} = 0, \quad (10.155)$$

$$\frac{\partial}{\partial t}\mathbf{q}(x,t) + \frac{\partial}{\partial x}\mathbf{f}(\mathbf{q}(x,t)) = \mathbf{s}(\mathbf{q}(x,t)), \quad (10.156)$$

which applies away from jumps.

10.1.9 Galilean transformation

We know that Newtonian[9] mechanics have been constructed so as to be invariant under a so-called Galilean[10] transformation which takes one from a fixed laboratory frame to a constant velocity frame with respect to the fixed frame. The Galilean transformation is such that our original coordinate system in the laboratory frame, (x,t), transforms to a steady travelling wave frame, $(\hat{x}, \hat{t})$, via

$$\hat{x} = x - Dt, \quad (10.157)$$

$$\hat{t} = t. \quad (10.158)$$

---

[9]after Isaac Newton, 1643-1727, English polymath.
[10]after Galileo Galilei, 1564-1642, Italian polymath.

We now seek to see how our derivatives transform under this coordinate change. We shall arrive at the same result via two methods: 1) a direct approach, and 2) a more formal approach based on notions from differential geometry. The first is more straightforward; the second gives greater cohesion with a more general theory of coordinate transformations.

10.1.9.1   Direct approach

For the direct approach, we first take differentials of Eqs. (10.157,10.158) and get

$$
d\hat{x} \;=\; \frac{\partial \hat{x}}{\partial x}dx + \frac{\partial \hat{x}}{\partial t}dt = dx - D\,dt, \tag{10.159}
$$

$$
d\hat{t} \;=\; \frac{\partial \hat{t}}{\partial x}dx + \frac{\partial \hat{t}}{\partial t}dt = dt. \tag{10.160}
$$

Scaling $d\hat{x}$ by $d\hat{t}$ gives us then

$$
\frac{d\hat{x}}{d\hat{t}} = \frac{dx}{dt} - D. \tag{10.161}
$$

Taking as usual the particle velocity in the fixed frame to be $u = dx/dt$ and defining the particle velocity in the laboratory frame to be $\hat{u} = d\hat{x}/d\hat{t}$, we see that

$$
\hat{u} = u - D. \tag{10.162}
$$

Now, a dependent variable ψ has a representation in the original space of $\psi(x,t)$, and in the transformed space as $\psi(\hat{x},\hat{t})$. And they must both map to the same value of ψ and the same point. And there is a differential of ψ in both spaces which must be equal:

$$
d\psi = \left.\frac{\partial \psi}{\partial x}\right|_{t} dx + \left.\frac{\partial \psi}{\partial t}\right|_{x} dt \;=\; \left.\frac{\partial \psi}{\partial \hat{x}}\right|_{\hat{t}} d\hat{x} + \left.\frac{\partial \psi}{\partial \hat{t}}\right|_{\hat{x}} d\hat{t}, \tag{10.163}
$$

$$
=\; \left.\frac{\partial \psi}{\partial \hat{x}}\right|_{\hat{t}} (dx - D\,dt) + \left.\frac{\partial \psi}{\partial \hat{t}}\right|_{\hat{x}} dt, \tag{10.164}
$$

$$
=\; \left.\frac{\partial \psi}{\partial \hat{x}}\right|_{\hat{t}} dx + \left(\left.\frac{\partial \psi}{\partial \hat{t}}\right|_{\hat{x}} - D \left.\frac{\partial \psi}{\partial \hat{x}}\right|_{\hat{t}} \right) dt. \tag{10.165}
$$

Now, consider Eq. (10.165) for constant x, thus $dx = 0$, and divide by dt:

$$
\left.\frac{\partial \psi}{\partial t}\right|_{x} = \left.\frac{\partial \psi}{\partial \hat{t}}\right|_{\hat{x}} - D \left.\frac{\partial \psi}{\partial \hat{x}}\right|_{\hat{t}}. \tag{10.166}
$$

More generally the partial with respect to t becomes

$$
\left.\frac{\partial}{\partial t}\right|_{x} = \left.\frac{\partial}{\partial \hat{t}}\right|_{\hat{x}} - D \left.\frac{\partial}{\partial \hat{x}}\right|_{\hat{t}}. \tag{10.167}
$$

Now, consider Eq. (10.165) for constant t, thus $dt = 0$, and divide by dx:

$$\left.\frac{\partial \psi}{\partial x}\right|_t = \left.\frac{\partial \psi}{\partial \hat{x}}\right|_{\hat{t}} . \tag{10.168}$$

More generally,

$$\left.\frac{\partial}{\partial x}\right|_t = \left.\frac{\partial}{\partial \hat{x}}\right|_{\hat{t}} . \tag{10.169}$$

10.1.9.2 Differential geometry approach

For the differential geometry approach, we view the transformation in light of notions from linear theory where such concepts as the Jacobian, metric tensor, co- and contravariant representations are often used. These ideas are traditionally confined to spatial systems. Here, we will adapt them in a non-traditional way to account for our spatio-temporal transformation. First, we invert Eqs. (10.157,10.158) to form

$$x = \hat{x} + D\hat{t}, \tag{10.170}$$
$$t = \hat{t}. \tag{10.171}$$

Now, physically, x and t have different units. For dimensional consistency between the two independent variables, let us choose to consider the independent variables in the untransformed and transformed coordinates to be $(x, c_o t)$, and $(\hat{x}, c_o \hat{t})$, respectively. It is thus trivial to see that Eqs. (10.170),10.171) can be rewritten as

$$x = \hat{x} + \frac{D}{c_o}\left(c_o \hat{t}\right), \tag{10.172}$$
$$c_o t = c_o \hat{t}. \tag{10.173}$$

In matrix form, we could say

$$\underbrace{\begin{pmatrix} x \\ c_o t \end{pmatrix}}_{\boldsymbol{\xi}} = \underbrace{\begin{pmatrix} 1 & \frac{D}{c_o} \\ 0 & 1 \end{pmatrix}}_{\mathbf{J}} \cdot \underbrace{\begin{pmatrix} \hat{x} \\ c_o \hat{t} \end{pmatrix}}_{\hat{\boldsymbol{\xi}}} . \tag{10.174}$$

Here, we have defined a vector containing our untransformed independent variables as

$$\boldsymbol{\xi} = \begin{pmatrix} \xi^1 \\ \xi^2 \end{pmatrix} = \begin{pmatrix} x \\ c_o t \end{pmatrix} . \tag{10.175}$$

The superscripts are not exponents, but indices. The transformed independent variables are

$$\hat{\boldsymbol{\xi}} = \begin{pmatrix} \hat{\xi}^1 \\ \hat{\xi}^2 \end{pmatrix} = \begin{pmatrix} \hat{x} \\ c_o \hat{t} \end{pmatrix} . \tag{10.176}$$

These are linked by the linear transformation

$$\boldsymbol{\xi} = \mathbf{J} \cdot \hat{\boldsymbol{\xi}}, \tag{10.177}$$

where the constant Jacobian matrix, $\mathbf{J}$ is

$$\mathbf{J} = \frac{\partial \boldsymbol{\xi}}{\partial \hat{\boldsymbol{\xi}}} = \begin{pmatrix} \left.\frac{\partial \xi^1}{\partial \hat{\xi}^1}\right|_{\hat{\xi}^2} & \left.\frac{\partial \xi^1}{\partial \hat{\xi}^2}\right|_{\hat{\xi}^1} \\ \left.\frac{\partial \xi^2}{\partial \hat{\xi}^1}\right|_{\hat{\xi}^2} & \left.\frac{\partial \xi^2}{\partial \hat{\xi}^2}\right|_{\hat{\xi}^1} \end{pmatrix} = \begin{pmatrix} 1 & \frac{D}{c_o} \\ 0 & 1 \end{pmatrix}. \tag{10.178}$$

It is easily shown that the ratio of generalized areas between the two coordinate systems is given by $J = \det \mathbf{J}$. Here, we have

$$J = \det \mathbf{J} = 1, \tag{10.179}$$

so that generalized areas are preserved in the mapping. Moreover, it can be shown that because $J > 0$, the transformation is orientation-preserving.

We also have, by differentiating Eqs. (10.175-10.177), the differentials

$$d\boldsymbol{\xi} = \begin{pmatrix} dx \\ c_o dt \end{pmatrix}, \qquad d\hat{\boldsymbol{\xi}} = \begin{pmatrix} d\hat{x} \\ c_o d\hat{t} \end{pmatrix}, \tag{10.180}$$

as well as the transformation rule

$$d\boldsymbol{\xi} = \mathbf{J} \cdot d\hat{\boldsymbol{\xi}}. \tag{10.181}$$

The metric tensor $\mathbf{G}$ of the transformation is

$$\mathbf{G} = \mathbf{J}^T \cdot \mathbf{J} = \begin{pmatrix} 1 & 0 \\ \frac{D}{c_o} & 1 \end{pmatrix} \cdot \begin{pmatrix} 1 & \frac{D}{c_o} \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & \frac{D}{c_o} \\ \frac{D}{c_o} & 1 + \frac{D}{c_o}^2 \end{pmatrix}. \tag{10.182}$$

A generalized distance in the untransformed space is deduced from the Pythagorean formula

$$(ds)^2 = d\boldsymbol{\xi}^T \cdot d\boldsymbol{\xi} = \begin{pmatrix} dx & c_o dt \end{pmatrix} \begin{pmatrix} dx \\ c_o dt \end{pmatrix} = dx^2 + c_o^2 dt^2. \tag{10.183}$$

In the transformed space, Eq. (10.183) becomes, after using Eqs. (10.181,10.182),

$$(ds)^2 = \left(\mathbf{J} \cdot d\hat{\boldsymbol{\xi}} \right)^T \cdot \left(\mathbf{J} \cdot d\hat{\boldsymbol{\xi}} \right), \tag{10.184}$$

$$= d\hat{\boldsymbol{\xi}}^T \cdot \underbrace{\mathbf{J}^T \cdot \mathbf{J}}_{\mathbf{G}} \cdot d\hat{\boldsymbol{\xi}}, \tag{10.185}$$

$$= \underbrace{d\hat{\boldsymbol{\xi}}^T \cdot \mathbf{G}}_{d\hat{\xi}_j} \cdot \underbrace{d\hat{\boldsymbol{\xi}}}_{d\hat{\xi}^j}. \tag{10.186}$$

Using upstairs-downstairs index notation, we can define our covariant metric tensor as

$$\mathbf{G} = g_{ij}, \tag{10.187}$$

the contravariant $d\hat{\xi}^j$ as

$$d\hat{\boldsymbol{\xi}} = \begin{pmatrix} d\hat{x} \\ c_o d\hat{t} \end{pmatrix} = d\hat{\xi}^j, \tag{10.188}$$

and the covariant $d\hat{\xi}_j$ as

$$d\hat{\boldsymbol{\xi}}^T \cdot \mathbf{G} = \begin{pmatrix} d\hat{x} & c_o d\hat{t} \end{pmatrix} \begin{pmatrix} 1 & \frac{D}{c_o} \\ \frac{D}{c_o} & 1 + \frac{D}{c_o}^2 \end{pmatrix} = \begin{pmatrix} d\hat{x} + D d\hat{t} & \frac{D}{c_o} d\hat{x} + \left(1 + \frac{D^2}{c_o^2}\right) c_o d\hat{t} \end{pmatrix} = d\hat{\xi}_j. \tag{10.189}$$

For a general function ψ, the chain rule tells us

$$\underbrace{\begin{pmatrix} \frac{\partial \psi}{\partial \hat{\xi}^1}\Big|_{\hat{\xi}^2} \\ \frac{\partial \psi}{\partial \hat{\xi}^2}\Big|_{\hat{\xi}^1} \end{pmatrix}}_{\nabla_{\hat{\boldsymbol{\xi}}}\psi} = \underbrace{\begin{pmatrix} \frac{\partial \xi^1}{\partial \hat{\xi}^1}\Big|_{\hat{\xi}^2} & \frac{\partial \xi^2}{\partial \hat{\xi}^1}\Big|_{\hat{\xi}^2} \\ \frac{\partial \xi^1}{\partial \hat{\xi}^2}\Big|_{\hat{\xi}^1} & \frac{\partial \xi^2}{\partial \hat{\xi}^2}\Big|_{\hat{\xi}^1} \end{pmatrix}}_{\mathbf{J}^T} \cdot \underbrace{\begin{pmatrix} \frac{\partial \psi}{\partial \xi^1}\Big|_{\xi^2} \\ \frac{\partial \psi}{\partial \xi^2}\Big|_{\xi^1} \end{pmatrix}}_{\nabla_{\boldsymbol{\xi}}\psi}. \tag{10.190}$$

Equation (10.190) can be expressed in terms of the space-time gradients $\nabla_{\hat{\boldsymbol{\xi}}}$ and $\nabla_{\boldsymbol{\xi}}$

$$\nabla_{\hat{\boldsymbol{\xi}}}\psi = \mathbf{J}^T \cdot \nabla_{\boldsymbol{\xi}}\psi. \tag{10.191}$$

Inverting Eq. 10.191), we get

$$\nabla_{\boldsymbol{\xi}}\psi = \left(\mathbf{J}^T\right)^{-1} \cdot \nabla_{\hat{\boldsymbol{\xi}}}\psi. \tag{10.192}$$

Transposing then inverting $\mathbf{J}$ from Eq. (10.178), we get

$$\left(\mathbf{J}^T\right)^{-1} = \begin{pmatrix} 1 & 0 \\ -\frac{D}{c_o} & 1 \end{pmatrix}. \tag{10.193}$$

For our particular independent variables, Eq. (10.192) becomes

$$\begin{pmatrix} \frac{\partial \psi}{\partial x}\Big|_{c_o t} \\ \frac{\partial \psi}{\partial (c_o t)}\Big|_{x} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ -\frac{D}{c_o} & 1 \end{pmatrix} \cdot \begin{pmatrix} \frac{\partial \psi}{\partial \hat{x}}\Big|_{c_o \hat{t}} \\ \frac{\partial \psi}{\partial (c_o \hat{t})}\Big|_{\hat{x}} \end{pmatrix}. \tag{10.194}$$

In scalar form, Eq. (10.194) becomes

$$\frac{\partial \psi}{\partial x}\Big|_{c_o t} = \frac{\partial \psi}{\partial \hat{x}}\Big|_{c_o \hat{t}}, \tag{10.195}$$

$$\frac{\partial \psi}{\partial (c_o t)}\Big|_{x} = \frac{\partial \psi}{\partial (c_o \hat{t})}\Big|_{\hat{x}} - \frac{D}{c_o} \frac{\partial \psi}{\partial \hat{x}}\Big|_{c_o \hat{t}}. \tag{10.196}$$

And because c_o is a constant, Eqs. (10.195, 10.196) reduce to

$$\frac{\partial \psi}{\partial x}\Big|_{t} = \frac{\partial \psi}{\partial \hat{x}}\Big|_{\hat{t}}, \tag{10.197}$$

$$\frac{\partial \psi}{\partial t}\Big|_{x} = \frac{\partial \psi}{\partial \hat{t}}\Big|_{\hat{x}} - D \frac{\partial \psi}{\partial \hat{x}}\Big|_{\hat{t}}. \tag{10.198}$$

Equations (10.197, 10.198) are identical to those found using the direct method, Eqs. (10.168, 10.166).

10.1.9.3   Transformed equations

Applying either approach, we can quickly write our non-conservative form, Eqs. (10.64-10.67) in the transformed frame. First, let us consider how a material derivative transforms then

$$\left.\frac{\partial}{\partial t}\right|_x + u\left.\frac{\partial}{\partial x}\right|_t = \left(\left.\frac{\partial}{\partial \hat{t}}\right|_{\hat{x}} - D\left.\frac{\partial}{\partial \hat{x}}\right|_{\hat{t}}\right) + (\hat{u} + D)\left.\frac{\partial}{\partial \hat{x}}\right|_{\hat{t}}, \tag{10.199}$$

$$= \left.\frac{\partial}{\partial \hat{t}}\right|_{\hat{x}} + \hat{u}\left.\frac{\partial}{\partial \hat{x}}\right|_{\hat{t}}. \tag{10.200}$$

With this, we can then say

$$\frac{\partial \rho}{\partial \hat{t}} + \hat{u}\frac{\partial \rho}{\partial \hat{x}} + \rho\frac{\partial \hat{u}}{\partial \hat{x}} = 0, \tag{10.201}$$

$$\frac{\partial \hat{u}}{\partial \hat{t}} + \hat{u}\frac{\partial \hat{u}}{\partial \hat{x}} + \frac{1}{\rho}\frac{\partial P}{\partial \hat{x}} = 0, \tag{10.202}$$

$$\frac{\partial e}{\partial \hat{t}} + \hat{u}\frac{\partial e}{\partial \hat{x}} - P\left(\frac{\partial v}{\partial \hat{t}} + \hat{u}\frac{\partial v}{\partial \hat{x}}\right) = 0, \tag{10.203}$$

$$\frac{\partial \lambda}{\partial \hat{t}} + \hat{u}\frac{\partial \lambda}{\partial \hat{x}} = \mathsf{r}. \tag{10.204}$$

Moreover, we can write these equations in conservative form. Leaving out the details, which amounts to reversing our earlier steps which led to the non-conservative form, we get

$$\frac{\partial \rho}{\partial \hat{t}} + \frac{\partial}{\partial \hat{x}}(\rho\hat{u}) = 0, \tag{10.205}$$

$$\frac{\partial}{\partial \hat{t}}(\rho\hat{u}) + \frac{\partial}{\partial \hat{x}}\left(\rho\hat{u}^2 + P\right) = 0, \tag{10.206}$$

$$\frac{\partial}{\partial \hat{t}}\left(\rho\left(e + \frac{1}{2}\hat{u}^2\right)\right) + \frac{\partial}{\partial \hat{x}}\left(\rho\hat{u}\left(e + \frac{1}{2}\hat{u}^2 + \frac{P}{\rho}\right)\right) = 0, \tag{10.207}$$

$$\frac{\partial}{\partial \hat{t}}(\rho\lambda) + \frac{\partial}{\partial \hat{x}}(\rho\hat{u}\lambda) = \rho\mathsf{r}. \tag{10.208}$$

10.2   One-dimensional, steady solutions

Let us consider a steadily propagating disturbance in a one dimensional flow field. In the laboratory frame, the disturbance is observed to propagate with constant velocity D. Let us analyze such a disturbance.

10.2.1 Steady shock jumps

In the steady frame, our jump conditions, Eq. (10.151) have $U = 0$ and reduce to

$$
\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \rho_2 \hat{u}_2 - \rho_1 \hat{u}_1 \\ \rho_2 \hat{u}_2^2 + P_2 - \rho_1 \hat{u}_1^2 - P_1 \\ \rho_2 \hat{u}_2 \left(e_2 + \frac{1}{2}\hat{u}_2^2 + \frac{P_2}{\rho_2} \right) - \rho_1 \hat{u}_1 \left(e_1 + \frac{1}{2}\hat{u}_1^2 + \frac{P_1}{\rho_1} \right) \\ \rho_2 \hat{u}_2 \lambda_2 - \rho_1 \hat{u}_1 \lambda_1 \end{pmatrix}.
\tag{10.209}
$$

The mass jump equation can be used to quickly simplify the energy and species jump equations to get a revised set

$$
\begin{aligned}
\rho_2 \hat{u}_2 &= \rho_1 \hat{u}_1, \\
\rho_2 \hat{u}_2^2 + P_2 &= \rho_1 \hat{u}_1^2 + P_1, \\
e_2 + \frac{1}{2}\hat{u}_2^2 + \frac{P_2}{\rho_2} &= e_1 + \frac{1}{2}\hat{u}_1^2 + \frac{P_1}{\rho_1}, \\
\lambda_2 &= \lambda_1.
\end{aligned}
\tag{10.210}
$$

10.2.2 Ordinary differential equations of motion

10.2.2.1 Conservative form

Let us now assert that in the steady laboratory frame that no variable has dependence on $\hat{t}$, so $\partial/\partial \hat{t} = 0$, and $\partial/\partial \hat{x} = d/d\hat{x}$. With this assumption our partial differential equations of motion, Eqs. (10.205-10.208), become ordinary differential equations:

$$
\frac{d}{d\hat{x}}(\rho \hat{u}) = 0,
\tag{10.211}
$$

$$
\frac{d}{d\hat{x}}\left(\rho \hat{u}^2 + P\right) = 0,
\tag{10.212}
$$

$$
\frac{d}{d\hat{x}}\left(\rho \hat{u}\left(e + \frac{1}{2}\hat{u}^2 + \frac{P}{\rho}\right)\right) = 0,
\tag{10.213}
$$

$$
\frac{d}{d\hat{x}}(\rho \hat{u}\lambda) = \rho\mathsf{r},
\tag{10.214}
$$

$$
e = e(P, \rho, \lambda),
\tag{10.215}
$$

$$
\mathsf{r} = \mathsf{r}(P, \rho, \lambda).
\tag{10.216}
$$

We shall take the following conditions for the undisturbed fluid just before the shock at $\hat{x} = 0_-$:

$$
\rho(\hat{x} = 0_-) = \rho_o,
\tag{10.217}
$$

$$
\hat{u}(\hat{x} = 0_-) = -D,
\tag{10.218}
$$

$$
P(\hat{x} = 0_-) = P_o,
\tag{10.219}
$$

$$
e(\hat{x} = 0_-) = e_o,
\tag{10.220}
$$

$$
\lambda(\hat{x} = 0_-) = 0.
\tag{10.221}
$$

Note that in the laboratory frame, this corresponds to a material at rest since $u = \hat{u} + D = (-D) + D = 0$.

10.2.2.2   Unreduced non-conservative form

We can gain insights into how the differential equations, Eqs. (10.211-10.214) behave by writing them in a non-conservative form. Let us in fact write them, taking advantage of the reductions we used to acquire the characteristic form, Eqs. (10.86-10.89) to write those equations after transformation to the steady Galilean transformed frame as

$$\rho \frac{d\hat{u}}{d\hat{x}} + \hat{u}\frac{d\rho}{d\hat{x}} = 0, \tag{10.222}$$

$$\hat{u}\frac{d\hat{u}}{d\hat{x}} + \frac{1}{\rho}\frac{dP}{d\hat{x}} = 0, \tag{10.223}$$

$$\hat{u}\frac{dP}{d\hat{x}} - c^2\hat{u}\frac{d\rho}{d\hat{x}} = \rho c^2 \sigma \mathsf{r}, \tag{10.224}$$

$$\hat{u}\frac{d\lambda}{d\hat{x}} = \mathsf{r}. \tag{10.225}$$

Let us attempt next to get explicit representations for the first derivatives of each equation. In matrix form, we can say our system is

$$\begin{pmatrix} \hat{u} & \rho & 0 & 0 \\ 0 & \hat{u} & \frac{1}{\rho} & 0 \\ -c^2\hat{u} & 0 & \hat{u} & 0 \\ 0 & 0 & 0 & \hat{u} \end{pmatrix} \begin{pmatrix} \frac{d\rho}{d\hat{x}} \\ \frac{d\hat{u}}{d\hat{x}} \\ \frac{d\hat{P}}{d\hat{x}} \\ \frac{d\lambda}{d\hat{x}} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \rho c^2 \sigma \mathsf{r} \\ \mathsf{r} \end{pmatrix}. \tag{10.226}$$

We can use Cramer's[11] rule to invert the coefficient matrix to solve for the evolution of each state variable. This first requires the determinant of the coefficient matrix Δ.

$$\Delta = \begin{vmatrix} \hat{u} & \rho & 0 & 0 \\ 0 & \hat{u} & \frac{1}{\rho} & 0 \\ -c^2\hat{u} & 0 & \hat{u} & 0 \\ 0 & 0 & 0 & \hat{u} \end{vmatrix}, \tag{10.227}$$

$$= \hat{u}\begin{vmatrix} \hat{u} & \rho & 0 \\ 0 & \hat{u} & \frac{1}{\rho} \\ -c^2\hat{u} & 0 & \hat{u} \end{vmatrix}, \tag{10.228}$$

$$= \hat{u}\left(\hat{u}(\hat{u}^2) - \rho\frac{c^2\hat{u}}{\rho}\right), \tag{10.229}$$

$$= \hat{u}^2(\hat{u}^2 - c^2). \tag{10.230}$$

As Δ appears in the denominator after application of Cramer's rule, we see immediately that *when the waveframe velocity $\hat{u}$ becomes locally sonic ($\hat{u} = c$) that our system of differential equations is potentially singular.*

---

[11]Gabriel Cramer, 1704-1752, Swiss mathematician.

Now, by Cramer's rule, $d\rho/d\hat{x}$ is found via

$$\frac{d\rho}{d\hat{x}} = \frac{\begin{vmatrix} 0 & \rho & 0 & 0 \\ 0 & \hat{u} & \frac{1}{\rho} & 0 \\ \rho c^2 \sigma r & 0 & \hat{u} & 0 \\ r & 0 & 0 & \hat{u} \end{vmatrix}}{\Delta}, \tag{10.231}$$

$$= \frac{\hat{u}\begin{vmatrix} 0 & \rho & 0 \\ 0 & \hat{u} & \frac{1}{\rho} \\ \rho c^2 \sigma r & 0 & \hat{u} \end{vmatrix}}{\hat{u}^2(\hat{u}^2 - c^2)}, \tag{10.232}$$

$$= \frac{\hat{u}(-\rho)(-c^2 \sigma r)}{\hat{u}^2(\hat{u}^2 - c^2)}, \tag{10.233}$$

$$= \frac{\rho c^2 \sigma r}{\hat{u}(\hat{u}^2 - c^2)}. \tag{10.234}$$

Similarly, solving for $d\hat{u}/d\hat{x}$ we get

$$\frac{d\hat{u}}{d\hat{x}} = \frac{\begin{vmatrix} \hat{u} & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{\rho} & 0 \\ -c^2\hat{u} & \rho c^2 \sigma r & \hat{u} & 0 \\ 0 & r & 0 & \hat{u} \end{vmatrix}}{\Delta}, \tag{10.235}$$

$$= \frac{\hat{u}\begin{vmatrix} \hat{u} & 0 & 0 \\ 0 & 0 & \frac{1}{\rho} \\ -c^2\hat{u} & \rho c^2 \sigma r & \hat{u} \end{vmatrix}}{\hat{u}^2(\hat{u}^2 - c^2)}, \tag{10.236}$$

$$= \frac{\hat{u}^2(-c^2 \sigma r)}{\hat{u}^2(\hat{u}^2 - c^2)}, \tag{10.237}$$

$$= -\frac{c^2 \sigma r}{\hat{u}^2 - c^2}. \tag{10.238}$$

For $dP/d\hat{x}$, we get

$$\frac{dP}{d\hat{x}} = \frac{\begin{vmatrix} \hat{u} & \rho & 0 & 0 \\ 0 & \hat{u} & 0 & 0 \\ -c^2\hat{u} & 0 & \rho c^2 \sigma r & 0 \\ 0 & 0 & r & \hat{u} \end{vmatrix}}{\Delta}, \tag{10.239}$$

$$= \frac{\hat{u}\begin{vmatrix} \hat{u} & \rho & 0 \\ 0 & \hat{u} & 0 \\ -c^2\hat{u} & 0 & \rho c^2 \sigma r \end{vmatrix}}{\hat{u}^2(\hat{u}^2 - c^2)}, \tag{10.240}$$

$$= \quad \frac{\hat{u}\rho c^2 \sigma \mathsf{r}\hat{u}^2}{\hat{u}^2(\hat{u}^2 - c^2)}, \tag{10.241}$$

$$= \quad \frac{\hat{u}\rho c^2 \sigma \mathsf{r}}{\hat{u}^2 - c^2}. \tag{10.242}$$

Lastly, we have by inspection

$$\frac{d\lambda}{d\hat{x}} = \frac{\mathsf{r}}{\hat{u}}. \tag{10.243}$$

We can employ the local Mach number in the steady wave frame,

$$\hat{\mathsf{M}}^2 \equiv \frac{\hat{u}^2}{c^2}, \tag{10.244}$$

to write our system of ordinary differential equations as

$$\frac{d\rho}{d\hat{x}} = -\frac{\rho \sigma \mathsf{r}}{\hat{u}(1 - \hat{\mathsf{M}}^2)}, \tag{10.245}$$

$$\frac{d\hat{u}}{d\hat{x}} = \frac{\sigma \mathsf{r}}{1 - \hat{\mathsf{M}}^2}, \tag{10.246}$$

$$\frac{dP}{d\hat{x}} = -\frac{\rho\hat{u}\sigma \mathsf{r}}{1 - \hat{\mathsf{M}}^2}, \tag{10.247}$$

$$\frac{d\lambda}{d\hat{x}} = \frac{\mathsf{r}}{\hat{u}}. \tag{10.248}$$

We note the when the flow is locally sonic, $\hat{\mathsf{M}} = 1$, that our equations are singular. Recalling an analogy from compressible flow with area change, which is really an application of l'Hôpital's rule, in order for the flow to be locally sonic, we must insist that simultaneously the numerator must be zero; thus, we might demand that at a sonic point, $\sigma \mathsf{r} = 0$. So, an end state with $\mathsf{r} = 0$ may in fact be a sonic point. For multi-step reactions, each with their own thermicity and reaction progress, we require the generalization $\boldsymbol{\sigma} \cdot \mathbf{r} = 0$ at a local sonic point. Here, $\boldsymbol{\sigma}$ is the vector of thermicities and $\mathbf{r}$ is the vector of reaction rates. This condition will be important later when we consider so-called eigenvalue detonations.

10.2.2.3   Reduced non-conservative form

Let us use the mass equation, Eq. (10.211) to simplify the reaction equation, Eq. (10.214), then integrate our differential equations for mass momentum and energy conservation, apply the initial conditions, and thus reduce our system of four differential and two algebraic equations to one differential and five algebraic equations:

$$\rho\hat{u} = -\rho_o D, \tag{10.249}$$

$$P + \rho\hat{u}^2 = P_o + \rho_o D^2, \tag{10.250}$$

$$\rho \hat{u} \left(e + \frac{1}{2} \hat{u}^2 + \frac{P}{\rho} \right) = -\rho_o D \left(e_o + \frac{1}{2} D^2 + \frac{P_o}{\rho_o} \right), \tag{10.251}$$

$$\frac{d\lambda}{d\hat{x}} = \frac{1}{\hat{u}} \mathsf{r}, \tag{10.252}$$

$$e = e(P, \rho, \lambda), \tag{10.253}$$

$$\mathsf{r} = \mathsf{r}(P, \rho, \lambda). \tag{10.254}$$

With some effort, we can unravel these equations to form one ordinary differential equation in one unknown. But let us delay that analysis until after we have examined the consequences of the algebraic constraints

10.2.3 Rankine-Hugoniot analysis

Let us first analyze our steady mass, momentum, and energy equations, Eqs. (10.249-10.251). Our analysis here will be valid both within, $(0 < \lambda < 1)$ and at the end of the reaction zone $(\lambda = 1)$.

10.2.3.1 Rayleigh line

Let us get what is known as the *Rayleigh*[12] *line* by considering only the mass and linear momentum equations, Eqs. (10.249-10.250). Let us first rewrite Eq. (10.250) as

$$P + \frac{\rho^2 \hat{u}^2}{\rho} = P_o + \frac{\rho_o^2 D^2}{\rho_o}. \tag{10.255}$$

Then, the mass equation, Eq. (10.22) allows us to rewrite the momentum equation, Eq. (10.255) as

$$P + \frac{\rho_o^2 D^2}{\rho} = P_o + \frac{\rho_o^2 D^2}{\rho_o}. \tag{10.256}$$

Rearranging to solve for P, we find

$$P = P_o - \rho_o^2 D^2 \left(\frac{1}{\rho} - \frac{1}{\rho_o} \right). \tag{10.257}$$

In terms of $v = 1/\rho$, and a slight rearrangement, Eq. (10.257) can be re-stated as

$$P = P_o - \frac{D^2}{v_o^2} (v - v_o), \tag{10.258}$$

$$\frac{P}{P_o} = 1 - \frac{D^2}{P_o v_o} \left(\frac{v}{v_o} - 1 \right). \tag{10.259}$$

Note:

---

[12]John William Strutt, 3rd Baron Rayleigh, 1842-1919, English physicist.
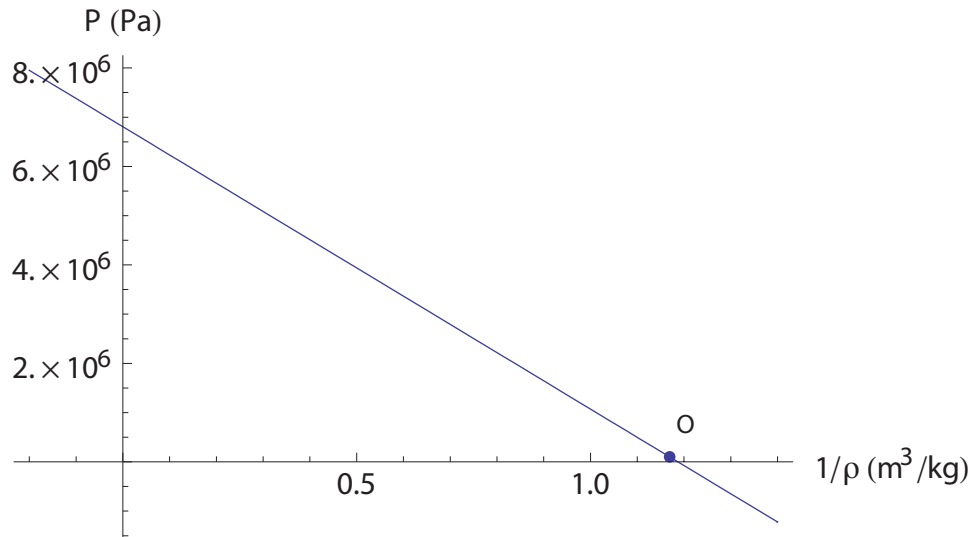
Figure 10.1:   Plot of Rayleigh line for parameters of Table 10.1 and $D = 2800 \ m/s$. Slope is $-\rho_o^2 D^2 < 0$.

- This is a line in $(P, 1/\rho)$ space, the Rayleigh line.

- The slope of the Rayleigh line is strictly negative.

- The magnitude of the slope of the Rayleigh line is proportional the square of the wave speed; high wave speeds induce steep slopes.

- The Rayleigh line passes through the ambient state $(P_o, 1/\rho_o)$.

- Small volume leads to high pressure.

- These conclusions are a consequence of mass and momentum conservation *alone*. No consideration of energy has been made.

- The Rayleigh line equation is valid at all stages of the reaction: the inert state, a shocked stated, an intermediate reacted state, and a completely reacted state. It is always the same line.

A plot of a Rayleigh line for $D = 2800 \ m/s$ and the parameters of Table 10.1 is shown in Fig. 10.1. Here, the point labeled "O" is the ambient state $(1/\rho_o, P_o)$.

10.2.3.2   Hugoniot curve

Let us next focus on the energy equation, Eq. (10.251). We shall use the mass and momentum equations (10.249,10.250) to cast the energy equation in a form which is independent of both

velocities and wave speeds. From Eq. (10.249), we can easily see that Eq. (10.251) first reduces to

$$e + \frac{1}{2}\hat{u}^2 + \frac{P}{\rho} \;=\; e_o + \frac{1}{2}D^2 + \frac{P_o}{\rho_o}. \tag{10.260}$$

Now, the mass equation (10.249) also tells us that

$$\hat{u} = -\frac{\rho_o}{\rho}D, \tag{10.261}$$

so Eq. (10.260) can be recast as

$$e + \frac{1}{2}\left(\frac{\rho_o}{\rho}\right)^2 D^2 + \frac{P}{\rho} \;=\; e_o + \frac{1}{2}D^2 + \frac{P_o}{\rho_o}, \tag{10.262}$$

$$e - e_o + \frac{1}{2}D^2\left(\left(\frac{\rho_o}{\rho}\right)^2 - 1\right) + \frac{P}{\rho} - \frac{P_o}{\rho_o} \;=\; 0, \tag{10.263}$$

$$e - e_o + \frac{1}{2}D^2\left(\frac{(\rho_o - \rho)(\rho_o + \rho)}{\rho^2}\right) + \frac{P}{\rho} - \frac{P_o}{\rho_o} \;=\; 0. \tag{10.264}$$

Now, the Rayleigh line, Eq. (10.257) can be used to solve for D^2,

$$D^2 = \frac{P_o - P}{\rho_o^2}\left(\frac{1}{\rho} - \frac{1}{\rho_o}\right)^{-1} = \frac{P_o - P}{\rho_o^2}\left(\frac{\rho\rho_o}{\rho_o - \rho}\right). \tag{10.265}$$

Now, use Eq. (10.265) to eliminate D^2 in Eq. (10.264):

$$e - e_o + \frac{1}{2}\underbrace{\left(\frac{P_o - P}{\rho_o^2}\left(\frac{\rho\rho_o}{\rho_o - \rho}\right)\right)}_{=D^2}\left(\frac{(\rho_o - \rho)(\rho_o + \rho)}{\rho^2}\right) + \frac{P}{\rho} - \frac{P_o}{\rho_o} \;=\; 0, \tag{10.266}$$

$$e - e_o + \frac{1}{2}\left(\frac{P_o - P}{\rho_o}\right)\left(\frac{\rho_o + \rho}{\rho}\right) + \frac{P}{\rho} - \frac{P_o}{\rho_o} \;=\; 0, \tag{10.267}$$

$$e - e_o + \frac{1}{2}(P_o - P)\left(\frac{1}{\rho} + \frac{1}{\rho_o}\right) + \frac{P}{\rho} - \frac{P_o}{\rho_o} \;=\; 0, \tag{10.268}$$

$$e - e_o + \frac{1}{2}\frac{P_o}{\rho} + \frac{1}{2}\frac{P_o}{\rho_o} - \frac{1}{2}\frac{P}{\rho} - \frac{1}{2}\frac{P}{\rho_o} + \frac{P}{\rho} - \frac{P_o}{\rho_o} \;=\; 0, \tag{10.269}$$

$$e - e_o + \frac{1}{2}\left(\frac{P_o}{\rho} - \frac{P_o}{\rho_o} + \frac{P}{\rho} - \frac{P}{\rho_o}\right) \;=\; 0, \tag{10.270}$$

$$e - e_o + \frac{1}{2}(P + P_o)\left(\frac{1}{\rho} - \frac{1}{\rho_o}\right) \;=\; 0. \tag{10.271}$$

Rearranging, we get

$$\underbrace{e - e_o}_{\text{change in energy}} \;=\; \underbrace{-\frac{P + P_o}{2}}_{\text{-average pressure}} \times \underbrace{\left(\frac{1}{\rho} - \frac{1}{\rho_o}\right)}_{\text{change in volume}}. \tag{10.272}$$

This is the Hugoniot equation for a general material. It applies for solid, liquid, or gas.
Note that

- This form of the Hugoniot does not depend on the state equation.

- The Hugoniot has no dependency on particle velocity or wave speed.

- The Hugoniot is valid for all $e(\lambda)$; that is it is valid for inert, partially reacted, and totally reacted material. Different degrees of reaction λ will induce shifts in the curve.

Now, let us specify an equation of state. For convenience and to more easily illustrate the features of the Rankine-Hugoniot analysis, let us focus on the simplest physically-based state equation, the calorically perfect ideal gas for our simple irreversible kinetics model. With that we adopt the perfect caloric state equation studied earlier, Eq. (8.7):

$$e \;=\; c_v T - \lambda q. \tag{10.273}$$

We also adopt an ideal gas assumption

$$P = \rho R T. \tag{10.274}$$

Solving for T, we get $T = P/\rho/R$. Thus, $c_v T = (c_v/R)(P/\rho)$. Recalling that $R = c_P - c_v$, we then get $c_v T = (c_v/(c_P - c_v))(P/\rho)$. And recalling that for the calorically perfect ideal gas

$$\gamma = \frac{c_P}{c_v}, \tag{10.275}$$

we get

$$c_v T = \frac{1}{\gamma - 1}\frac{P}{\rho}. \tag{10.276}$$

Thus, our caloric equation of state, Eq. (10.273), for our simple model becomes

$$e(P, \rho, \lambda) = \frac{1}{\gamma - 1}\frac{P}{\rho} - \lambda q. \tag{10.277}$$

In terms of v, Eq. (10.277) is

$$e(P, v, \lambda) = \frac{1}{\gamma - 1}Pv - \lambda q. \tag{10.278}$$

As an aside, we note that for this equation of state, the sound speed can be deduced from Eq. (10.16) as

$$\rho^2 c^2 = \frac{P + \left.\frac{\partial e}{\partial v}\right|_{P,\lambda}}{\left.\frac{\partial e}{\partial P}\right|_{v,\lambda}} = \frac{P + \frac{1}{\gamma - 1}P}{\frac{1}{\gamma - 1}v} = \frac{\gamma P}{v}. \tag{10.279}$$

$$c^2 = \gamma\frac{P}{v}\frac{1}{\rho^2} = \gamma Pv = \gamma\frac{P}{\rho}. \tag{10.280}$$

For the thermicity, we note that

$$P = \rho R T = \frac{R}{v} T = \frac{R}{v} \frac{e + \lambda q}{c_v}, \tag{10.281}$$

$$\left. \frac{\partial P}{\partial \lambda} \right|_{v,e} = \frac{R}{c_v} \frac{q}{v} = (\gamma - 1) \rho q, \tag{10.282}$$

$$\sigma = \frac{1}{\rho c^2} \left. \frac{\partial P}{\partial \lambda} \right|_{v,e} = \frac{1}{\rho c^2} (\gamma - 1) \rho q = (\gamma - 1) \frac{q}{c^2} = \frac{\gamma - 1}{\gamma} \frac{\rho q}{P}. \tag{10.283}$$

Now, at the initial state, we have $\lambda = 0$, and so Eq. (10.277) reduces to

$$e_o = \frac{1}{\gamma - 1} \frac{P_o}{\rho_o}. \tag{10.284}$$

We now use our caloric state relations, Eqs. (10.277,10.284) to specialize our Hugoniot relation, Eq. (10.272), to

$$\frac{1}{\gamma - 1} \left(\frac{P}{\rho} - \frac{P_o}{\rho_o} \right) - \lambda q = -\frac{P + P_o}{2} \left(\frac{1}{\rho} - \frac{1}{\rho_o} \right). \tag{10.285}$$

Employing $v = 1/\rho$, we get a more compact form:

$$\frac{1}{\gamma - 1} (Pv - P_o v_o) - \lambda q = -\frac{1}{2}(P + P_o)(v - v_o). \tag{10.286}$$

Let us next operate on Eq. (10.285) so as to see more clearly how the Hugoniot is represented in the $(P, v) = (P, 1/\rho)$ plane.

$$\frac{1}{\gamma - 1} (Pv - P_o v_o) + \frac{1}{2}(Pv + P_o v - Pv_o - P_o v_o) = \lambda q, \tag{10.287}$$

$$P \left(\frac{1}{\gamma - 1} v + \frac{1}{2} v - \frac{1}{2} v_o \right) - P_o \left(\frac{1}{\gamma - 1} v_o - \frac{1}{2} v + \frac{1}{2} v_o \right) = \lambda q, \tag{10.288}$$

$$\frac{P}{2} \left(\frac{\gamma + 1}{\gamma - 1} v - v_o \right) - \frac{P_o}{2} \left(\frac{\gamma + 1}{\gamma - 1} v_o - v \right) = \lambda q, \tag{10.289}$$

$$P = \frac{2\lambda q + P_o \left(\frac{\gamma + 1}{\gamma - 1} v_o - v \right)}{\left(\frac{\gamma + 1}{\gamma - 1} v - v_o \right)}. \tag{10.290}$$

Note that as

$$v \to \frac{\gamma - 1}{\gamma + 1} v_o, \qquad P \to \infty. \tag{10.291}$$

For $\gamma = 7/5$, this gives $v \to v_o/6$ induces and infinite pressure. In fact an ideal gas cannot be compressed beyond this limit, known as the *strong shock limit*. Note also that as

$$v \to \infty, \qquad -\frac{\gamma - 1}{\gamma + 1} P_o < 0. \tag{10.292}$$

So, very large volumes induce non-physical pressures.

Let us continue to operate to get a more compact form for the calorically perfect ideal gas Hugoniot curve. Let us add a common term to both sides of Eq. (10.290):

$$P + \frac{\gamma - 1}{\gamma + 1} P_o = \frac{2\lambda q + P_o \left(\frac{\gamma+1}{\gamma-1} v_o - v \right)}{\left(\frac{\gamma+1}{\gamma-1} v - v_o \right)} + \frac{\gamma - 1}{\gamma + 1} P_o, \quad (10.293)$$

$$\left(P + \frac{\gamma - 1}{\gamma + 1} P_o \right) \left(\frac{\gamma + 1}{\gamma - 1} v - v_o \right) = 2\lambda q + P_o \left(\frac{\gamma + 1}{\gamma - 1} v_o - v \right)$$

$$+ \frac{\gamma - 1}{\gamma + 1} P_o \left(\frac{\gamma + 1}{\gamma - 1} v - v_o \right), \quad (10.294)$$

$$= 2\lambda q + \frac{\gamma + 1}{\gamma - 1} P_o v_o - P_o v$$

$$+ P_o v - \frac{\gamma - 1}{\gamma + 1} P_o v_o, \quad (10.295)$$

$$= 2\lambda q + \frac{\gamma + 1}{\gamma - 1} P_o v_o - \frac{\gamma - 1}{\gamma + 1} P_o v_o, \quad (10.296)$$

$$= 2\lambda q + \frac{4\gamma}{\gamma^2 - 1} P_o v_o, \quad (10.297)$$

$$\left(\frac{P}{P_o} + \frac{\gamma - 1}{\gamma + 1} \right) \left(\frac{\gamma + 1}{\gamma - 1} \frac{v}{v_o} - 1 \right) = \frac{2\lambda q}{P_o v_o} + \frac{4\gamma}{\gamma^2 - 1}, \quad (10.298)$$

$$\left(\frac{P}{P_o} + \frac{\gamma - 1}{\gamma + 1} \right) \left(\frac{v}{v_o} - \frac{\gamma - 1}{\gamma + 1} \right) = \frac{\gamma - 1}{\gamma + 1} \frac{2\lambda q}{P_o v_o} + \frac{4\gamma}{(\gamma + 1)^2}. \quad (10.299)$$

Equation (10.299) represents a hyperbola in the $(P, v) = (P, 1/\rho)$ plane. As λ proceeds from 0 to 1, the Hugoniot moves. A plot of a series of Hugoniot curves for values of $\lambda = 0, 1/2, 1$ along with two Rayleigh lines for $D = 2800 \; m/s$ and $D = 1991.1 \; m/s$ is shown in Fig. 10.2. The $D = 1991.1 \; m/s$ Rayleigh line happens to be exactly tangent to the $\lambda = 1$ Hugoniot curve. We will see this has special significance.

Let us define, for convenience, the parameter $\hat{\mu}^2$ as

$$\hat{\mu}^2 \equiv \frac{\gamma - 1}{\gamma + 1}. \quad (10.300)$$

With this definition, we note that

$$1 - \hat{\mu}^4 = 1 - \left(\frac{\gamma - 1}{\gamma + 1} \right)^2 = \frac{\gamma^2 + 2\gamma + 1 - \gamma^2 + 2\gamma - 1}{(\gamma + 1)^2} = \frac{4\gamma}{(\gamma + 1)^2}. \quad (10.301)$$

With this definition, Eq. (10.299), the Hugoniot, becomes

$$\left(\frac{P}{P_o} + \hat{\mu}^2 \right) \left(\frac{v}{v_o} - \hat{\mu}^2 \right) = 2\hat{\mu}^2 \frac{\lambda q}{P_o v_o} + 1 - \hat{\mu}^4. \quad (10.302)$$
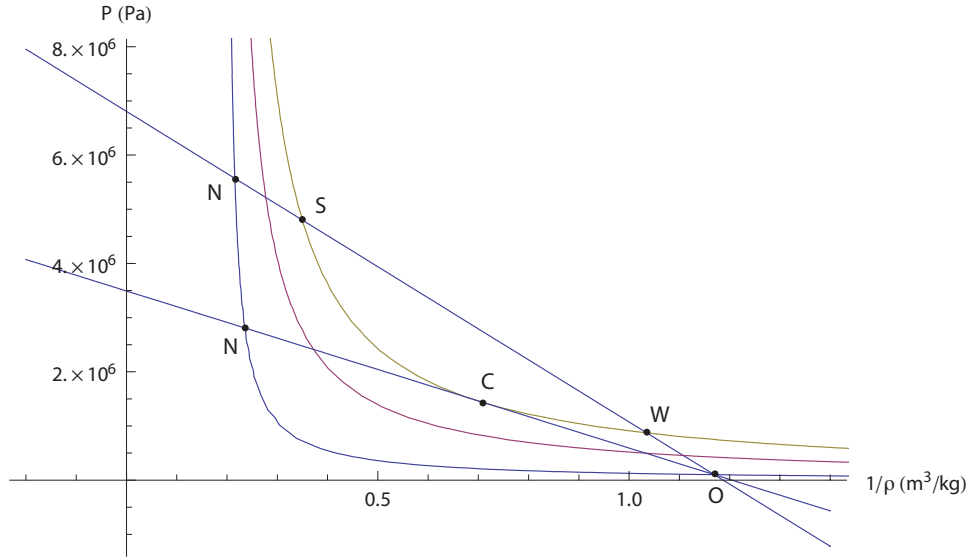
Figure 10.2: Plot of $\lambda = 0, 1/2, 1$ Hugoniot curves and two Rayleigh lines for $D = 2800 \ m/s$, $D = 1991.1 \ m/s$ and parameters of Table 10.1.

Now, let us seek to intersect the Rayleigh line with the Hugoniot curve and find the points of intersection. To do so, let us use the Rayleigh line, Eq. (10.259), to eliminate pressure in the Hugoniot, Eq. (10.302):

$$\left(1 - \frac{D^2}{P_o v_o} \left(\frac{v}{v_o} - 1\right) + \hat{\mu}^2\right)\left(\frac{v}{v_o} - \hat{\mu}^2\right) \ = \ 2\hat{\mu}^2 \frac{\lambda q}{P_o v_o} + 1 - \hat{\mu}^4. \qquad (10.303)$$

We now structure Eq. (10.303) so that it can be solved for v:

$$\left(1 + \hat{\mu}^2 - \frac{D^2}{P_o v_o}\frac{v}{v_o} + \frac{D^2}{P_o v_o}\right)\left(\frac{v}{v_o} - \hat{\mu}^2\right) \ = \ 2\hat{\mu}^2 \frac{\lambda q}{P_o v_o} + 1 - \hat{\mu}^4. \qquad (10.304)$$

Now, let us regroup to form

$$\left(\frac{v}{v_o}\right)^2 \left(-\frac{D^2}{P_o v_o}\right) + \left(\frac{v}{v_o}\right)\left((1 + \hat{\mu}^2)\left(1 + \frac{D^2}{P_o v_o}\right)\right) - \hat{\mu}^2\left(1 + \hat{\mu}^2 + \frac{D^2}{P_o v_o}\right)$$
$$-2\hat{\mu}^2 \frac{\lambda q}{P_o v_o} - 1 + \hat{\mu}^4 \ = \ 0,$$
$$(10.305)$$
$$\left(\frac{v}{v_o}\right)^2\left(-\frac{D^2}{P_o v_o}\right) + \left(\frac{v}{v_o}\right)\left((1 + \hat{\mu}^2)\left(1 + \frac{D^2}{P_o v_o}\right)\right) - \hat{\mu}^2\left(1 + \frac{D^2}{P_o v_o}\right) - 2\hat{\mu}^2 \frac{\lambda q}{P_o v_o} - 1 \ = \ 0.$$
$$(10.306)$$

This quadratic equation has two roots:

$$
\begin{aligned}
\left(\frac{v}{v_o}\right) &= \frac{\left(1+\frac{D^2}{P_o v_o}\right)(1+\hat{\mu}^2)}{2\frac{D^2}{P_o v_o}} \\
&\pm \frac{\sqrt{\left(1+\frac{D^2}{P_o v_o}\right)^2(1+\hat{\mu}^2)^2 - 4\frac{D^2}{P_o v_o}\left(1+\left(1+\frac{D^2}{P_o v_o}\right)\hat{\mu}^2 - 2\hat{\mu}^2\frac{\lambda q}{P_o v_o}\right)}}{2\frac{D^2}{P_o v_o}}.
\end{aligned}
\tag{10.307}
$$

For a given wave speed D, initial undisturbed conditions, P_o, v_o, and material properties, $\hat{\mu}$, q, Eq. (10.307) gives the specific volume as a function of reaction progress λ. Depending on these parameters, we can mathematically expect two distinct real solutions, two repeated solutions, or two complex solutions.

10.2.4   Shock solutions

We know from Eq. (10.210) that λ does not change through a shock. So, if $\lambda = 0$ before the shock, it has the same value after. So, we can get the shock state by enforcing the Rankine-Hugoniot jump conditions with $\lambda = 0$:

$$
\begin{aligned}
\left(\frac{v}{v_o}\right) &= \frac{\left(1+\frac{D^2}{P_o v_o}\right)(1+\hat{\mu}^2)}{2\frac{D^2}{P_o v_o}} \\
&\pm \frac{\sqrt{\left(1+\frac{D^2}{P_o v_o}\right)^2(1+\hat{\mu}^2)^2 - 4\frac{D^2}{P_o v_o}\left(1+\left(1+\frac{D^2}{P_o v_o}\right)\hat{\mu}^2\right)}}{2\frac{D^2}{P_o v_o}}.
\end{aligned}
\tag{10.308}
$$

With considerable effort, or alternatively, by direct calculation via computational algebra, the two roots of Eq. (10.308) can be shown to reduce to:

$$
\frac{v}{v_o} = 1,
\tag{10.309}
$$

$$
\frac{v}{v_o} = \hat{\mu}^2 + \frac{P_o v_o}{D^2}(1+\hat{\mu}^2).
\tag{10.310}
$$

The first is the ambient solution; the second is the shock solution. The shock solution can also be expressed as

$$
\frac{v}{v_o} = \frac{\gamma - 1}{\gamma + 1} + \frac{2\gamma}{\gamma + 1}\frac{P_o v_o}{D^2}.
\tag{10.311}
$$

In the limit as $P_o v_o/D^2 \to 0$, the so-called strong shock limit, we find

$$
\frac{v}{v_o} \to \frac{\gamma - 1}{\gamma + 1}.
\tag{10.312}
$$

The reciprocal gives the density ratio in the strong shock limit:

$$\frac{\rho}{\rho_o} \to \frac{\gamma+1}{\gamma-1}. \tag{10.313}$$

With the solutions for v/v_o, we can employ the Rayleigh line, Eq. (10.259) to get the pressure. Again, we find two solutions:

$$\frac{P}{P_o} = 1, \tag{10.314}$$

$$\frac{P}{P_o} = \frac{D^2}{P_o v_o}(1 - \hat{\mu}^2) - \hat{\mu}^2. \tag{10.315}$$

The first is the inert solution, and the second is the shock solution. The shock solution is rewritten as

$$\frac{P}{P_o} = \frac{2}{\gamma+1}\frac{D^2}{P_o v_o} - \frac{\gamma-1}{\gamma+1}. \tag{10.316}$$

In the strong shock limit, $P_o v_o / D^2 \to 0$, the shock state reduces to

$$\frac{P}{P_o} \to \frac{2}{\gamma+1}\frac{D^2}{P_o v_o}. \tag{10.317}$$

Note, this can also be rewritten as

$$\frac{P}{P_o} \to \frac{2\gamma}{\gamma+1}\frac{D^2}{\gamma P_o v_o}, \tag{10.318}$$

$$\to \frac{2\gamma}{\gamma+1}\frac{D^2}{c_o^2}. \tag{10.319}$$

Lastly, the particle velocity can be obtained via the mass equation, Eq. (10.261):

$$\frac{\hat{u}}{D} = -\frac{\rho_o}{\rho}, \tag{10.320}$$

$$= -\frac{v}{v_o}, \tag{10.321}$$

$$= -\frac{\gamma-1}{\gamma+1} - \frac{2\gamma}{\gamma+1}\frac{P_o v_o}{D^2}. \tag{10.322}$$

In the strong shock limit, $P_o v_o / D^2 \to 0$, we get

$$\frac{\hat{u}}{D} \to -\frac{\gamma-1}{\gamma+1}. \tag{10.323}$$

Note that in the laboratory frame, one gets

$$\frac{u-D}{D} \to -\frac{\gamma-1}{\gamma+1}, \tag{10.324}$$

$$\frac{u}{D} \to 1 - \frac{\gamma-1}{\gamma+1}, \tag{10.325}$$

$$\frac{u}{D} \to \frac{2}{\gamma+1}. \tag{10.326}$$

10.2.5 Equilibrium solutions

Our remaining differential equation, Eq. (10.252) is in equilibrium when $\mathsf{r} = 0$, which for one-step irreversible kinetics, Eq. (10.12), occurs when $\lambda = 1$. So, for equilibrium end states, we enforce $\lambda = 1$ in Eq. (10.307) and get

$$
\left(\frac{v}{v_o}\right) = \frac{\left(1 + \frac{D^2}{P_o v_o}\right)(1 + \hat{\mu}^2)}{2\frac{D^2}{P_o v_o}}
$$

$$
\pm \frac{\sqrt{\left(1 + \frac{D^2}{P_o v_o}\right)^2 (1 + \hat{\mu}^2)^2 - 4\frac{D^2}{P_o v_o}\left(1 + \left(1 + \frac{D^2}{P_o v_o}\right)\hat{\mu}^2 - 2\hat{\mu}^2\frac{q}{P_o v_o}\right)}}{2\frac{D^2}{P_o v_o}}. \tag{10.327}
$$

This has only one free parameter, D. There are two solutions for v/v_o at complete reaction. They can be distinct and real, repeated and real, or complex, depending on the value of D. We are most interested in D for which the solutions are real; these will be physically realizable.

10.2.5.1 Chapman-Jouguet solutions

Let us first consider solutions for which the two roots of Eq. (10.327) are repeated. This is known as a Chapman[13]-Jouguet[14] (CJ) solution. For a CJ solution, the Rayleigh line is tangent to the Hugoniot at $\lambda = 1$ if the reaction is driven by one-step irreversible kinetics.

We can find values of D for which the solutions are CJ by requiring the discriminant under the square root operator in Eq. (10.327) to be zero. We label such solutions with a CJ subscript and say

$$
\left(1 + \frac{D_{CJ}^2}{P_o v_o}\right)^2 (1 + \hat{\mu}^2)^2 - 4\frac{D_{CJ}^2}{P_o v_o}\left(1 + \left(1 + \frac{D_{CJ}^2}{P_o v_o}\right)\hat{\mu}^2 - 2\hat{\mu}^2\frac{q}{P_o v_o}\right) = 0. \tag{10.328}
$$

Equation (10.328) is quartic in D_{CJ} and quadratic in D_{CJ}^2. It has solutions

$$
\frac{D_{CJ}^2}{P_o v_o} = \frac{1 + 4\hat{\mu}^2\frac{q}{P_o v_o} - \hat{\mu}^4 \pm 2\sqrt{\frac{2q}{P_o v_o}\hat{\mu}^2(1 + 2\hat{\mu}^2 - \hat{\mu}^4)}}{(\hat{\mu}^2 - 1)^2}. \tag{10.329}
$$

The "+" root corresponds to a large value of D_{CJ}. This is known as the *detonation* branch. For the parameter values of Table 10.1, we find by substitution that $D_{CJ} = 1991.1\ m/s$ for our H_2-air mixture. It corresponds to a pressure increase and a volume decrease. The "-" root corresponds to a small value of D_{CJ}. It corresponds to a pressure decrease and a volume increase. It is known as the *deflagration* branch. For our H_2-air mixture, we find $D_{CJ} = 83.306\ m/s$. Here, we are most concerned with the detonation branch. The

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[13]David Leonard Chapman, 1869-1958, English chemist.
[14]Jacques Charles Émile Jouguet, 1871-1943, French engineer.

deflagration branch may be of interest, but neglected mechanisms, such as diffusion, may be of more importance for this branch. In fact laminar flames in hydrogen move much slower than that predicted by the CJ deflagration speed. We also note that for $q \to 0$, that $D_{CJ}^2/(P_o v_o) = (1 + \hat{\mu}^2)/(1 - \hat{\mu}^2) = \gamma$. Thus, for $q \to 0$, we have $D_{CJ}^2 \to \gamma P_o v_o$, and the wave speed is the ambient sound speed.

Taylor series expansion of the detonation branch in the strong shock limit, $P_o v_o / D_{CJ}^2 \to 0$ shows that

$$D_{CJ}^2 \to 2q(\gamma^2 - 1), \tag{10.330}$$

$$v_{CJ} \to \frac{\gamma}{\gamma + 1} v_o, \tag{10.331}$$

$$P_{CJ} \to 2(\gamma - 1)\frac{q}{v_o}, \tag{10.332}$$

$$\hat{u}_{CJ} \to -\frac{\gamma}{\gamma + 1}\sqrt{2q(\gamma^2 - 1)}, \tag{10.333}$$

$$u_{CJ} \to \frac{\sqrt{2q(\gamma^2 - 1)}}{\gamma + 1}. \tag{10.334}$$

Importantly the Mach number in the wave frame at the CJ state is

$$\hat{\mathsf{M}}_{CJ}^2 = \frac{\hat{u}_{CJ}^2}{c_{CJ}^2}, \tag{10.335}$$

$$= \frac{\hat{u}_{CJ}^2}{\gamma P_{CJ} v_{CJ}}, \tag{10.336}$$

$$= \frac{\frac{\gamma^2}{(\gamma+1)^2}2q(\gamma^2 - 1)}{\gamma \frac{2q}{v_o}(\gamma - 1)v_o \frac{\gamma}{\gamma+1}}, \tag{10.337}$$

$$= \frac{\frac{\gamma^2}{(\gamma+1)^2}(\gamma^2 - 1)}{\gamma(\gamma - 1)\frac{\gamma}{\gamma+1}}, \tag{10.338}$$

$$= \frac{\frac{\gamma^2}{(\gamma+1)^2}(\gamma + 1)(\gamma - 1)}{\gamma(\gamma - 1)\frac{\gamma}{\gamma+1}}, \tag{10.339}$$

$$= 1. \tag{10.340}$$

In the strong shock limit, the local Mach number in the wave frame is sonic at the end of the reaction zone. This can be shown to hold away from the strong shock limit as well.

10.2.5.2 Weak and strong solutions

For $D < D_{CJ}$ there are no real solutions on the detonation branch. For $D > D_{CJ}$, there are two real solutions. These are known as the *weak* and *strong* solution. These solutions are represent the intersection of the Rayleigh line with the complete reaction Hugoniot at two points. The higher pressure solution is known as the strong solution. The lower pressure
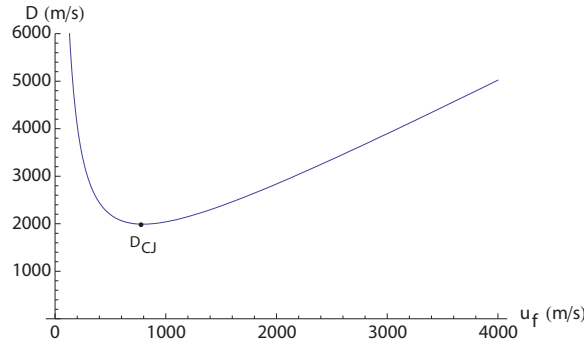
Figure 10.3:   Plot of detonation wave speed D versus piston velocity u_f; parameters from Table 10.1 loosely model H_2-air detonation.

solution is known as the weak solution. Equilibrium end state analysis cannot determine which of the solutions, strong or weak, is preferred if $D > D_{CJ}$.

We can understand much about detonations, weak, strong, and CJ, by considering how they behave as the final velocity in the laboratory frame is changed. We can think of the final velocity in the laboratory frame as that of a piston which is pushing the detonation. While we could analyze this on the basis of the theory we have already developed, the algebra is complicated. Let us instead return to a more primitive form. Consider the Rankine-Hugoniot jump equations, Eqs. (10.249-10.251) with caloric state equation, Eq. (10.277) with the final state, denoted by the subscript f, being $\lambda = 1$ and the initial state being $\lambda = 0$, Eq. (10.249) being used to simplify Eq. (10.251), and the laboratory frame velocity u used in place of $\hat{u}$:

$$\rho_f(u_f - D) = -\rho_o D, \tag{10.341}$$

$$P_f + \rho_f(u_f - D)^2 = P_o + \rho_o D^2, \tag{10.342}$$

$$\underbrace{\frac{1}{\gamma - 1}\frac{P_f}{\rho_f} - q}_{e_f} + \frac{1}{2}(u_f - D)^2 + \frac{P_f}{\rho_f} = \underbrace{\frac{1}{\gamma - 1}\frac{P_o}{\rho_o}}_{=e_o} + \frac{1}{2}D^2 + \frac{P_o}{\rho_o}. \tag{10.343}$$

Let us consider the unknowns to be P_f, ρ_f, and D. Computer algebra solution of these three equations yields two sets of solutions. The relevant physical branch has a solution for D of

$$D = u_f \left(\frac{\gamma + 1}{4} + \frac{\gamma - 1}{2}\frac{q}{u_f^2} + \sqrt{\gamma\frac{P_o}{\rho_o u_f^2} + \left(\frac{\gamma + 1}{4} + \frac{\gamma - 1}{2}\frac{q}{u_f^2}\right)^2} \right). \tag{10.344}$$

We give a plot of D as a function of the supporting piston velocity u_f in Figure 10.3. We notice on Fig. 10.3 that there is a clear minimum D. This value of D is the CJ value of $D_{CJ} = 1991.1\ m/s$. It corresponds to a piston velocity of $u_f = 794.9\ m/s$.

A piston driving at $u_f = 794.9\ m/s$ will just drive the wave at the CJ speed. At this piston speed, all of the energy to drive the wave is supplied by the combustion process itself.

As u_f increases beyond 794.9 m/s, the wave speed D increases. For such piston velocities, the piston itself is supplying energy to drive the wave. For $u_f < 794.9$ m/s, our formula predicts an increase in D, but that is not what is observed in experiment. Instead, a wave propagating at D_{CJ} is observed.

We last note that in the inert, $q = 0$, small piston velocity, $u_f \to 0$, limit that Eq. (10.344) reduces to $D = \sqrt{\gamma P_o/\rho_o}$. That is, the wave speed is the ambient sound speed.

10.2.5.3 Summary of solution properties

Here is a summary of the properties of solutions for various values of D that can be obtained by equilibrium end state analysis:

- $D < D_{CJ}$: No Rayleigh line intersects a complete reaction Hugoniot on the detonation branch. There is no real equilibrium detonation solution.

- $D = D_{CJ}$: There is a two repeated solutions at a single point, which we will call C, the Chapman-Jouguet point. At C, the Rayleigh line is tangent to the complete reaction Hugoniot. Some properties of this solution are

  - $\hat{u}_{CJ}/c_{CJ} = 1$; the flow is sonic in the wave frame at complete reaction.
  - This is the unique speed of propagation of a wave without piston support if the reaction is one-step irreversible.
  - At this wave speed, $D = D_{CJ}$, all the energy from the reaction is *just sufficient* to drive the wave forward.
  - Because the end of the reaction zone is sonic, downstream acoustic disturbances cannot overtake the reaction zone.

- $D > D_{CJ}$; Two solutions are admitted at the equilibrium end state, the strong solution at point S, and the weak solution at point W.

  - The strong solution S has
    * $\hat{u}/c < 1$, subsonic.
    * piston support is required to drive the wave forward
    * some energy to drive the wave comes from the reaction, some comes from the piston.
    * if the piston support is withdrawn, acoustic disturbances will overtake and weaken the wave.
  - The weak solution W has
    * $\hat{u}/c > 1$, supersonic.
    * often thought to be non-physical, at least for one-step irreversible kinetics because of no initiation mechanism.
    * exceptions exist.

10.2.6   ZND solutions: One-step irreversible kinetics

We next consider the structure of the reaction zone. Structure was first considered contemporaneously and independently by Zel'dovich, von Neumann[15] and Döring[16] Equation (10.307) gives $v(\lambda)$ for either the strong or weak branches of the solution. Knowing $v(\lambda)$ and thus $\rho(\lambda)$, since $v = 1/\rho$, we can use the integrated mass equation, Eq. (10.249) to write an explicit equation for $\hat{u}(\lambda)$. Our Rankine-Hugoniot analysis also give $T(\lambda)$. These can be employed in the reaction kinetics equation, Eq. (10.252, 10.13) to form a single ordinary differential equation for the evolution of λ of the form

$$\frac{d\lambda}{d\hat{x}} = \frac{a(T(\lambda))^\beta \exp\left(-\frac{\mathcal{E}}{RT(\lambda)}\right)(1-\lambda)}{\hat{u}(\lambda)}, \qquad \lambda(0) = 0. \tag{10.345}$$

We consider the initial unshocked state to be labeled O. We label the point after the shock N for the Neumann point, named after von Neumann, one of the pioneers of detonation theory. Recall $\lambda = 0$ both at O and at N. But the state variables, e.g. P, ρ, $\hat{u}$, change from O to N.

Before we actually solve the differential equations, we can learn much by considering how P varies with λ in the reaction zone by using Rankine-Hugoniot analysis. Consider the Rankine-Hugoniot equations, Eqs. (10.249-10.251) with caloric state equation, Eq. (10.277), Eq. (10.249) being used to simplify Eq. (10.251):

$$\rho\hat{u} = -\rho_o D, \tag{10.346}$$

$$P + \rho\hat{u}^2 = P_o + \rho_o D^2, \tag{10.347}$$

$$\underbrace{\frac{1}{\gamma - 1}\frac{P}{\rho}}_{e} - \lambda q + \frac{1}{2}\hat{u}^2 + \frac{P}{\rho} = \underbrace{\frac{1}{\gamma - 1}\frac{P_o}{\rho_o}}_{=e_o} + \frac{1}{2}D^2 + \frac{P_o}{\rho_o}. \tag{10.348}$$

Computer algebra reveals the solution for $P(\lambda)$ to be

$$P(\lambda) = \frac{1}{\gamma + 1}\left(P_o + \rho_o D^2\left(1 \pm \sqrt{\left(1 - \frac{\gamma P_o}{\rho_o D^2}\right)^2 - \frac{2(\gamma^2 - 1)\lambda q}{D^2}}\right)\right). \tag{10.349}$$

In Fig. (10.4), we plot P versus λ for three different values of D: $D = 2800\ m/s > D_{CJ}$, $D = 1991.1\ m/s = D_{CJ}$, $D = 1800\ m/s < D_{CJ}$.

We can also, via detailed algebraic analysis get an algebraic expression for $\hat{\mathsf{M}}$ as a function of λ. We omit that here, but do get a plot for our system. In Fig. (10.5), we plot $\hat{\mathsf{M}}$ versus λ for three different values of D: $D = 2800\ m/s > D_{CJ}$, $D = 1991.1\ m/s = D_{CJ}$, $D = 1800\ m/s < D_{CJ}$. The plot of $\hat{\mathsf{M}}$ versus λ is log-log so that the sonic condition may be clearly exhibited.

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[15]John von Neumann, 1903-1957, Hungarian-American genius.
[16] Werner Döring, 1911-2006, German physicist.
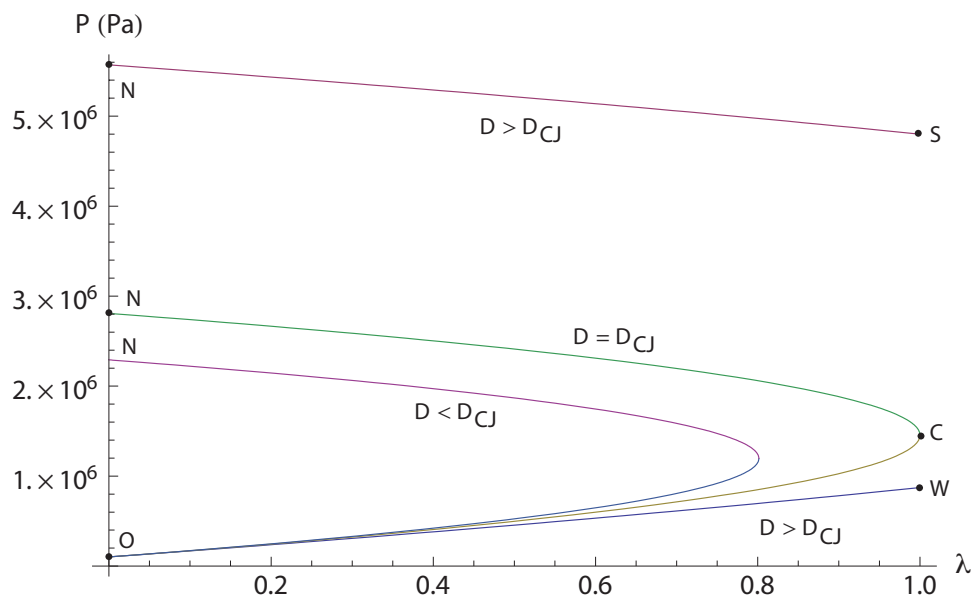
Figure 10.4: P versus λ from Rankine-Hugoniot analysis for one-step irreversible reaction for $D = 2800 \ m/s > D_{CJ}$, $D = 1991.1 \ m/s = D_{CJ}$, $D = 1800 \ m/s < D_{CJ}$ for H_2/air-based parameters of Table 10.1.
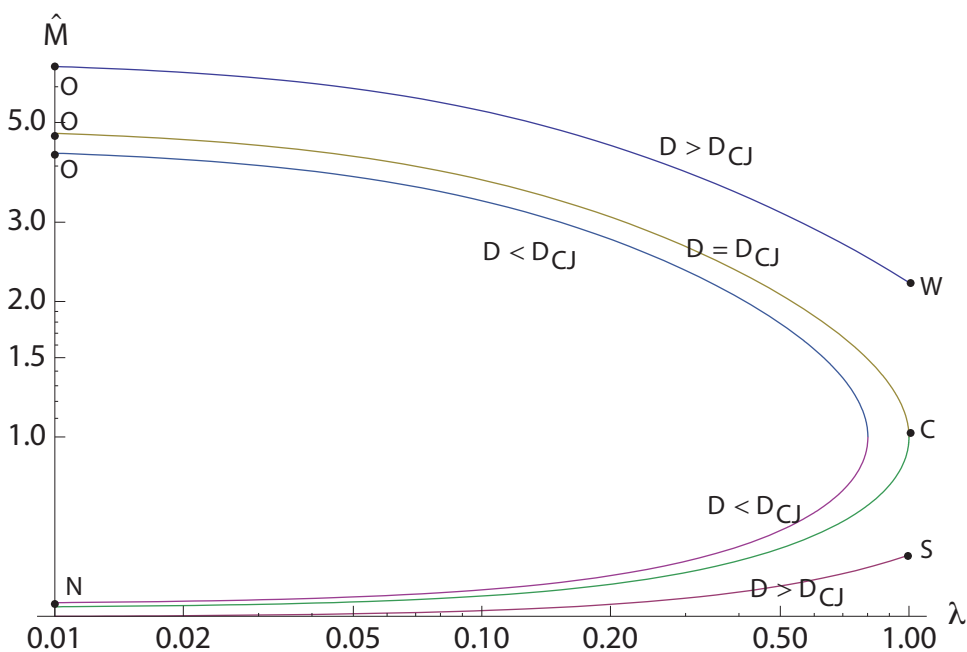
Figure 10.5: $\hat{M}$ versus λ from Rankine-Hugoniot analysis for one-step irreversible reaction for $D = 2800 \ m/s > D_{CJ}$, $D = 1991.1 \ m/s = D_{CJ}$, $D = 1800 \ m/s < D_{CJ}$ for H_2/air-based parameters of Table 10.1.

For $D = 2800 \ m/s > D_{CJ}$, there are two branches, the strong and the weak. The strong branch commences at N where $\lambda = 0$ and proceeds to decrease to $\lambda = 1$ where the equilibrium point S is encountered at a subsonic state. There other branch commences at O and pressure increases until the supersonic W is reached at $\lambda = 1$.

For $D = 1991.1 \ m/s = D_{CJ}$, the behavior is similar, except that the branches commencing at N and O both reach complete reaction at the same point C. The point C can be shown to be sonic with $\hat{\mathsf{M}} = 1$. We recall from our earlier discussion regarding Eqs. (10.245-10.248) that sonic points are admitted only if $\sigma \mathsf{r} = 0$. For one-step irreversible reaction, $\mathsf{r} = 0$ when $\lambda = 1$, so a sonic condition is admissible.

For $D = 1800 \ m/s < D_{CJ}$, the strong and weak branches merge at a point of incomplete reaction. At the point of merger, near $\lambda = 0.8$, the flow is locally sonic; however, this is not a point of complete reaction, so there can be no real-valued detonation structure for this value of D.

Finally, we write an alternate differential-algebraic equations which can be integrated for the detonation structure:

$$\rho \hat{u} = -\rho_o D, \tag{10.350}$$

$$P + \rho \hat{u}^2 = P_o + \rho_o D^2, \tag{10.351}$$

$$e + \frac{1}{2}\hat{u}^2 + \frac{P}{\rho} = e_o + \frac{1}{2}D^2 + \frac{P_o}{\rho_o}, \tag{10.352}$$

$$e = \frac{1}{\gamma - 1}\frac{P}{\rho} - \lambda q, \tag{10.353}$$

$$P = \rho R T, \tag{10.354}$$

$$\frac{d\lambda}{d\hat{x}} = \frac{1 - \lambda}{\hat{u}} a \exp\left(-\frac{\mathcal{E}}{RT}\right). \tag{10.355}$$

We need the condition $\lambda(0) = 0$. These form six equations for the six unknowns ρ, $\hat{u}$, P, e, T, and λ.

10.2.6.1   CJ ZND structures

We now fix $D = D_{CJ} = 1991.1 \ m/s$ and integrate Eq. (10.345) from the shocked state N to a complete reaction point, C, the Chapman-Jouguet detonation state. We could also integrate from O to C, but this is not observed in nature. After obtaining $\lambda(\hat{x})$, we can use our Rankine-Hugoniot analysis results to plot all state variables as functions of $\hat{x}$.

In Fig. (10.6), we plot the density and pressure versus $\hat{x}$. The density first jumps discontinuously from O to its shocked value at N. From there it slowly drops through the reaction zone until it relaxes near $\hat{x} \sim -0.01 \ m$ to its equilibrium value at complete reaction. Thus, the reaction zone has a thickness of roughly $1 \ cm$. Similar behavior is seen for the pressure.

The wave frame-based fluid particle velocity is shown in Fig. 10.7. Since the unshocked fluid is at rest in the laboratory frame with $u = 0 \ m/s$, the fluid in the wave frame has velocity $\hat{u} = 0 - 1991.1 \ m/s = -1991.1 \ m/s$. It is shocked to a lower velocity and then relaxes to its equilibrium value.
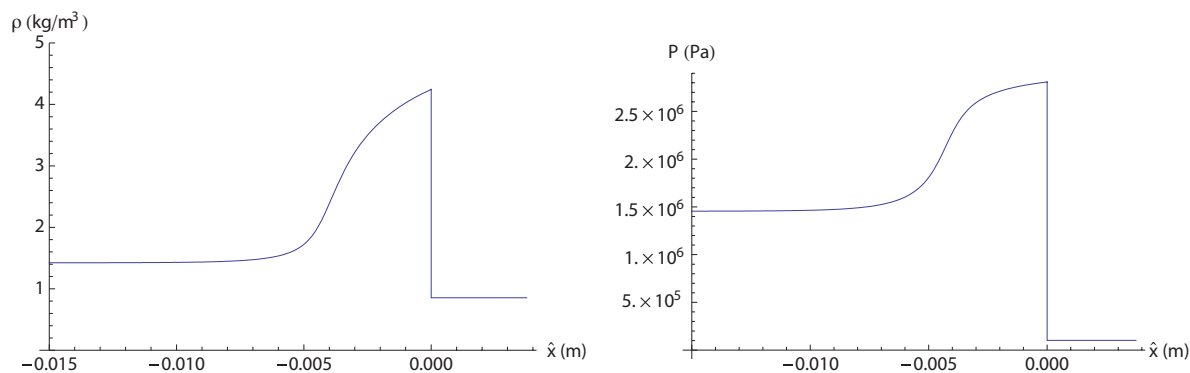
Figure 10.6: ZND structure of $\rho(\hat{x})$ and $P(\hat{x})$ for $D = D_{CJ} = 1991.1$ m/s for one-step irreversible reaction for H_2/air-based parameters of Table 10.1.
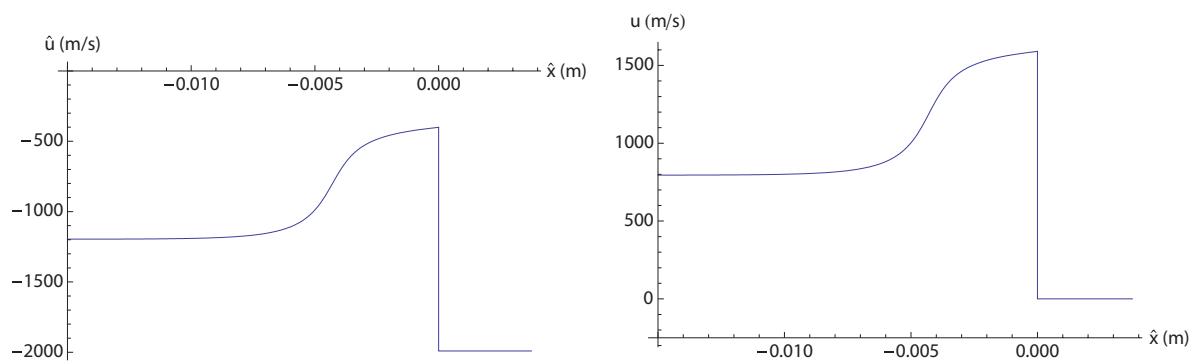
Figure 10.7: ZND structure of wave frame-based fluid particle velocity $\hat{u}(\hat{x})$ and laboratory frame-based particle velocity $u(\hat{x})$ for $D = D_{CJ} = 1991.1$ m/s for one-step irreversible reaction for H_2/air-based parameters of Table 10.1.
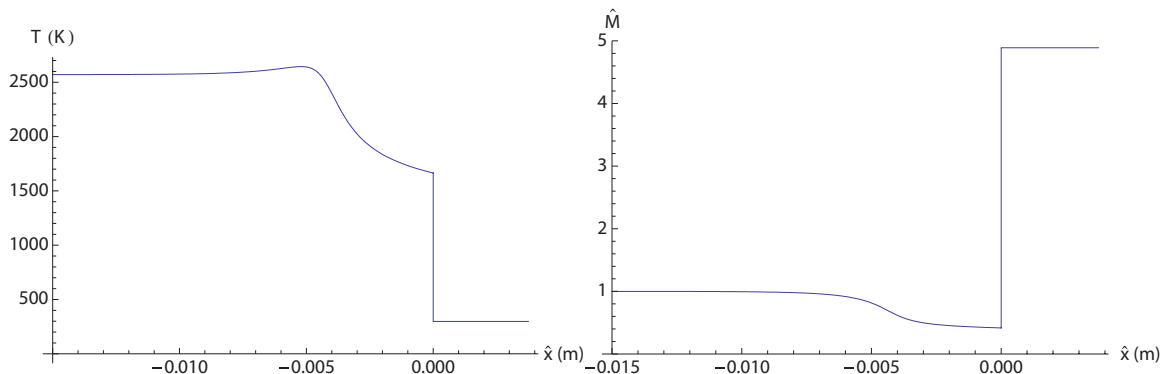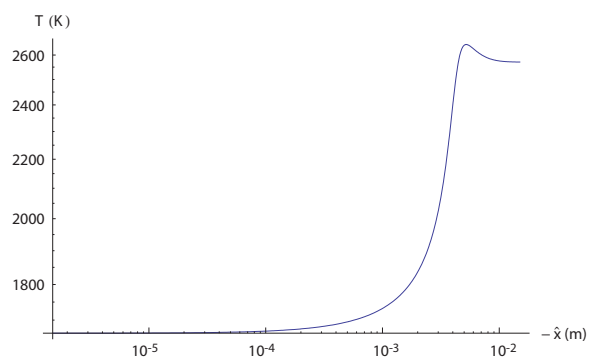
Figure 10.8:   ZND structure of $T(\hat{x})$ and wave frame-based Mach number $\hat{\mathsf{M}}$ for $D = D_{CJ} = 1991.1\ m/s$ for one-step irreversible reaction for H_2/air-based parameters of Table 10.1.

The structure of the velocity profiles is easier to understand in the laboratory frame, as also shown in Fig. 10.7. Here, we see the unshocked fluid velocity of $u = 0\ m/s$. The fluid is shocked to a high velocity, which then decreases to a value at the end of the reaction zone. The final velocity can be associated with that of a supporting piston, $u_f = 794.9\ m/s$.

The temperature and wave frame-based Mach number are plotted in Fig. 10.8. It is shocked from 298 K to a high value, then continues to mainly increase through the reaction zone. Near the end of the reaction zone, there is a final decrease as it reaches its equilibrium value. The Mach number calculated in the wave frame, $\hat{\mathsf{M}}$, goes from an initial value of $\hat{\mathsf{M}} = 4.88887$, which we call the CJ detonation Mach number, $\mathsf{M}_{CJ} = 4.88887$, to a post-shock value of $\mathsf{M} = 0.41687$. Note this result confirms a standard result from compressible flow that a standing normal shock must bring a flow from a supersonic state to a subsonic state. At equilibrium it relaxes to $\mathsf{M} = 1$. This relaxation to a sonic state when $\lambda = 1$ is what defines the CJ state. We recall that this result is similar to that obtained in so-called "Rayleigh flow" of one-dimensional gas dynamics. Rayleigh flow admits heat transfer to a one-dimensional channel, and it is well known that the addition of heat always induces the flow to move to a sonic (or "choked") state. So, we can think of the CJ detonation wave as a thermally choked flow.

The reaction progress variable λ is plotted in Fig. 10.9. Note that it undergoes no shock jump and simply relaxes to its equilibrium value of $\lambda = 1$ near $\hat{x} = 0.01\ m$. Lastly, we plot $T(-\hat{x})$ on a log-log scale in Fig. (10.10). The sign of $\hat{x}$ is reversed so as to avoid the plotting of the logarithms of negative numbers. We notice on this scale that the temperature is roughly that of the shock until $-\hat{x} = 0.001\ m$, at which point a steep rise begins. We call this length the induction length, ℓ_{ind}. When we compare this figure to Fig. 2 of Powers and Paolucci, 2005, we see a somewhat similar behavior. However the detailed kinetics model shows $\ell_{ind} \sim 0.0001\ m$. The overall reaction zone length ℓ_{rxn} is predicted well by the simple model. Its value of $\ell_{rxn} \sim 0.01\ m$ is also predicted by the detailed model. Some of the final values at the end state are different as well. This could be due to a variety of factors,
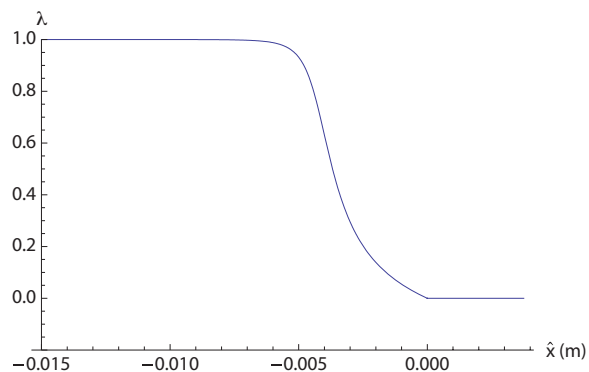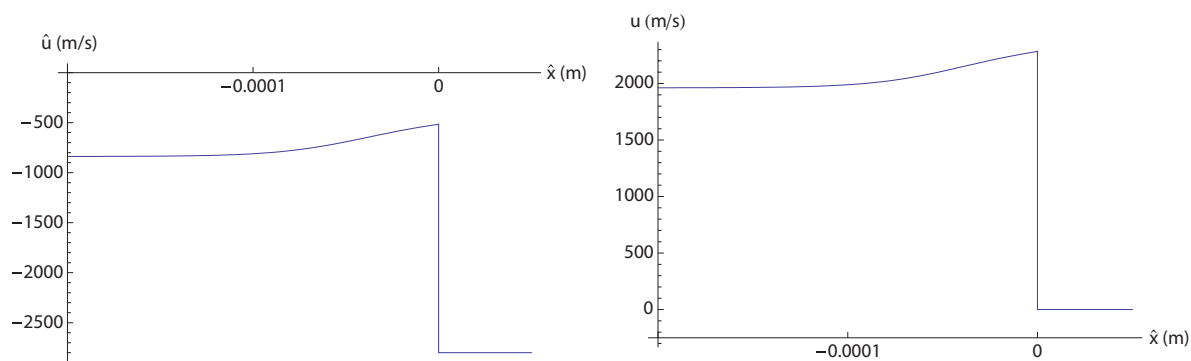
Figure 10.9: ZND structure of $\lambda(\hat{x})$ for $D = D_{CJ} = 1991.1\ m/s$ for one-step irreversible reaction for H_2/air-based parameters of Table 10.1.

Figure 10.10: ZND structure on a log-log scale of $T(\hat{x})$ for $D = D_{CJ} = 1991.1\ m/s$ for one-step irreversible reaction for H_2/air-based parameters of Table 10.1.

parameter	simple	detailed
ℓ_{rxn}	$10^{-2}\ m$	$10^{-2}\ m$
ℓ_{ind}	$10^{-3}\ m$	$10^{-4}\ m$
D_{CJ}	$1991.1\ m/s$	$1979.7\ m/s$
P_s	$2.80849 \times 10^6\ Pa$	$2.8323 \times 10^6\ Pa$
P_{CJ}	$1.4553 \times 10^6\ Pa$	$1.6483 \times 10^6\ Pa$
T_s	$1664.4\ K$	$1542.7\ K$
T_{CJ}	$2570.86\ K$	$2982.1\ K$
ρ_s	$4.244\ kg/m^3$	$4.618\ kg/m^3$
ρ_{CJ}	$1.424\ kg/m^3$	$1.5882\ kg/m^3$
$\hat{\mathsf{M}}_o$	4.88887	4.8594
$\hat{\mathsf{M}}_s$	0.41687	0.40779
$\hat{\mathsf{M}}_{CJ}$	1	0.93823

Table 10.2: Numerical values of parameters which roughly model CJ H_2-air detonation.

especially differences in the state equations. Comparisons between values predicted by the detailed model of Powers and Paolucci, 2005, against those of the simple model here are given in Table 10.2.

10.2.6.2   Strong ZND structures

We increase the detonation velocity D to $D > D_{CJ}$ and obtain strong detonation structures. These have a path from O to N to the equilibrium point S. These detonations require piston support to propagate, as the energy supplied by heat release alone is insufficient to maintain their steady speed.

Similar to our plots of the CJ structures, we give plots of the strong, $D = 2800\ m/s$ structures of $\rho(\hat{x})$, $P(\hat{x})$, $\hat{u}(\hat{x})$, $u(\hat{x})$, $T(\hat{x})$, $\hat{\mathsf{M}}(\hat{x})$, $\lambda(\hat{x})$ in Figs. 10.11-10.14, respectively. The behavior of the plots is qualitatively similar to that for CJ detonations. We see however that the reaction zone has become significantly thinner, $\ell_{rxn} \sim 0.0001\ m$. This is because the higher temperatures associated with the stronger shock induce faster reactions, thus thinning the reaction zone. Comparison with Fig. 10.2 reveals that the shocked and final values of pressure agree with those of the Rankine-Hugoniot jump analysis. We also note the final value of $\hat{\mathsf{M}}$ is subsonic. This allows information to propagate from the supporting piston all the way to the shock front.
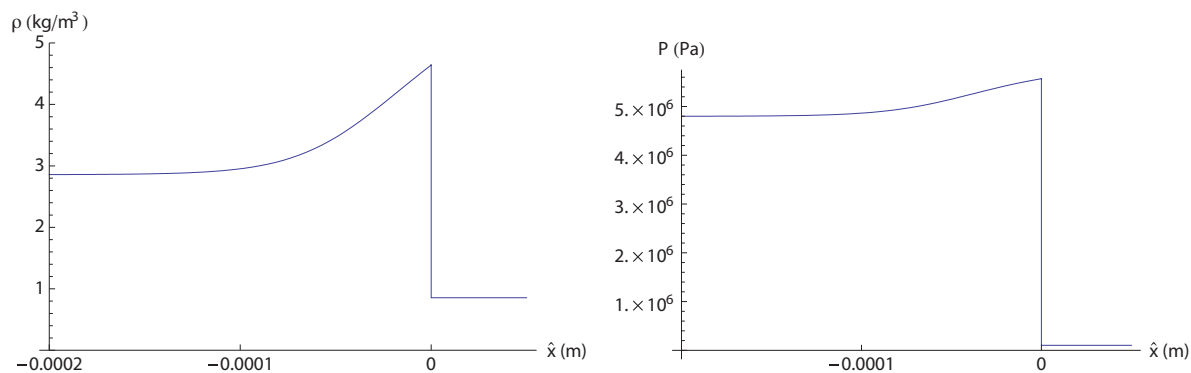
Figure 10.11: ZND structure of $\rho(\hat{x})$ and $P(\hat{x})$ for strong $D = 2800 \; m/s > D_{CJ}$ for one-step irreversible reaction for H_2/air-based parameters of Table 10.1.


Figure 10.12: ZND structure of wave frame-based fluid particle velocity $\hat{u}(\hat{x})$ and laboratory frame-based fluid particle velocity $u(\hat{x})$ for strong $D = 2800 \; m/s > D_{CJ}$ for one-step irreversible reaction for H_2/air-based parameters of Table 10.1.
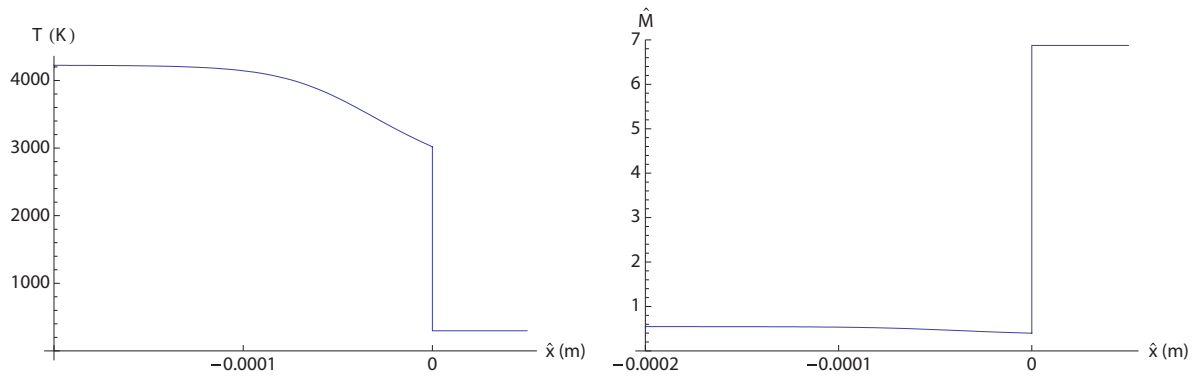
Figure 10.13:   ZND structure of $T(\hat{x})$ and $\hat{M}(\hat{x})$ for strong $D = 2800 \, m/s > D_{CJ}$ for one-step irreversible reaction for H_2/air-based parameters of Table 10.1.
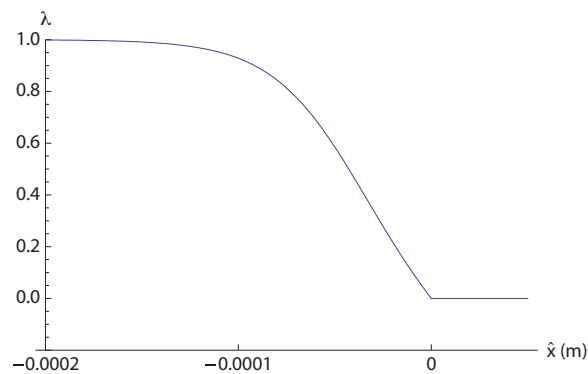
Figure 10.14:   ZND structure of $\lambda(\hat{x})$ for strong $D = 2800 \, m/s > D_{CJ}$ for one-step irreversible reaction for H_2/air-based parameters of Table 10.1.
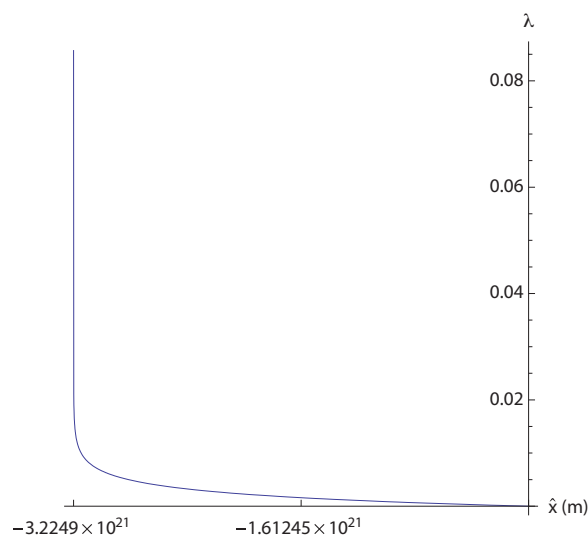
Figure 10.15:   ZND structure of $\lambda(\hat{x})$ for unshocked, weak $D = 2800 \ m/s > D_{CJ}$ for one-step irreversible reaction for H_2/air-based parameters of Table 10.1. The galactic distance scales are far too large to be realistic representations of reality!

10.2.6.3   Weak ZND structures

For the simple one-step irreversible kinetics model, there is no path from O through the shocked state N to the weak solution W. There is a direct path from O to W; however, it is physically unrealistic. For $D = 2800 \ m/s$, we plot λ versus $\hat{x}$ in Fig. 10.15. Numerical solution was available only until $\lambda \sim 0.02$. Numerical precision issues arose at this point. Note, importantly, that $\ell_{rxn} \sim 10^{21} \ m$ is unrealistically large! Note the distance from Earth to the Large Magellanic Cloud, a dwarf galaxy orbiting the Milky Way, is $10^{21} \ m$. Our combustion model is not well calibrated to those distances, so it is entirely unreliable to predict this class of weak detonation!

10.2.6.4   Piston problem

We can understand the physics of the one-step kinetics problem better in the context of a piston problem, where the supporting piston connects to the final laboratory frame fluid velocity $u_p = u(\hat{x} \to -\infty)$. Let us consider pistons with high velocity and then lower them and examine the changes of structure.

- $u_p > u_{p,CJ}$. This high velocity piston will drive a strong shock into the fluid at a speed $D > D_{CJ}$. The solution will proceed from O to N to S and be subsonic throughout. Therefore changes at the piston face will be able to be communicated all the way to the shock front. The energy to drive the wave comes from a combination of energy released during combustion and energy supplied by the piston support.

- $u_p = u_{p,CJ}$ At a critical value of piston velocity, $u_{p,CJ}$, the solution will go from O to

N to C, and where it is locally sonic.

- $u_p < u_{p,CJ}$ For such flows, the detonation wave is self-supporting. There is no means to communicate with the supporting piston. The detonation wave proceeds at $D = D_{CJ}$. *We note that D_{CJ} is not a function of the specific kinetic mechanism. So, for a one-step irreversible kinetics model*, the conclusion the D_{CJ} is the unique speed of propagation of an unsupported wave is verified. It should be noted that nearly any complication added to the model, *e.g.* reversibility, multi-step kinetics, multi-dimensionality, diffusion, etc., will alter this conclusion.

10.2.7   Detonation structure: Two-step irreversible kinetics

Let us consider a small change to the one-step model of the previous sections. We will now consider a two-step irreversible kinetics model. The first reaction will be exothermic and the second endothermic. Both reactions will be driven to completion, and when they are complete, the global heat release will be identical to that of the one-step reaction. All other parameters will remain the same from the one-step model. This model is discussed in detail by Fickett and Davis, and in a two-dimensional extension by Powers and Gonthier.[17]

We will see that this simple modification has profound effects on what is a preferred detonation structure. In particular, we will see that *for such a two-step model*

- the CJ structure is no longer the preferred state of an unsupported detonation wave,

- the steady speed of the unsupported detonation wave is unique and greater than the CJ speed,

- there is a path from the unshocked state O to the shocked state N through a sonic incomplete reaction pathological point P to the weak equilibrium end state W,

- there is a strong analog to steady compressible one-dimensional inert flow with area change, *i.e.* rocket nozzle flow.

Let us pose the two step irreversible kinetics model of

$$1: \quad A \quad \rightarrow \quad B, \tag{10.356}$$
$$2: \quad B \quad \rightarrow \quad C. \tag{10.357}$$

Let us insist that A, B, and C each have the same molecular mass, $M_A = M_B = M_C = M$, and the same constant specific heats, $c_{PA} = c_{PB} = c_{PC} = c_P$. Let us also insist that both reactions have the same kinetic parameters, $\mathcal{E}_1 = \mathcal{E}_2 = \mathcal{E}$, $a_1 = a_2 = a$, $\beta_1 = \beta_2 = 0$. Therefore the reaction rates are such that

$$k_1 = k_2 = k. \tag{10.358}$$

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[17]Powers, J. M., and Gonthier, K. A., 1992, "Reaction Zone Structure for Strong, Weak Overdriven, and Weak Underdriven Oblique Detonations," *Physics of Fluids A*, 4(9): 2082-2089.

Let us assume at the initial state that we have all A and no B or C: $\overline{\rho}_A(0) = \hat{\overline{\rho}}_A$, $\overline{\rho}_B(0) = 0$, $\overline{\rho}_C(0) = 0$. Since $J = 2$, we have a reaction vector r_j of length 2:

$$r_j = \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{10.359}$$

Our stoichiometric matrix ν_{ij} has dimension 3×2 since $N = 3$ and $J = 2$:

$$\nu_{ij} = \begin{pmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{pmatrix}. \tag{10.360}$$

For species production rates, from $\dot{\omega}_i = \sum_{j=1}^{J} \nu_{ij} r_j$ we have

$$\frac{d}{dt} \begin{pmatrix} \overline{\rho}_A/\rho \\ \overline{\rho}_B/\rho \\ \overline{\rho}_C/\rho \end{pmatrix} = \frac{1}{\rho} \begin{pmatrix} \dot{\omega}_A \\ \dot{\omega}_B \\ \dot{\omega}_C \end{pmatrix} = \frac{1}{\rho} \begin{pmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix} = \frac{1}{\rho} \begin{pmatrix} -r_1 \\ r_1 - r_2 \\ r_2 \end{pmatrix}. \tag{10.361}$$

We recall here that d/dt denotes the material derivative following a fluid particle, $d/dt = \partial/\partial t + \hat{u}\partial/\partial\hat{x}$. For our steady waves, we will have $d/dt = \hat{u}d/d\hat{x}$. We next recall that $\overline{\rho}_i/\rho = Y_i/M_i$, which for us is Y_i/M, since the molecular masses are constant. So, we have

$$\frac{d}{dt} \begin{pmatrix} Y_A \\ Y_B \\ Y_C \end{pmatrix} = \frac{M}{\rho} \begin{pmatrix} \dot{\omega}_A \\ \dot{\omega}_B \\ \dot{\omega}_C \end{pmatrix} = \frac{M}{\rho} \begin{pmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix} = \frac{M}{\rho} \begin{pmatrix} -r_1 \\ r_1 - r_2 \\ r_2 \end{pmatrix}. \tag{10.362}$$

Elementary row operations gives us the row echelon form

$$\frac{d}{dt} \begin{pmatrix} Y_A \\ Y_A + Y_B \\ Y_A + Y_B + Y_C \end{pmatrix} = \frac{M}{\rho} \begin{pmatrix} -1 & 0 \\ 0 & -1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{10.363}$$

We can integrate the homogeneous third equation and apply the initial condition to get

$$Y_A + Y_B + Y_C = 1. \tag{10.364}$$

This can be thought of as an unusual matrix equation:

$$(1 \quad 1 \quad 1) \begin{pmatrix} Y_A \\ Y_B \\ Y_C \end{pmatrix} = (1). \tag{10.365}$$

We can perform an analogous exercise to finding the form $\overline{\boldsymbol{\rho}} = \hat{\overline{\boldsymbol{\rho}}} + \mathbf{D} \cdot \overline{\boldsymbol{\xi}}$ and get

$$\begin{pmatrix} Y_A \\ Y_B \\ Y_C \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \underbrace{\begin{pmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{pmatrix}}_{=\mathbf{F}} \begin{pmatrix} \lambda_1 \\ \lambda_2 \end{pmatrix}. \tag{10.366}$$

The column vectors of $\mathbf{F}$ are linearly independent and lie in the right null space of the coefficient matrix $(1, 1, 1)$. The choices for $\mathbf{F}$ are not unique, but are convenient. We can think of the independent variables λ_1, λ_2 as reaction progress variables. Thus, for reaction 1, we have λ_1, and for reaction 2, we have λ_2. Both $\lambda_1(0) = 0$ and $\lambda_2(0) = 0$. The mass fraction of each species can be related to the reaction progress via

$$
\begin{align}
Y_A &= 1 - \lambda_1, \tag{10.367}\\
Y_B &= \lambda_1 - \lambda_2, \tag{10.368}\\
Y_C &= \lambda_2. \tag{10.369}
\end{align}
$$

When the reaction is complete, we have $\lambda_1 \to 1$, $\lambda_2 \to 1$, and $Y_A \to 0$, $Y_B \to 0$, $Y_C \to 1$. Now, our reaction law is

$$
\frac{d}{dt}\begin{pmatrix} Y_A \\ Y_B \\ Y_C \end{pmatrix} = \frac{M}{\rho}\begin{pmatrix} -r_1 \\ r_1 - r_2 \\ r_2 \end{pmatrix} = \frac{M}{\rho}\begin{pmatrix} -k\overline{\rho}_A \\ k\overline{\rho}_A - k\overline{\rho}_B \\ k\overline{\rho}_B \end{pmatrix} = k\begin{pmatrix} -Y_A \\ Y_A - Y_B \\ Y_B \end{pmatrix}. \tag{10.370}
$$

Eliminating Y_A, Y_B and Y_C in favor of λ_1 and λ_2, we get

$$
\frac{d}{dt}\begin{pmatrix} 1 - \lambda_1 \\ \lambda_1 - \lambda_2 \\ \lambda_2 \end{pmatrix} = k\begin{pmatrix} -(1 - \lambda_1) \\ (1 - \lambda_1) - (\lambda_1 - \lambda_2) \\ \lambda_1 - \lambda_2 \end{pmatrix}. \tag{10.371}
$$

This reduces to

$$
\frac{d}{dt}\begin{pmatrix} \lambda_1 \\ \lambda_1 - \lambda_2 \\ \lambda_2 \end{pmatrix} = k\begin{pmatrix} 1 - \lambda_1 \\ 1 - 2\lambda_1 + \lambda_2 \\ \lambda_1 - \lambda_2 \end{pmatrix}. \tag{10.372}
$$

The second of these equations is the difference of the first and the third, so it is redundant and we need only consider

$$
\frac{d}{dt}\begin{pmatrix} \lambda_1 \\ \lambda_2 \end{pmatrix} = k\begin{pmatrix} 1 - \lambda_1 \\ \lambda_1 - \lambda_2 \end{pmatrix}. \tag{10.373}
$$

In the steady wave frame, this is written as

$$
\begin{align}
\hat{u}\frac{d\lambda_1}{d\hat{x}} &= (1 - \lambda_1)k, \tag{10.374}\\
\hat{u}\frac{d\lambda_2}{d\hat{x}} &= (\lambda_1 - \lambda_2)k. \tag{10.375}
\end{align}
$$

Because the rates $k_1 = k_2 = k$ have been taken to be identical, we can actually get $\lambda_2(\lambda_1)$. Dividing our two kinetic equations gives

$$
\frac{d\lambda_2}{d\lambda_1} = \frac{\lambda_1 - \lambda_2}{1 - \lambda_1}. \tag{10.376}
$$

Because $\lambda_1(0) = 0$ and $\lambda_2(0) = 0$, we can say that $\lambda_2(\lambda_1 = 0) = 0$. We rearrange this differential equation to get

$$\frac{d\lambda_2}{d\lambda_1} + \frac{1}{1 - \lambda_1}\lambda_2 = \frac{\lambda_1}{1 - \lambda_1}. \tag{10.377}$$

This equation is first order and linear. It has an integrating factor of

$$\exp\left(\int \frac{d\lambda_1}{1 - \lambda_1}\right) = \exp\left(-\ln(1 - \lambda_1)\right) = \frac{1}{1 - \lambda_1}.$$

Multiplying both sides by the integrating factor, we get

$$\frac{1}{1 - \lambda_1}\frac{d\lambda_2}{d\lambda_1} + \left(\frac{1}{1 - \lambda_1}\right)^2 \lambda_2 = \frac{\lambda_1}{(1 - \lambda_1)^2}. \tag{10.378}$$

Using the product rule, we then get

$$\frac{d}{d\lambda_1}\left(\frac{\lambda_2}{1 - \lambda_1}\right) = \frac{\lambda_1}{(1 - \lambda_1)^2}, \tag{10.379}$$

$$\frac{\lambda_2}{1 - \lambda_1} = \int \frac{\lambda_1}{(1 - \lambda_1)^2}d\lambda_1. \tag{10.380}$$

Taking $u = \lambda_1$ and $dv = d\lambda_1/(1 - \lambda_1)^2$ and integrating the right side by parts, we get

$$\frac{\lambda_2}{1 - \lambda_1} = \frac{\lambda_1}{1 - \lambda_1} - \int \frac{d\lambda_1}{1 - \lambda_1}, \tag{10.381}$$

$$= \frac{\lambda_1}{1 - \lambda_1} + \ln(1 - \lambda_1) + C, \tag{10.382}$$

$$\lambda_2 = \lambda_1 + (1 - \lambda_1)\ln(1 - \lambda_1) + C(1 - \lambda_1). \tag{10.383}$$

Now, since $\lambda_2(\lambda_1 = 0) = 0$, we get $C = 0$, so

$$\lambda_2(\hat{x}) = \lambda_1(\hat{x}) + (1 - \lambda_1(\hat{x}))\ln(1 - \lambda_1(\hat{x})). \tag{10.384}$$

Leaving out details of the derivation, our state equation becomes

$$e(T, \lambda_1, \lambda_2) = c_v(T - T_o) - \lambda_1 q_1 - \lambda_2 q_2. \tag{10.385}$$

We find it convenient to define $Q(\lambda_1, \lambda_2)$ as

$$Q(\lambda_1, \lambda_2) \equiv \lambda_1 q_1 + \lambda_2 q_2. \tag{10.386}$$

So, the equation of state can be written as

$$e(T, \lambda_1, \lambda_2) = c_v(T - T_o) - Q(\lambda_1, \lambda_2). \tag{10.387}$$

Parameter	Value	Units
γ	1.4	
M	20.91	$kg/kmole$
R	397.58	$J/kg/K$
P_o	1.01325×10^5	Pa
T_o	298	K
ρ_o	0.85521	kg/m^3
v_o	1.1693	m^3/kg
q_1	7.58265×10^6	J/kg
q_2	-5.68698×10^6	J/kg
$\mathcal{E}$	8.29352×10^6	J/kg
a	5×10^9	$1/s$
β	0	

Table 10.3: Numerical values of parameters for two-step irreversible kinetics.

The frozen sound speed remains

$$c^2 = \gamma P v = \gamma \frac{P}{\rho}. \tag{10.388}$$

There are now two thermicities:

$$\sigma_1 = \left. \frac{1}{\rho c^2} \frac{\partial P}{\partial \lambda_1} \right|_{v,e,\lambda_2} = \frac{\gamma}{\gamma - 1} \frac{\rho q_1}{P}, \tag{10.389}$$

$$\sigma_2 = \left. \frac{1}{\rho c^2} \frac{\partial P}{\partial \lambda_2} \right|_{v,e,\lambda_1} = \frac{\gamma}{\gamma - 1} \frac{\rho q_2}{P}. \tag{10.390}$$

Parameters for our two step model are identical to those of our one step model, except for the heat releases. The parameters are listed in Table 10.3. Note that at complete reaction $Q(\lambda_1, \lambda_2) = Q(1, 1) = q_1 + q_2 = 1.89566 \times 10^6$ J/kg. Thus, the overall heat release at complete reaction $\lambda_1 = \lambda_2 = 1$ is identical to our earlier one-step kinetic model.

Let us do some new Rankine-Hugoniot analysis. We can write a set of mass, momentum, energy, and state equations as

$$\rho \hat{u} = -\rho_o D, \tag{10.391}$$

$$P + \rho \hat{u}^2 = P_o + \rho_o D^2, \tag{10.392}$$

$$e + \frac{1}{2}\hat{u}^2 + \frac{P}{\rho} = e_o + \frac{1}{2}D^2 + \frac{P_o}{\rho_o}, \tag{10.393}$$

$$e = \frac{1}{\gamma - 1} \frac{P}{\rho} - \lambda_1 q_1 - \lambda_2 q_2, \tag{10.394}$$

$$\lambda_2 = \lambda_1 + (1 - \lambda_1) \ln(1 - \lambda_1). \tag{10.395}$$
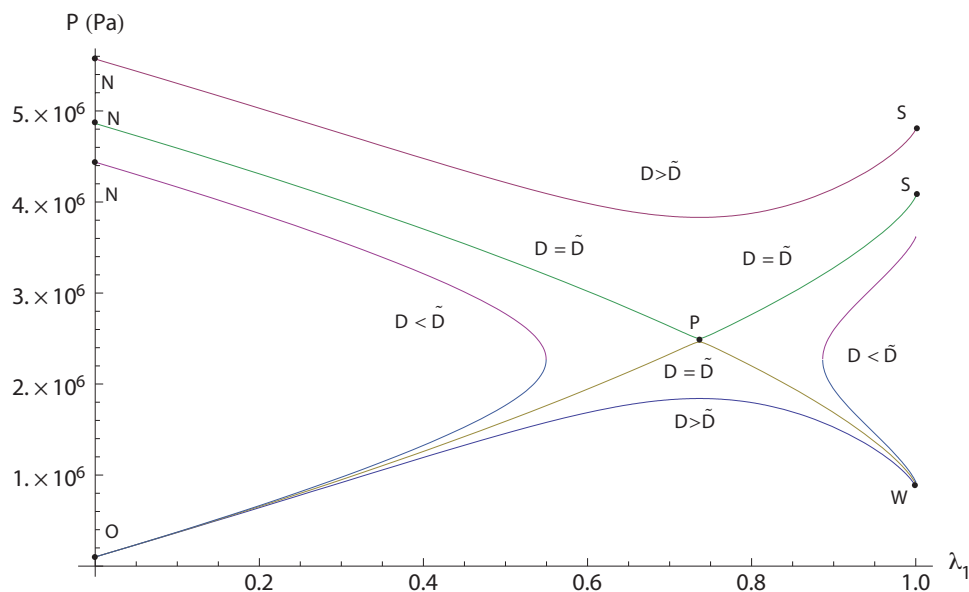
Figure 10.16: Pressure versus λ_1 for two-step kinetics problem for three different values of D: $D = 2800\ m/s > \tilde{D}$, $D = 2616.5\ m/s = \tilde{D}$, $D = 2500\ m/s < \tilde{D}$; parameters are from Table 10.3.

Let us consider D and λ_1 to be unspecified but known parameters for this analysis. These equations are five equations for the five unknowns, ρ, $\hat{u}$, P, e, and λ_2. They can be solved for $\rho(D, \lambda_1)$, $\hat{u}(D, \lambda_1)$, $P(D, \lambda_1)$, $e(D, \lambda_1)$, and $\lambda_2(\lambda_1)$.

The solution is lengthy, but the plot is revealing. For three different values of D, pressure as a function of λ_1 is shown in in Fig. 10.16. There are three important classes of D, each shown in Fig. 10.16, depending on how D compares to a critical value we call $\tilde{D}$.

- $D > \tilde{D}$. There are two potentially paths here. The important physical branch starts at point O, and is immediately shocked to state N, the Neumann point. From N the pressure first decreases as λ_1 increases. Near $\lambda_1 = 0.75$, the pressure reaches a local minimum, and then increases to the complete reaction point at S. This is a strong solution. There is a second branch which commences at O and is unshocked. On this branch the pressure increases to a maximum, then decreases to the end state at W. While this branch is admissible mathematically, its length scales are unphysically long, and this branch is discarded.

- $D = \tilde{D}$. Let us only consider branches which are shocked from O to N. The unshocked branches are again non-physical. On this branch, the pressure decreases from N to the pathological point P. At P, the flow is locally sonic, with $\hat{M} = 1$. Here, the pressure can take two distinct paths. The one chosen will depend on the velocity of the supporting piston at the end state. On one path the pressure increases to its final value at the strong point S. On the other the pressure decreases to its final value at the weak point W.
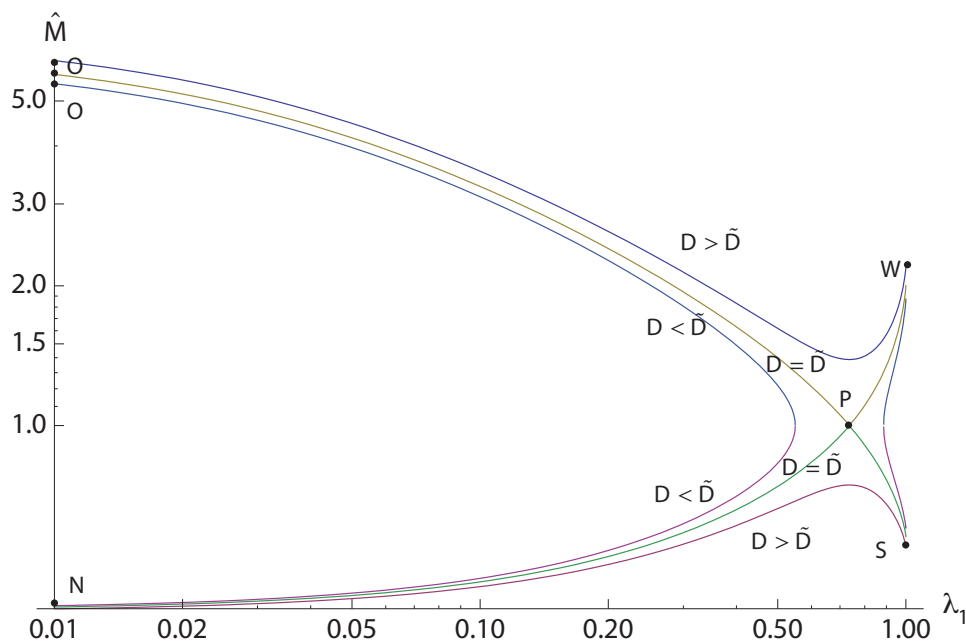
Figure 10.17:   Mach number $\hat{M}$ versus λ_1 for two-step kinetics problem for three different values of D: $D = 2800 \ m/s > \tilde{D}$, $D = 2616.5 \ m/s = \tilde{D}$, $D = 2500 \ m/s < \tilde{D}$; parameters are from Table 10.3.

- $D < \tilde{D}$. For such values of D, there is no physical structure for the entire reaction zone $0 < \lambda_1 < 1$. This branch is discarded.

Mach number in the wave frame, $\hat{M}$ as a function of λ_1 is shown in in Fig. 10.17. The results here are similar to those in Fig. 10.16. Note the ambient point O is always supersonic, and the Neumann point N is always subsonic. For flows originating at N, if $D > \tilde{D}$, the flow remains subsonic throughout until its termination at S. For $D = \tilde{D}$, the flow can undergo a subsonic to supersonic transition at the pathological point P. The weak point W is a supersonic end state.

The important Fig. 10.16 bears remarkable similarity to curves of $P(x)$ in compressible inert flow in a converging-diverging nozzle. We recall that for such flows, a subsonic to supersonic transition is only realized at an area minimum. This can be explained because the equation for evolution of pressure for such flows takes the form $dP/dx \sim (dA/dx)/(1 - M^2)$. So, if the flow is locally sonic, it must encounter a critical point in area, $dA/dx = 0$ in order to avoid infinite pressure gradients. This is what is realized in actual nozzles.

For us the analogous equation is the two-step version of Eq. (10.247), which can be shown to be

$$\frac{dP}{d\hat{x}} = -\frac{\rho \hat{u}(\sigma_1 r_1 + \sigma_2 r_2)}{1 - \hat{M}^2}. \tag{10.396}$$

Because the first reaction is exothermic, we have $\sigma_1 > 0$, and because the second reaction

is endothermic, we have $\sigma_2 < 0$. With $r_1 > 0$, $r_2 > 0$, this gives rise to the possibility that $\sigma_1 r_1 + \sigma_2 r_2 = 0$ at a point where the reaction is incomplete. The point P is just such a point; it is realized when $D = \tilde{D}$.

Finally, we write our differential-algebraic equations which are integrated for the detonation structure:

$$\rho \hat{u} = -\rho_o D, \tag{10.397}$$

$$P + \rho \hat{u}^2 = P_o + \rho_o D^2, \tag{10.398}$$

$$e + \frac{1}{2}\hat{u}^2 + \frac{P}{\rho} = e_o + \frac{1}{2}D^2 + \frac{P_o}{\rho_o}, \tag{10.399}$$

$$e = \frac{1}{\gamma - 1}\frac{P}{\rho} - \lambda_1 q_1 - \lambda_2 q_2, \tag{10.400}$$

$$P = \rho R T, \tag{10.401}$$

$$\lambda_2 = \lambda_1 + (1 - \lambda_1)\ln(1 - \lambda_1), \tag{10.402}$$

$$\frac{d\lambda_1}{d\hat{x}} = \frac{1 - \lambda_1}{\hat{u}} a \exp\left(-\frac{\mathcal{E}}{RT}\right). \tag{10.403}$$

We need the condition $\lambda_1(0) = 0$. These form seven equations for the seven unknowns ρ, $\hat{u}$, P, e, T, λ_1, and λ_2. We also realize that the algebraic solutions are multi-valued and must take special care to be on the proper branch. This becomes particularly important for solutions which pass through P.

10.2.7.1 Strong structures

Here, we consider strong structures for two cases: $D > \tilde{D}$ and $D = \tilde{D}$. All of these will proceed from O to N through a pressure minimum, and finish at the strong point S.

10.2.7.1.1 $D > \tilde{D}$ Structures for a strong detonation with $D = 2800 \; m/s > \tilde{D}$ are given in Figs. 10.18-10.21. The structure of all of these can be compared directly to those of the one-step kinetics model at the same $D = 2800 \; m/s$, Figs. 10.11-10.14. Note the shock values are identical. The reaction zone thicknesses are similar as well at $\ell_{rxn} \sim 0.0001 \; m$. The structures themselves have some differences; most notably, the two-step model structures display interior critical points before complete reaction.

We take special note of the pressure plot of Fig. 10.18, which can be compared with Fig. 10.16. We see in both figures the shock from O to N, followed by a drop of pressure to a minimum, followed by a final relaxation to an equilibrium value at S. Note that the two curves have the opposite sense of direction as λ_1 commences at 0 and goes to 1, while $\hat{x}$ commences at 0 and goes to $-0.0002 \; m$.

We can also compare the $\hat{M}(\hat{x})$ plot of Fig. 10.20 with that of $\hat{M}(\lambda_1)$ of Fig. 10.17. In both the supersonic O is shocked to a subsonic N. The Mach number rises slightly then falls in the reaction zone to its equilibrium value at S. It never returns to a supersonic state.
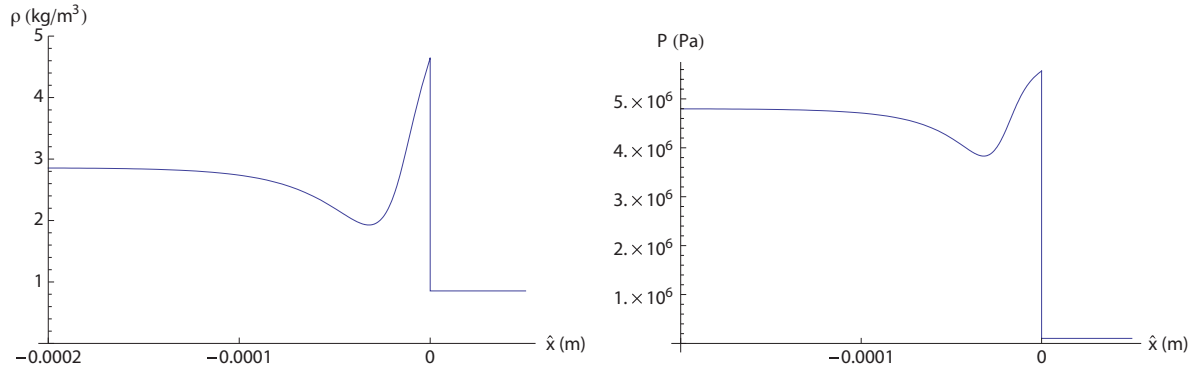
Figure 10.18: ZND structure of $\rho(\hat{x})$ and $P(\hat{x})$ for strong $D = 2800 \ m/s > \tilde{D}$ for two-step irreversible reaction with parameters of Table 10.3.
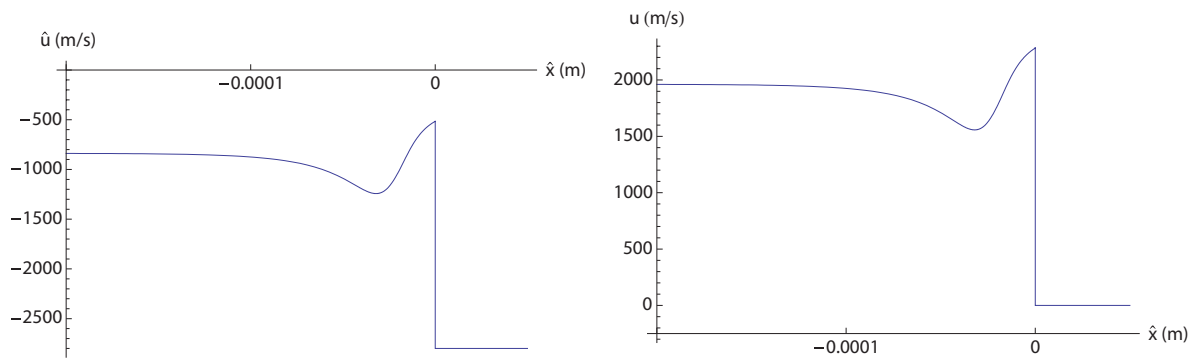

Figure 10.19: ZND structure of $\hat{u}(\hat{x})$ and $u(\hat{x})$ for strong $D = 2800 \ m/s > \tilde{D}$ for two-step irreversible reaction with parameters of Table 10.3.
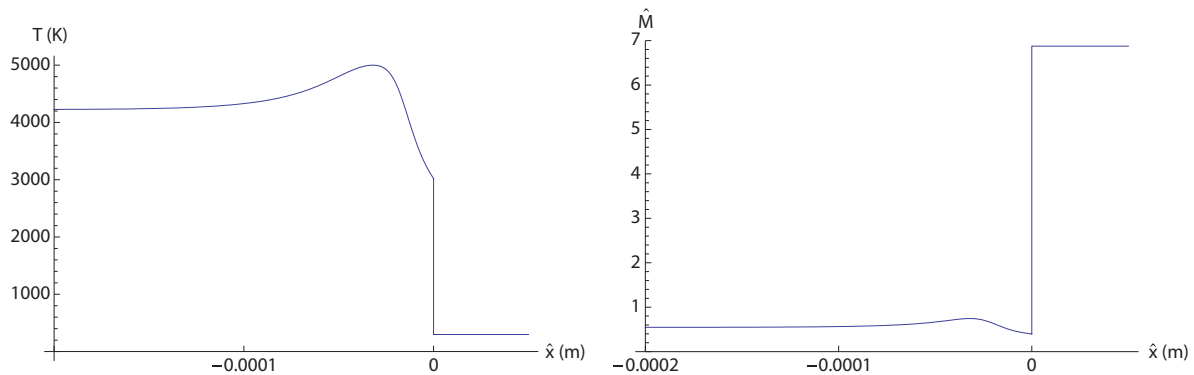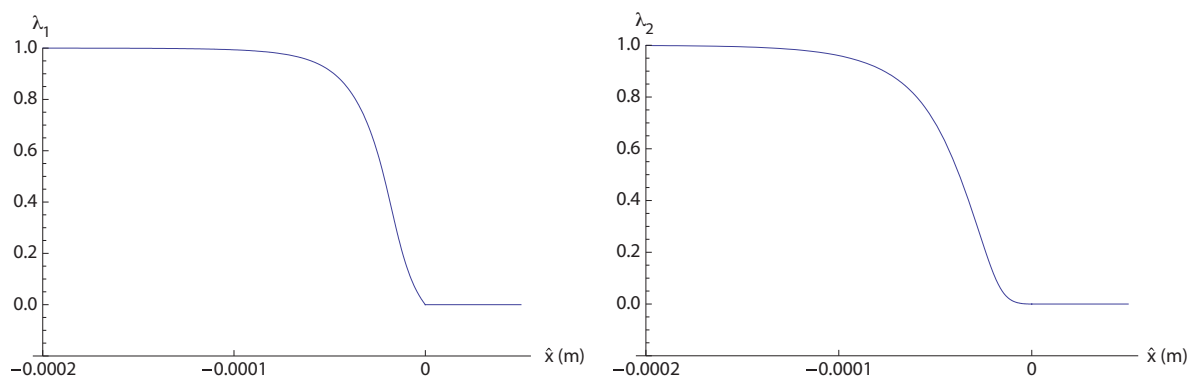

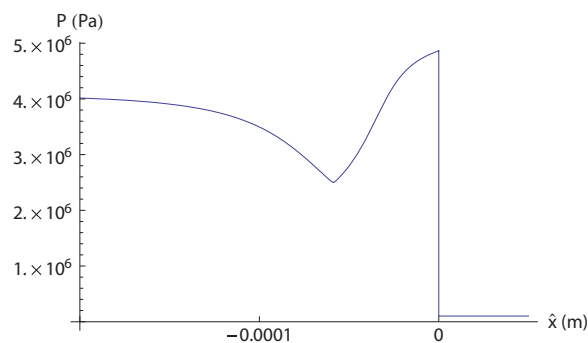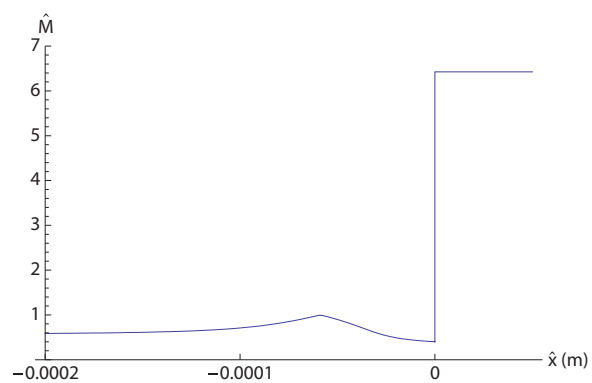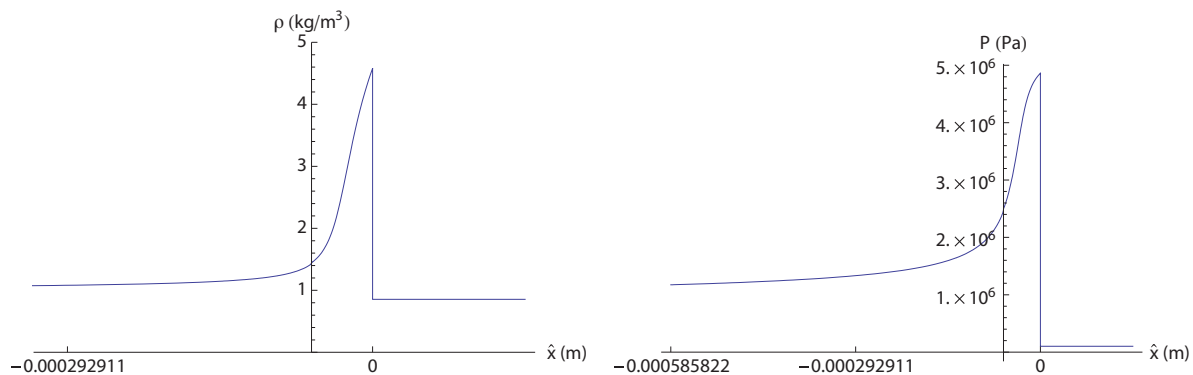Figure 10.20: ZND structure of $T(\hat{x})$ and $\hat{M}(\hat{x})$ for strong $D = 2800 \ m/s > \tilde{D}$ for two-step irreversible reaction with parameters of Table 10.3.

Figure 10.21: ZND structure of $\lambda_1(\hat{x})$ and $\lambda_2(\hat{x})$ for strong $D = 2800 \; m/s > \tilde{D}$ for two-step irreversible reaction with parameters of Table 10.3.

Figure 10.22: ZND structure of $P(\hat{x})$ for strong $D = 2616.5 \; m/s = \tilde{D}$ for two-step irreversible reaction with parameters of Table 10.3.

10.2.7.1.2 $D = \tilde{D}$ For $D = \tilde{D} = 2616.5 \; m/s$, we can find a strong structure with a path from O to N to S. Pressure P and Mach number $\hat{M}$ are plotted in Figures 10.22-10.23. Note that at an interior point in the structure, a cusp in the P and $\hat{M}$ profile is seen. At this point, the flow is locally sonic with $\hat{M} = 1$.

Figure 10.23:   ZND structure of $\hat{M}(\hat{x})$ for strong $D = 2616.5 \ m/s = \tilde{D}$ for two-step irreversible reaction with parameters of Table 10.3.
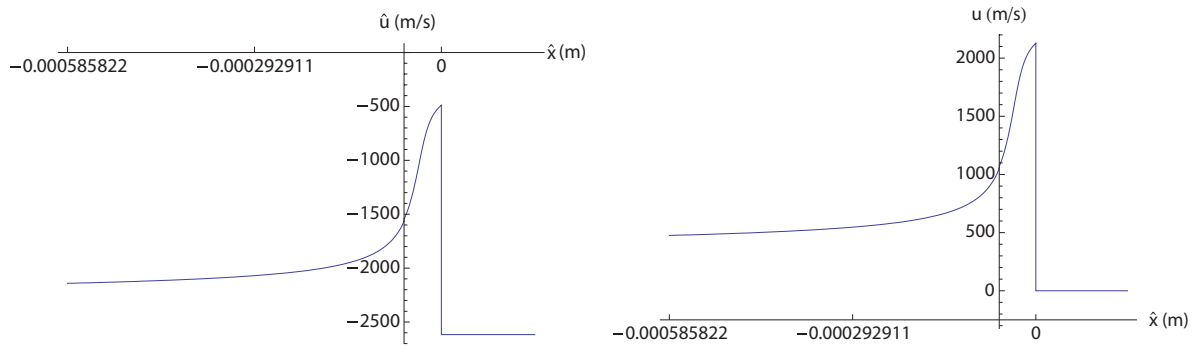
Figure 10.24: ZND structure of $\rho(\hat{x})$ and $P(\hat{x})$ for weak $D = 2616.5 \ m/s = \tilde{D}$ for two-step irreversible reaction with parameters of Table 10.3.

### 10.2.7.2 Weak, eigenvalue structures

Let us now consider weak structures with $D = \tilde{D} = 2616.5 \ m/s$. Special care must be taken in integrating the governing equations. In general one must integrate to very near the pathological point P, then halt. While there are more sophisticated techniques involving further coordinate transformations, one can record the values near P on its approach from N. Then, one can perturb slightly all state variables so that the $\hat{M}$ is just greater than unity and recommence the integration.

Figures of the structures which commence at O, are shocked to N, pass through sonic point P, and finish at the supersonic W are shown in Figs. 10.24-10.27. One may again compare the pressure and Mach number plots of Figs. 10.24,10.26 with those of Figs. 10.16,10.17.

Figure 10.25:   ZND structure of $\hat{u}(\hat{x})$ and $u(\hat{x})$ for weak $D = 2616.5 \ m/s = \tilde{D}$ for two-step irreversible reaction with parameters of Table 10.3.
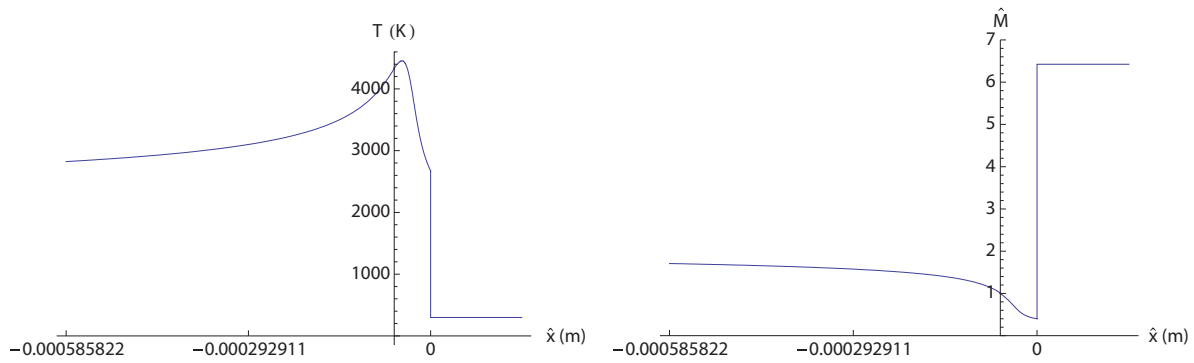
Figure 10.26:   ZND structure of $T(\hat{x})$ and $\hat{M}(\hat{x})$ for weak $D = 2616.5 \ m/s = \tilde{D}$ for two-step irreversible reaction with parameters of Table 10.3.
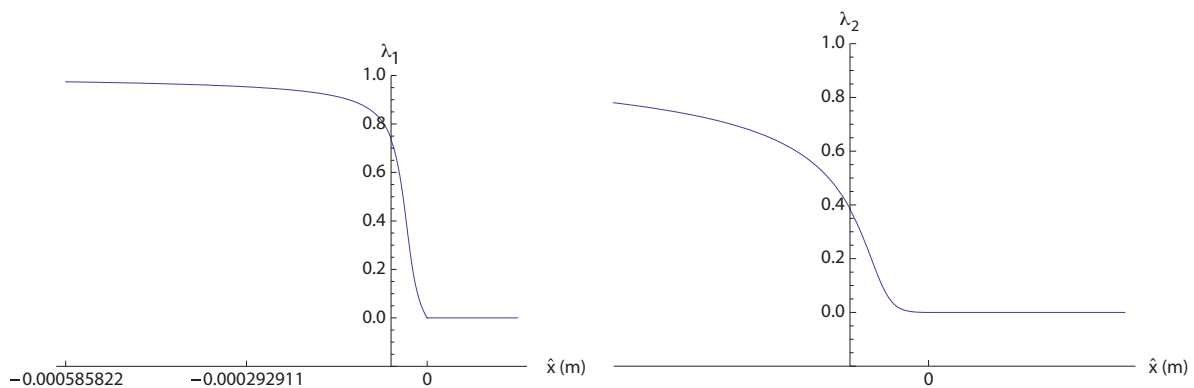
Figure 10.27:   ZND structure of $\lambda_1(\hat{x})$ and $\lambda_2(\hat{x})$ for weak $D = 2616.5 \ m/s = \tilde{D}$ for two-step irreversible reaction with parameters of Table 10.3.

10.2.7.3   Piston problem

We can understand the physics of the two-step kinetics problem better in the context of a piston problem, where the supporting piston connects to the final laboratory frame fluid velocity $u_p = u(\hat{x} \to -\infty)$. Let us consider pistons with high velocity and then lower them and examine the changes of structure.

- $u_p > \tilde{u}_{ps}$. This high velocity piston will drive a strong shock into the fluid at a speed $D > \tilde{D}$. The solution will proceed from O to N to S and be subsonic throughout. Therefore changes at the piston face will be able to be communicated all the way to the shock front. The energy to drive the wave comes from a combination of energy released during combustion and energy supplied by the piston support.

- $u_p = \tilde{u}_{ps}$. At a critical value of piston velocity, $\tilde{u}_{ps}$, the solution will go from O to N to P to S, and be locally sonic. This is analogous to the "subsonic design" condition for a converging-diverging nozzle.

- $u_p \in [\tilde{u}_{ps}, \tilde{u}_{pw}]$. Here, the flow can be complicated. Analogous to flow in a nozzle, there can be standing shock waves in the supersonic portion of the flow which decelerate the flow so as to match the piston velocity at the end of the reaction. Such flows will proceed from O to N through P, and then are shocked back onto the subsonic branch to terminate at S.

- $u_p = \tilde{u}_{pw}$. This state is analogous to the "supersonic design" condition of flow in a converging-diverging nozzle. The fluid proceeds from O to N through P and terminates at W. All of the energy to propagate the wave comes from the reaction.

- $u_p < \tilde{u}_{pw}$. For such flows, the detonation wave is self-supporting. There is no means to communicate with the supporting piston. The detonation wave proceeds at $D = \tilde{D}$. *We note that $\tilde{D}$ is a function of the specific kinetic mechanism. This non-classical result contradicts the conclusion from CJ theory with simpler kinetics in which the wave speed of an unsupported detonation is independent of the kinetics.* Note for our problem that $\tilde{D} = 2616.5 \ m/s$. This stands in contrast to the CJ velocity, independently computed of $D_{CJ} = 1991.1 \ m/s$ for the same mixture.

10.2.8   Detonation structure: Detailed $H_2 - O_2 - N_2$ kinetics

These same notions for detonation with simple kinetics and state equations can easily be extended to more complex models. Let us consider a one-dimensional steady detonation in a stoichiometric hydrogen-air mixture with the detailed kinetics model of Table 1.2. We shall consider a case almost identical to that studied by Powers and Paolucci.[18] The mixture is thus taken to be $2H_2 + O_2 + 3.76N_2$. As we did in our modelling of the same mixture

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[18]Powers, J. M., and Paolucci, S., 2005, "Accurate Spatial Resolution Estimates for Reactive Supersonic Flow with Detailed Chemistry," *AIAA Journal*, 43(5): 1088-1099.

under spatially homogeneous isochoric, adiabatic conditions in Sec. 1.2.2, we will take the number of moles of each of the minor species to be a small number near machine precision. This has the effect of removing some numerical roundoff errors in the very early stages of reaction. Our model will be the steady one-dimensional reactive Euler equations, obtained by considering the reactive Navier-Stokes equations in the limit as $\boldsymbol{\tau}$, $\mathbf{j}_i^m$, $\mathbf{j}^q$ all go to zero.

Our model then is 1) the integrated mass, momentum, and energy equations, Eqs. (10.249-10.251) with an opposite sign on D to account for the left-running wave, 2) the one-dimensional, steady, diffusion-free version of species evolution, Eq. (6.54), 3) the calorically imperfect ideal gas state equations of Eqs. (6.69), (6.77), and 4) the law of mass action with Arrhenius kinetics of Eqs. (6.82-6.85). In order to cleanly plot the results on a logarithmic scale, we will, in contrast to the previous right-running detonations, consider left-running waves with detonation velocity D. The governing equations are as follows:

$$\rho \hat{u} = \rho_o D, \tag{10.404}$$

$$P + \rho \hat{u}^2 = P_o + \rho_o D^2, \tag{10.405}$$

$$\rho \hat{u}\left(e + \frac{1}{2}\hat{u}^2 + \frac{P}{\rho}\right) = \rho_o D\left(e_o + \frac{1}{2}D^2 + \frac{P_o}{\rho_o}\right), \tag{10.406}$$

$$\rho \hat{u}\frac{dY_i}{d\hat{x}} = M_i \dot{\omega}_i, \tag{10.407}$$

$$P = \rho \overline{R} T \sum_{i=1}^{N} \frac{Y_i}{M_i}, \tag{10.408}$$

$$e = \sum_{i=1}^{N} Y_i \left(e_{T_o,i}^o + \int_{T_o}^{T} c_{vi}(\hat{T})d\hat{T}\right), \tag{10.409}$$

$$\dot{\omega}_i = \sum_{j=1}^{J} \nu_{ij} r_j, \tag{10.410}$$

$$r_j = k_j \prod_{k=1}^{N} \overline{\rho}_k^{\nu'_{kj}} \left(1 - \frac{1}{K_{c,j}} \prod_{k=1}^{N} \overline{\rho}_k^{\nu_{kj}}\cdot\right), \tag{10.411}$$

$$k_j = a_j T^{\beta_j} \exp\left(\frac{-\overline{\mathcal{E}}_j}{\overline{R}T}\right), \tag{10.412}$$

$$K_{c,j} = \left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^{N}\nu_{ij}} \exp\left(-\frac{\Delta G_j^o}{\overline{R}T}\right). \tag{10.413}$$

This differential-algebraic system must be solved numerically. One can use standard methods to achieve this. Alternatively, and with significant effort, one can remove all of the algebraic constraints. Part of this requires a numerical iteration to find certain roots. After this effort, one can in principle write a set of $N - L$ differential equations for evolution of the $N - L$ independent species.

Here, we chose $D \sim D_{CJ} = 1979.70 \ m/s$. Because this model is not a simple one-step model, we cannot expect to find the equilibrium state to be exactly sonic. However, it is

possible to slightly overdrive the wave and achieve a nearly sonic state at the equilibrium state. Here, our final Mach number was $\hat{M} = 0.9382$. Had we weakened the overdrive further, we would have encountered an interior sonic point at a non-equilibrium point, thus inducing a non-physical sonic singularity.

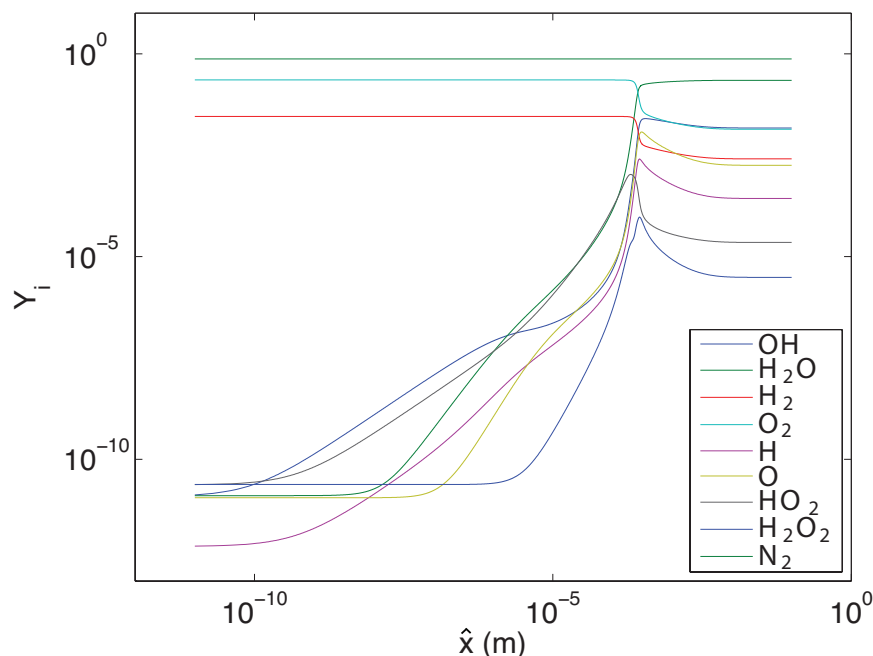Numerical solution for species mass fraction is given in Fig. (10.28). The figure is plot-

Figure 10.28: Detailed kinetics ZND structure of species mass fractions for near CJ detonation, $D_{CJ} \sim D = 1979.70 \ m/s$, in $2H_2 + O_2 + 3.76N_2$, $P_o = 1.01325 \times 10^5 \ Pa$, $T_o = 298 \ K$, $T_s = 1542.7 \ K$, $P_s = 2.83280 \times 10^6 \ Pa$.

ted on a log-log scale because of the wide range of length scales and mass fraction scales encountered. Note that the minor species begin to change at a very small length scale. At a value of $\hat{x} \sim 2.6 \times 10^{-4} \ m$, a significant event occurs, known as a thermal explosion. This length is known as the induction length, $\ell_{ind} = 2.6 \times 10^{-4} \ m$. We get a rough estimate of the induction time by the formula $t_{ind} \sim \ell_{ind}/\hat{u}_s = 7.9 \times 10^{-7} \ s$. Here, $\hat{u}_s$ is the post shock velocity in the wave frame. Its value is $\hat{u}_s = 330.54 \ m/s$. All species contribute to the reaction dynamics here. This is followed by a relaxation to chemical equilibrium, achieved around $0.1 \ m$.

The pressure profile is given in Fig. (10.2.8). We artificially located the shock just away from $\hat{x} = 0$, so as to ease the log-log plot. The pressure is shocked from its atmospheric value to $2.83280 \times 10^6 \ Pa$ (see Table 10.2). After the shock, the pressure holds nearly constant for several decades of distance. Once the thermal explosion commences, the pressure relaxes to its equilibrium value. This figure can be compared with its one-step equivalent of Fig. 10.11.

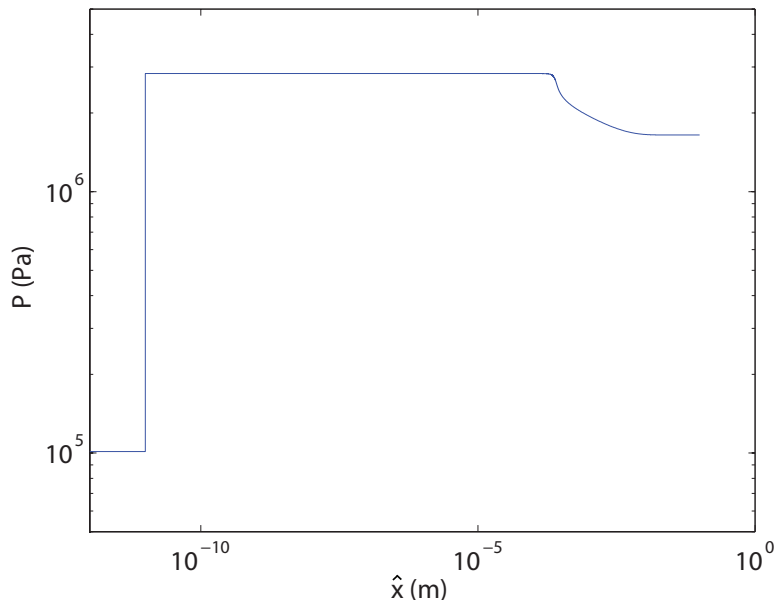Similar behavior is seen in the temperature plot of Fig. 10.30. The temperature is shocked

Figure 10.29:   Detailed kinetics ZND structure of pressure for near CJ detonation, $D_{CJ} \sim D = 1979.70\ m/s$, in $2H_2 + O_2 + 3.76N_2$, $P_o = 1.01325 \times 10^5\ Pa$, $T_o = 298\ K$, $T_s = 1542.7\ K$ $P_s = 2.83280 \times 10^6\ Pa$.

to $T_s = 1542.7\ K$, stays constant in the induction zone, and then increases to its equilibrium value after the thermal explosion. This figure can be compared with its one-step equivalent of Fig. 10.13.

It is interesting to compare these results to those obtained earlier in Sec. 1.2.2. There, an isochoric, adiabatic combustion of precisely the same stoichiometric hydrogen-air mixture with precisely the same kinetics was conducted. The adiabatic/isochoric mixture had an initial temperature and pressure identical to the post-shock pressure and temperature here. We compare the induction time of the spatially homogeneous problem, $t_{ind} = 6.6 \times 10^{-7}\ s$, Eq. (1.373) to our estimate from the detonation found earlier, $t_{ind} \sim \ell_{ind}/\hat{u}_s = 7.9 \times 10^{-7}\ s$. The two are remarkably similar!

We compare some other relevant values in Table 10.4. Note that these mixtures are identical at the onset of the calculation. The detonating mixture has reached the same initial state after the shock. And a fluid particle advecting through the detonation reaction zone with undergo a thermal explosion at nearly the same time a particle that was stationary in the closed vessel will. After that the two fates are different. This is because there is no kinetic energy in the spatially homogeneous problem. Thus, all the chemical energy is transformed into thermal energy. This is reflected in the higher final temperature and pressure of the spatially homogeneous problem relative to the detonating flow. Because the final temperature is different, the two systems relax to a different chemical equilibrium, as reflected in the different mass fractions. For example, note that the cooler detonating flow

Parameter	Spatially Homogeneous	Detonation
T_o	$1542.7\ K$	$298\ K$
T_s	$-$	$1542.7\ K$
P_o	$2.83280 \times 10^6\ Pa$	$1.01325 \times 10^5\ Pa$
P_s	$-$	$2.83280 \times 10^6\ Pa$
t_{ind}	$6.6 \times 10^{-7}\ s$	$7.9 \times 10^{-7}\ s$
T^{eq}	$3382.3\ K$	$2982.1\ K$
P^{eq}	$5.53 \times 10^6\ Pa$	$1.65 \times 10^6\ Pa$
ρ^{eq}	$4.62\ kg/m^3$	$1.59\ kg/m^3$
$\hat{u}^{eq}$	$0\ m/s$	$1066\ m/s$
$Y_{O_2}^{eq}$	1.85×10^{-2}	1.38×10^{-2}
Y_{H}^{eq}	5.41×10^{-4}	2.71×10^{-4}
Y_{OH}^{eq}	2.45×10^{-2}	1.48×10^{-2}
Y_{O}^{eq}	3.88×10^{-3}	1.78×10^{-3}
$Y_{H_2}^{eq}$	3.75×10^{-3}	2.57×10^{-3}
$Y_{H_2O}^{eq}$	2.04×10^{-1}	2.22×10^{-1}
$Y_{HO_2}^{eq}$	6.84×10^{-5}	2.23×10^{-5}
$Y_{H_2O_2}^{eq}$	1.04×10^{-5}	3.08×10^{-6}
$Y_{N_2}^{eq}$	7.45×10^{-1}	7.45×10^{-1}

Table 10.4: Comparison of relevant predictions of a spatially homogeneous model with those of a near CJ detonation in the same mixture.
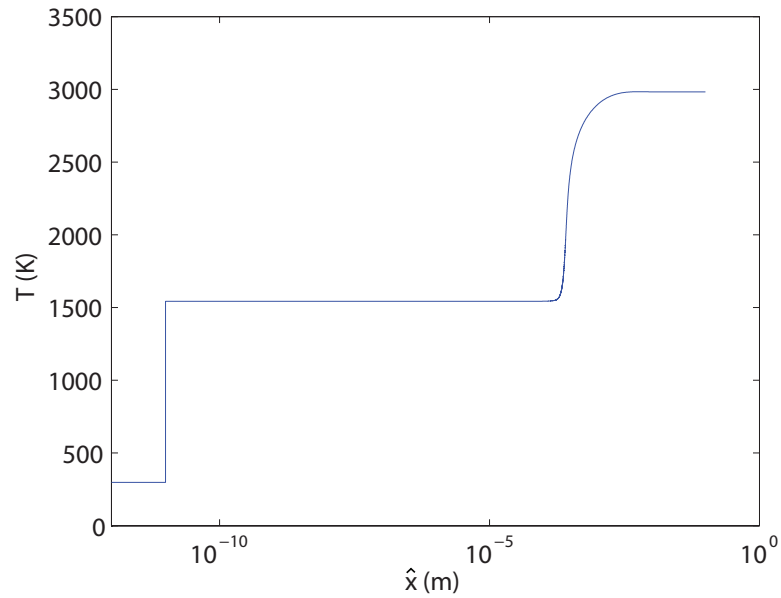
Figure 10.30: Detailed kinetics ZND structure of temperature for near CJ, $D_{CJ} \sim D = 1979.70\ m/s$, detonation in $2H_2 + O_2 + 3.76N_2$, $P_o = 1.01325 \times 10^5\ Pa$, $T_o = 298\ K$, $T_s = 1542.7\ K$, $P_s = 2.83280 \times 10^6\ Pa$. Shock at $\hat{x} = 0$ artificially translated to $\hat{x} = 10^{-11}\ m$.

has a higher final mass fraction of H_2O.

Chapter 11

Blast waves

Here, we will study the Taylor[1]-Sedov[2] blast wave solution. We will follow most closely two papers of Taylor[3][4] from 1950. Taylor notes that the first of these was actually written in 1941, but was classified. Sedov's complementary study[5] is also of interest. One may also consult other articles by Taylor for background.[6][7]

Consider a point source of energy which at $t = 0$ is released into a calorically perfect ideal gas. The point source could be the combustion products of an intense reaction event. We shall follow Taylor's analysis and obtain what is known as *self-similar solutions.* Though there are more general approaches which may in fact expose more details of how self-similar solutions are obtained, we will confine ourselves to Taylor's approach and use his notation.

The self-similar solution will be enabled by studying the Euler equations in what is known as the *strong shock limit* for a spherical shock wave. Now, a shock wave will raise both the internal and kinetic energy of the ambient fluid into which it is propagating. We would like to consider a scenario in which the total energy, kinetic and internal, enclosed by the strong spherical shock wave is a constant. The ambient fluid is initially at rest, and a point source of energy exists at $r = 0$. For $t > 0$, this point source of energy is distributed to the mechanical and thermal energy of the surrounding fluid.

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[1]Geoffrey Ingram Taylor, 1886-1975, English physicist.

[2]Leonid Ivanovitch Sedov, 1907-1999, Soviet physicist.

[3]Taylor, G. I., 1950, "The Formation of a Blast Wave by a Very Intense Explosion. I. Theoretical Discussion," *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* 201(1065): 159-174.

[4]Taylor, G. I., 1950, "The Formation of a Blast Wave by a Very Intense Explosion. II. The Atomic Explosion of 1945," *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 201(1065): 175-186.

[5]Sedov, L. I., 1946, "Rasprostraneniya Sil'nykh Vzryvnykh Voln," *Prikladnaya Matematika i Mekhanika* 10: 241-250.

[6]Taylor, G. I., 1950, "The Dynamics of the Combustion Products Behind Plane and Spherical Detonation Fronts in Explosives," *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 200(1061): 235-247.

[7]Taylor, G. I., 1946, "The Air Wave Surrounding an Expanding Sphere," *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 186(1006): 273-292.

Let us follow now Taylor's analysis from his 1950 Part I "Theoretical Discussion" paper. We shall

- write the governing inert one-dimensional unsteady Euler equations in spherical coordinates,

- reduce the partial differential equations in r and t to ordinary differential equations in an appropriate similarity variable,

- solve the ordinary differential equations numerically, and

- show our transformation guarantees constant total energy in the region $r \in [0, R(t)]$, where $R(t)$ is the locus of the moving shock wave.

We shall also refer to specific equations in Taylor's first 1950 paper.

11.1   Governing equations

The non-conservative formulation of the governing equations is as follows:

$$\frac{\partial \rho}{\partial t} + u\frac{\partial \rho}{\partial r} + \rho\frac{\partial u}{\partial r} = -\frac{2\rho u}{r}, \tag{11.1}$$

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial r} + \frac{1}{\rho}\frac{\partial P}{\partial r} = 0, \tag{11.2}$$

$$\left(\frac{\partial e}{\partial t} + u\frac{\partial e}{\partial r}\right) - \frac{P}{\rho^2}\left(\frac{\partial \rho}{\partial t} + u\frac{\partial \rho}{\partial r}\right) = 0, \tag{11.3}$$

$$e = \frac{1}{\gamma - 1}\frac{P}{\rho}, \tag{11.4}$$

$$P = \rho RT. \tag{11.5}$$

For review, let us look at the energy equation in a little more detail. Recall the material derivative is $d/dt = \partial/\partial t + u\partial/\partial r$, so the energy equation, Eq. (11.3) can be rewritten as

$$\frac{de}{dt} - \frac{P}{\rho^2}\frac{d\rho}{dt} = 0. \tag{11.6}$$

Let us now substitute the caloric energy equation, Eq. (11.4) into the energy equation, Eq. (11.6):

$$\frac{1}{\gamma - 1}\frac{d}{dt}\left(\frac{P}{\rho}\right) - \frac{P}{\rho^2}\frac{d\rho}{dt} = 0, \tag{11.7}$$

$$-\frac{1}{\gamma - 1}\frac{P}{\rho^2}\frac{d\rho}{dt} + \frac{1}{\gamma - 1}\frac{1}{\rho}\frac{dP}{dt} - \frac{P}{\rho^2}\frac{d\rho}{dt} = 0, \tag{11.8}$$

$$-\frac{P}{\rho^2}\frac{d\rho}{dt} + \frac{1}{\rho}\frac{dP}{dt} - (\gamma - 1)\frac{P}{\rho^2}\frac{d\rho}{dt} = 0, \tag{11.9}$$

$$\frac{1}{\rho}\frac{dP}{dt} - \gamma\frac{P}{\rho^2}\frac{d\rho}{dt} = 0, \tag{11.10}$$

$$\frac{dP}{dt} - \gamma\frac{P}{\rho}\frac{d\rho}{dt} = 0, \tag{11.11}$$

$$\frac{1}{\rho^\gamma}\frac{dP}{dt} - \gamma\frac{P}{\rho^{\gamma+1}}\frac{d\rho}{dt} = 0, \tag{11.12}$$

$$\frac{d}{dt}\left(\frac{P}{\rho^\gamma}\right) = 0, \tag{11.13}$$

$$\frac{\partial}{\partial t}\left(\frac{P}{\rho^\gamma}\right) + u\frac{\partial}{\partial r}\left(\frac{P}{\rho^\gamma}\right) = 0. \tag{11.14}$$

11.2 Similarity transformation

We shall next make some non-intuitive and non-obvious choices for a transformed coordinate system and transformed dependent variables. These choices can be systematically studied with the techniques of group theory, not discussed here.

11.2.1 Independent variables

Let us transform the independent variables $(r, t) \to (\eta, \tau)$ with

$$\eta = \frac{r}{R(t)}, \tag{11.15}$$

$$\tau = t. \tag{11.16}$$

We will seek solutions such that the dependent variables are functions of η, the distance relative to the time-dependent shock, only. We will have little need for the transformed time τ since it is equivalent to the original time t.

11.2.2 Dependent variables

Let us also define new dependent variables as

$$\frac{P}{P_o} = y = R^{-3}f_1(\eta), \tag{11.17}$$

$$\frac{\rho}{\rho_o} = \psi(\eta), \tag{11.18}$$

$$u = R^{-3/2}\phi_1(\eta). \tag{11.19}$$

These amount to definitions of a scaled pressure f_1, a scaled density ψ, and a scaled velocity ϕ_1, with the assumption that each is a function of η only. Here, P_o, and ρ_o are constant ambient values of pressure and density, respectively.

We also assume the shock velocity to be of the form

$$U = \frac{dR}{dt} = AR^{-3/2}. \tag{11.20}$$

The constant A is to be determined.

11.2.3   Derivative transformations

By the chain rule we have

$$\frac{\partial}{\partial t} = \frac{\partial \eta}{\partial t} \frac{\partial}{\partial \eta} + \frac{\partial \tau}{\partial t} \frac{\partial}{\partial \tau}. \tag{11.21}$$

Now, by Eq. (11.15) we get

$$\frac{\partial \eta}{\partial t} = -\frac{r}{R^2} \frac{dR}{dt}, \tag{11.22}$$

$$= -\frac{\eta}{R(t)} \frac{dR}{dt}, \tag{11.23}$$

$$= -\frac{\eta}{R} AR^{-3/2}, \tag{11.24}$$

$$= -\frac{A\eta}{R^{5/2}}. \tag{11.25}$$

From Eq. (11.16) we simply get

$$\frac{\partial \tau}{\partial t} = 1. \tag{11.26}$$

Thus, the chain rule, Eq. (11.21), can be written as

$$\frac{\partial}{\partial t} = -\frac{A\eta}{R^{5/2}} \frac{\partial}{\partial \eta} + \frac{\partial}{\partial \tau}. \tag{11.27}$$

As we are insisting the $\partial/\partial \tau = 0$, we get

$$\frac{\partial}{\partial t} = -\frac{A\eta}{R^{5/2}} \frac{d}{d\eta}. \tag{11.28}$$

In the same way, we get

$$\frac{\partial}{\partial r} = \frac{\partial \eta}{\partial r} \frac{\partial}{\partial \eta} + \frac{\partial \tau}{\partial r} \underbrace{\frac{\partial}{\partial \tau}}_{=0}, \tag{11.29}$$

$$= \frac{1}{R} \frac{d}{d\eta}. \tag{11.30}$$

11.3 Transformed equations

Let us now apply our rules for derivative transformation, Eqs. (11.25,11.30), and our transformed dependent variables, Eqs. (11.17-11.19), to the governing equations.

11.3.1 Mass

First, we shall consider the mass equation, Eq. (11.1). We get

$$\underbrace{-\frac{A\eta}{R^{5/2}}\frac{d}{d\eta}}_{=\partial/\partial t}\underbrace{(\rho_o\psi)}_{=\rho} + \underbrace{R^{-3/2}\phi_1}_{=u}\underbrace{\frac{1}{R}\frac{d}{d\eta}}_{=\partial/\partial r}\underbrace{(\rho_o\psi)}_{=\rho} + \underbrace{\rho_o\psi}_{=\rho}\underbrace{\frac{1}{R}\frac{d}{d\eta}}_{=\partial/\partial r}\underbrace{\left(R^{-3/2}\phi_1\right)}_{=u} = -\frac{2}{r}\underbrace{\rho_o\psi}_{=\rho}\underbrace{R^{-3/2}\phi_1}_{=u}. \quad (11.31)$$

Realizing the $R(t) = R(\tau)$ is not a function of η, canceling the common factor of ρ_o, and eliminating r with Eq. (11.15), we can write

$$-\frac{A\eta}{R^{5/2}}\frac{d\psi}{d\eta} + \frac{\phi_1}{R^{5/2}}\frac{d\psi}{d\eta} + \frac{\psi}{R^{5/2}}\frac{d\phi_1}{d\eta} = -\frac{2}{\eta}\frac{\psi\phi_1}{R^{5/2}}, \quad (11.32)$$

$$-A\eta\frac{d\psi}{d\eta} + \phi_1\frac{d\psi}{d\eta} + \psi\frac{d\phi_1}{d\eta} = -\frac{2}{\eta}\psi\phi_1, \quad (11.33)$$

$$-A\eta\frac{d\psi}{d\eta} + \phi_1\frac{d\psi}{d\eta} + \psi\left(\frac{d\phi_1}{d\eta} + \frac{2}{\eta}\phi_1\right) = 0, \qquad \text{mass.} \quad (11.34)$$

Equation (11.34) is number 9 in Taylor's paper, which we will call here Eq. T(9).

11.3.2 Linear momentum

Now, consider the linear momentum equation, Eq. (11.2), and apply the same transformations:

$$\frac{\partial}{\partial t}\underbrace{\left(R^{-3/2}\phi_1\right)}_{=u} + \underbrace{R^{-3/2}\phi_1}_{=u}\frac{\partial}{\partial r}\underbrace{\left(R^{-3/2}\phi_1\right)}_{=u} + \underbrace{\frac{1}{\rho_o\psi}}_{=1/\rho}\frac{\partial}{\partial r}\underbrace{\left(P_oR^{-3}f_1\right)}_{=P} = 0, \quad (11.35)$$

$$\underbrace{R^{-3/2}\frac{\partial\phi_1}{\partial t} - \frac{3}{2}R^{-5/2}\frac{dR}{dt}\phi_1}_{=\partial u/\partial t} + R^{-3/2}\phi_1\frac{\partial}{\partial r}\left(R^{-3/2}\phi_1\right) + \frac{1}{\rho_o\psi}\frac{\partial}{\partial r}\left(P_oR^{-3}f_1\right) = 0, \quad (11.36)$$

$$R^{-3/2}\left(-\frac{A\eta}{R^{5/2}}\right)\frac{d\phi_1}{d\eta} - \frac{3}{2}R^{-5/2}\left(AR^{-3/2}\right)\phi_1 + R^{-3/2}\phi_1\frac{\partial}{\partial r}\left(R^{-3/2}\phi_1\right)$$

$$+\frac{1}{\rho_o\psi}\frac{\partial}{\partial r}\left(P_oR^{-3}f_1\right) = 0, \quad (11.37)$$

$$-\frac{A\eta}{R^4}\frac{d\phi_1}{d\eta} - \frac{3}{2}\frac{A}{R^4}\phi_1 + R^{-3/2}\phi_1\frac{\partial}{\partial r}\left(R^{-3/2}\phi_1\right) + \frac{1}{\rho_o\psi}\frac{\partial}{\partial r}\left(P_oR^{-3}f_1\right) = 0, \quad (11.38)$$

$$-\frac{A\eta}{R^4}\frac{d\phi_1}{d\eta} - \frac{3}{2}\frac{A}{R^4}\phi_1 + R^{-3/2}\phi_1\frac{1}{R}\frac{d}{d\eta}\left(R^{-3/2}\phi_1\right) + \frac{1}{\rho_o\psi}\frac{1}{R}\frac{d}{d\eta}\left(P_oR^{-3}f_1\right) = 0, \quad (11.39)$$

$$-\frac{A\eta}{R^4}\frac{d\phi_1}{d\eta} - \frac{3}{2}\frac{A}{R^4}\phi_1 + \frac{\phi_1}{R^4}\frac{d\phi_1}{d\eta} + \frac{P_o}{\rho_o\psi}\frac{1}{R^4}\frac{df_1}{d\eta} = 0, \quad (11.40)$$

$$-A\eta\frac{d\phi_1}{d\eta} - \frac{3}{2}A\phi_1 + \phi_1\frac{d\phi_1}{d\eta} + \frac{P_o}{\rho_o\psi}\frac{df_1}{d\eta} = 0. \quad (11.41)$$

Our final form is

$$-A\left(\frac{3}{2}\phi_1 + \eta\frac{d\phi_1}{d\eta}\right) + \phi_1\frac{d\phi_1}{d\eta} + \frac{P_o}{\rho_o}\frac{1}{\psi}\frac{df_1}{d\eta} = 0, \qquad \text{linear momentum.} \quad (11.42)$$

Equation (11.42) is T(7).

11.3.3   Energy

Let us now consider the energy equation. It is best to begin with a form in which the equation of state has already been imposed. So, we will start by expanding Eq. (11.11) in terms of partial derivatives:

$$\underbrace{\frac{\partial P}{\partial t} + u\frac{\partial P}{\partial r}}_{=dP/dt} - \gamma\frac{P}{\rho}\underbrace{\left(\frac{\partial\rho}{\partial t} + u\frac{\partial\rho}{\partial r}\right)}_{=d\rho/dt} = 0, \qquad (11.43)$$

$$\frac{\partial}{\partial t}\left(P_oR^{-3}f_1\right) + R^{-3/2}\phi_1\frac{\partial}{\partial r}\left(P_oR^{-3}f_1\right)$$
$$-\gamma\frac{P_oR^{-3}f_1}{\rho_o\psi}\left(\frac{\partial}{\partial t}\left(\rho_o\psi\right) + R^{-3/2}\phi_1\frac{\partial}{\partial r}\left(\rho_o\psi\right)\right) = 0, \qquad (11.44)$$

$$\frac{\partial}{\partial t}\left(R^{-3}f_1\right) + R^{-3/2}\phi_1\frac{\partial}{\partial r}\left(R^{-3}f_1\right)$$
$$-\gamma\frac{R^{-3}f_1}{\psi}\left(\frac{\partial\psi}{\partial t} + R^{-3/2}\phi_1\frac{\partial\psi}{\partial r}\right) = 0, \qquad (11.45)$$

$$R^{-3}\frac{\partial f_1}{\partial t} - 3R^{-4}\frac{dR}{dt}f_1 + R^{-3/2}\phi_1\frac{\partial}{\partial r}\left(R^{-3}f_1\right)$$
$$-\gamma\frac{R^{-3}f_1}{\psi}\left(\frac{\partial\psi}{\partial t} + R^{-3/2}\phi_1\frac{\partial\psi}{\partial r}\right) = 0, \qquad (11.46)$$

$$R^{-3}\left(-\frac{A\eta}{R^{5/2}}\right)\frac{df_1}{d\eta} - 3R^{-4}(AR^{-3/2})f_1 + R^{-3/2}\phi_1\frac{\partial}{\partial r}\left(R^{-3}f_1\right)$$
$$-\gamma\frac{R^{-3}f_1}{\psi}\left(\frac{\partial\psi}{\partial t} + R^{-3/2}\phi_1\frac{\partial\psi}{\partial r}\right) = 0. \qquad (11.47)$$

Carrying on, we have

$$-\frac{A\eta}{R^{11/2}}\frac{df_1}{d\eta} - 3\frac{A}{R^{11/2}}f_1 + R^{-3/2}\phi_1 R^{-3}\frac{1}{R}\frac{df_1}{d\eta}$$

$$-\gamma\frac{R^{-3}f_1}{\psi}\left(\left(-\frac{A\eta}{R^{5/2}}\right)\frac{d\psi}{d\eta}+R^{-3/2}\phi_1\frac{1}{R}\frac{d\psi}{d\eta}\right) = 0, \quad (11.48)$$

$$-\frac{A\eta}{R^{11/2}}\frac{df_1}{d\eta}-3\frac{A}{R^{11/2}}f_1+\frac{\phi_1}{R^{11/2}}\frac{df_1}{d\eta}-\gamma\frac{f_1}{\psi R^{11/2}}\left(-A\eta\frac{d\psi}{d\eta}+\phi_1\frac{d\psi}{d\eta}\right) = 0, \quad (11.49)$$

$$-A\eta\frac{df_1}{d\eta}-3Af_1+\phi_1\frac{df_1}{d\eta}-\gamma\frac{f_1}{\psi}\left(-A\eta\frac{d\psi}{d\eta}+\phi_1\frac{d\psi}{d\eta}\right) = 0. \quad (11.50)$$

Our final form is

$$A\left(3f_1+\eta\frac{df_1}{d\eta}\right)+\gamma\frac{f_1}{\psi}\left(-A\eta+\phi_1\right)\frac{d\psi}{d\eta}-\phi_1\frac{df_1}{d\eta} = 0, \qquad \text{energy.} \qquad (11.51)$$

Equation (11.51) is T(11), correcting for a typographical error replacing a r with γ.

11.4 Dimensionless equations

Let us now write our conservation principles in dimensionless form. We take the constant ambient sound speed c_o to be defined for the calorically perfect ideal gas as

$$c_o^2 \equiv \gamma\frac{P_o}{\rho_o}. \qquad (11.52)$$

Note, we have used our notation for sound speed here; Taylor uses a instead.

Let us also define

$$f \equiv \left(\frac{c_o}{A}\right)^2 f_1, \qquad (11.53)$$

$$\phi \equiv \frac{\phi_1}{A}. \qquad (11.54)$$

11.4.1 Mass

With these definitions, the mass equation, Eq. (11.34) becomes

$$-A\eta\frac{d\psi}{d\eta}+A\phi\frac{d\psi}{d\eta}+\psi\left(A\frac{d\phi}{d\eta}+\frac{2}{\eta}A\phi\right) = 0, \qquad (11.55)$$

$$-\eta\frac{d\psi}{d\eta}+\phi\frac{d\psi}{d\eta}+\psi\left(\frac{d\phi}{d\eta}+\frac{2}{\eta}\phi\right) = 0, \qquad (11.56)$$

$$\frac{d\psi}{d\eta}(\phi-\eta) = -\psi\left(\frac{d\phi}{d\eta}+\frac{2}{\eta}\phi\right), \qquad (11.57)$$

$$\frac{1}{\psi}\frac{d\psi}{d\eta} = \frac{\frac{d\phi}{d\eta}+\frac{2\phi}{\eta}}{\eta-\phi}, \qquad \text{mass.} \qquad (11.58)$$

Equation (11.58) is T(9a).

11.4.2   Linear momentum

With the same definitions, the momentum equation, Eq. (11.42) becomes

$$-A\left(\frac{3}{2}A\phi + A\eta\frac{d\phi}{d\eta}\right) + A^2\phi\frac{d\phi}{d\eta} + \frac{P_o}{\rho_o}\frac{1}{\psi}\frac{A^2}{c_o^2}\frac{df}{d\eta} = 0, \tag{11.59}$$

$$-\left(\frac{3}{2}\phi + \eta\frac{d\phi}{d\eta}\right) + \phi\frac{d\phi}{d\eta} + \frac{1}{\gamma}\frac{1}{\psi}\frac{df}{d\eta} = 0, \tag{11.60}$$

$$\frac{d\phi}{d\eta}(\phi - \eta) - \frac{3}{2}\phi + \frac{1}{\gamma\psi}\frac{df}{d\eta} = 0, \tag{11.61}$$

$$\frac{d\phi}{d\eta}(\eta - \phi) = \frac{1}{\gamma\psi}\frac{df}{d\eta} - \frac{3}{2}\phi, \text{ momentum.} \tag{11.62}$$

Equation (11.62) is T(7a).

11.4.3   Energy

The energy equation, Eq. (11.51) becomes

$$A\left(3\frac{A^2}{c_o^2}f + \eta\frac{A^2}{c_o^2}\frac{df}{d\eta}\right) + \gamma\frac{f}{\psi}\frac{A^2}{c_o^2}(-A\eta + A\phi)\frac{d\psi}{d\eta} - A\frac{A^2}{c_o^2}\phi\frac{df}{d\eta} = 0, \tag{11.63}$$

$$3f + \eta\frac{df}{d\eta} + \gamma\frac{f}{\psi}(-\eta + \phi)\frac{d\psi}{d\eta} - \phi\frac{df}{d\eta} = 0, \tag{11.64}$$

$$3f + \eta\frac{df}{d\eta} + \gamma\frac{1}{\psi}\frac{d\psi}{d\eta}f(-\eta + \phi) - \phi\frac{df}{d\eta} = 0, \text{ energy.} \tag{11.65}$$

Equation (11.65) is T(11a).

11.5   Reduction to non-autonomous form

Let us eliminate $d\psi/d\eta$ and $d\phi/d\eta$ from Eq. (11.65) with use of Eqs. (11.58,11.62).

$$3f + \eta\frac{df}{d\eta} + \gamma f\left(\frac{\frac{d\phi}{d\eta} + \frac{2\phi}{\eta}}{\eta - \phi}\right)(-\eta + \phi) - \phi\frac{df}{d\eta} = 0, \tag{11.66}$$

$$3f + \eta\frac{df}{d\eta} + \gamma f\left(\frac{\frac{\frac{1}{\gamma\psi}\frac{df}{d\eta} - \frac{3}{2}\phi}{\eta - \phi} + \frac{2\phi}{\eta}}{\eta - \phi}\right)(-\eta + \phi) - \phi\frac{df}{d\eta} = 0, \tag{11.67}$$

$$3f + (\eta - \phi)\frac{df}{d\eta} - \gamma f\left(\frac{\frac{1}{\gamma\psi}\frac{df}{d\eta} - \frac{3}{2}\phi}{\eta - \phi} + \frac{2\phi}{\eta}\right) = 0, \tag{11.68}$$

$$3f(\eta - \phi) + (\eta - \phi)^2\frac{df}{d\eta} - \gamma f\left(\frac{1}{\gamma\psi}\frac{df}{d\eta} - \frac{3}{2}\phi + \frac{2\phi}{\eta}(\eta - \phi)\right) = 0, \tag{11.69}$$

$$\left(\left(\eta - \phi\right)^2 - \frac{f}{\psi}\right)\frac{df}{d\eta} - f\left(-3(\eta - \phi) - \frac{3}{2}\gamma\phi + \frac{2\gamma\phi}{\eta}(\eta - \phi)\right) = 0, \qquad (11.70)$$

$$\left(\left(\eta - \phi\right)^2 - \frac{f}{\psi}\right)\frac{df}{d\eta} + f\left(3\eta - 3\phi + \frac{3}{2}\gamma\phi - 2\gamma\phi + \frac{2\gamma\phi^2}{\eta}\right) = 0, \qquad (11.71)$$

$$\left(\left(\eta - \phi\right)^2 - \frac{f}{\psi}\right)\frac{df}{d\eta} + f\left(3\eta - \phi\left(3 + \frac{1}{2}\gamma\right) + \frac{2\gamma\phi^2}{\eta}\right) = 0. \qquad (11.72)$$

Rearranging, we get

$$\left(\left(\eta - \phi\right)^2 - \frac{f}{\psi}\right)\frac{df}{d\eta} = f\left(-3\eta + \phi\left(3 + \frac{1}{2}\gamma\right) - \frac{2\gamma\phi^2}{\eta}\right). \qquad (11.73)$$

$$(11.74)$$

Equation (11.73) is T(14).

We can thus write an explicit non-autonomous ordinary differential equation for the evolution of f in terms of the state variables f, ψ, and ϕ, as well as the independent variable η.

$$\frac{df}{d\eta} = \frac{f\left(-3\eta + \phi\left(3 + \frac{1}{2}\gamma\right) - \frac{2\gamma\phi^2}{\eta}\right)}{(\eta - \phi)^2 - \frac{f}{\psi}}. \qquad (11.75)$$

Eq. (11.75) can be directly substituted into the momentum equation, Eq. (11.62) to get

$$\frac{d\phi}{d\eta} = \frac{\frac{1}{\gamma\psi}\frac{df}{d\eta} - \frac{3}{2}\phi}{\eta - \phi}. \qquad (11.76)$$

Then, Eq. (11.76) can be substituted into Eq. (11.58) to get

$$\frac{d\psi}{d\eta} = \psi\frac{\frac{d\phi}{d\eta} + \frac{2\phi}{\eta}}{\eta - \phi}. \qquad (11.77)$$

Equations (11.75-11.77) form a non-autonomous system of first order differential equations of the form

$$\frac{df}{d\eta} = g_1(f, \phi, \psi, \eta), \qquad (11.78)$$

$$\frac{d\phi}{d\eta} = g_2(f, \phi, \psi, \eta), \qquad (11.79)$$

$$\frac{d\psi}{d\eta} = g_3(f, \phi, \psi, \eta). \qquad (11.80)$$

They can be integrated with standard numerical software. One must of course provide conditions of all state variables at a particular point. We apply conditions not at $\eta = 0$, but

at $\eta = 1$, the locus of the shock front. Following Taylor, the conditions are taken from the Rankine-Hugoniot equations applied in the limit of a strong shock. We take the subscript s to denote the shock state at $\eta = 1$. For the density, one applies Eq. (10.313) and finds

$$\frac{\rho_s}{\rho_o} = \frac{\gamma + 1}{\gamma - 1}, \tag{11.81}$$

$$\frac{\rho_o \psi_s}{\rho_o} = \frac{\gamma + 1}{\gamma - 1}, \tag{11.82}$$

$$\psi_s = \psi(\eta = 1) = \frac{\gamma + 1}{\gamma - 1}. \tag{11.83}$$

For the pressure, one finds, by slight modification of Eq. (10.319) (taking $D^2 = (dR/dt)^2$), that

$$\frac{\frac{dR}{dt}^2}{c_o^2} = \frac{\gamma + 1}{2\gamma} \frac{P_s}{P_o}, \tag{11.84}$$

$$\frac{A^2 R^{-3}}{c_o^2} = \frac{\gamma + 1}{2\gamma} R^{-3} f_{1s}, \tag{11.85}$$

$$\frac{A^2 R^{-3}}{c_o^2} = \frac{\gamma + 1}{2\gamma} R^{-3} \frac{A^2}{c_o^2} f_s, \tag{11.86}$$

$$1 = \frac{\gamma + 1}{2\gamma} f_s, \tag{11.87}$$

$$f_s = f(\eta = 1) = \frac{2\gamma}{\gamma + 1}. \tag{11.88}$$

For the velocity, using Eq. (10.326), one finds

$$\frac{u_s}{\frac{dR}{dt}} = \frac{2}{\gamma + 1}, \tag{11.89}$$

$$\frac{R^{-3/2} \phi_{1s}}{A R^{-3/2}} = \frac{2}{\gamma + 1}, \tag{11.90}$$

$$\frac{R^{-3/2} A \phi_s}{A R^{-3/2}} = \frac{2}{\gamma + 1}, \tag{11.91}$$

$$\phi_s = \phi(\eta = 1) = \frac{2}{\gamma + 1}. \tag{11.92}$$

Equations (11.83, 11.88, 11.92) form the appropriate set of initial conditions for the integration of Eqs. (11.75-11.77).

11.6 Numerical solution

Solutions for $f(\eta)$, $\phi(\eta)$ and $\psi(\eta)$ are shown for $\gamma = 7/5$ in Figs. 11.1-11.3, respectively.
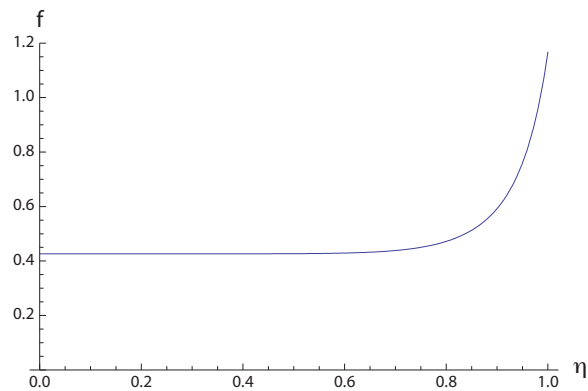
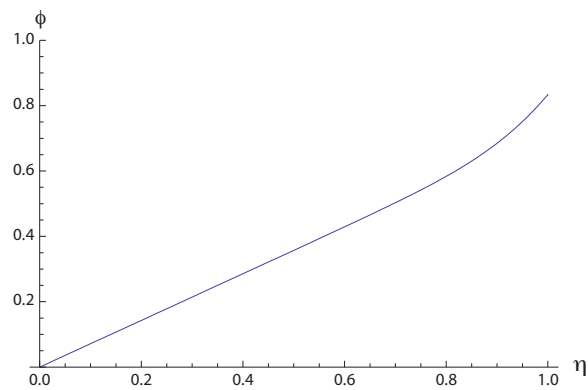Figure 11.1: Scaled pressure f versus similarity variable η for $\gamma = 7/5$ in Taylor-Sedov blast wave.

Figure 11.2: Scaled velocity ϕ versus similarity variable η for $\gamma = 7/5$ in Taylor-Sedov blast wave.
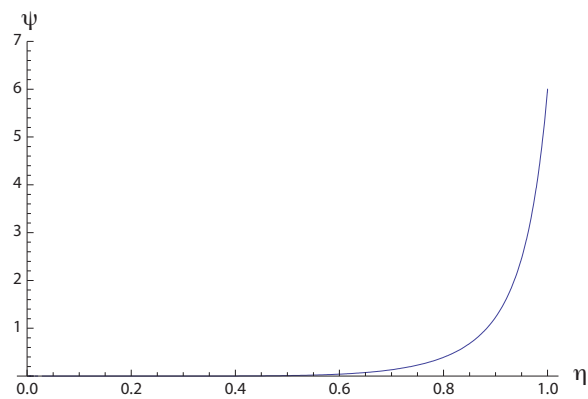

Figure 11.3: Scaled density ψ versus similarity variable η for $\gamma = 7/5$ in Taylor-Sedov blast wave.

So, we now have a similarity solution for the scaled variables. We need to relate this to physical dimensional quantities. Let us assign some initial conditions for $t = 0$, $r > 0$; that is, away from the point source. Take

$$u(r, 0) = 0, \quad \rho(r, 0) = \rho_o, \quad P(r, 0) = P_o. \tag{11.93}$$

We also have from the ideal gas law

$$T(r, 0) = \frac{P_o}{\rho_o R} = T_o. \tag{11.94}$$

For the calorically perfect gas we further have

$$e(r, 0) = \frac{1}{\gamma - 1} \frac{P_o}{\rho_o} = e_o. \tag{11.95}$$

11.6.1   Calculation of total energy

Now, as the point source expands, it will generate a strong shock wave. Material which has not been shocked is oblivious to the presence of the shock. Material which the shock wave has reached has been influenced by it. It stands to reason from energy conservation principles that we want the total energy, internal plus kinetic, to be *constant* in the shocked domain, $r \in (0, R(t)]$, where $R(t)$ is the shock front location.

Let us recall some spherical geometry so this energy conservation principle can be properly formulated. Consider a thin differential spherical shell of thickness dr located somewhere in the shocked region: $r \in (0, R(t)]$. The volume of the thin shell is

$$dV = \underbrace{4\pi r^2}_{\text{(surface area)}} \underbrace{dr}_{\text{(thickness)}} \tag{11.96}$$

The differential mass dm of this shell is

$$dm \;=\; \rho dV, \tag{11.97}$$

$$\;=\; 4\pi r^2 \rho dr. \tag{11.98}$$

Now, recall the mass-specific internal energy is e and the mass-specific kinetic energy is $u^2/2$. So, the total differential energy, internal plus kinetic, in the differential shell is

$$dE \;=\; \left(e + \frac{1}{2}u^2\right) dm, \tag{11.99}$$

$$\;=\; 4\pi\rho \left(e + \frac{1}{2}u^2\right) r^2 dr. \tag{11.100}$$

Now, the total energy E within the shock is the integral through the entire sphere,

$$E = \int_0^{R(t)} dE = \int_0^{R(t)} 4\pi\rho\left(e + \frac{1}{2}u^2\right)r^2 dr, \tag{11.101}$$

$$= \int_0^{R(t)} 4\pi\rho\left(\frac{1}{\gamma-1}\frac{P}{\rho} + \frac{1}{2}u^2\right)r^2 dr, \tag{11.102}$$

$$= \underbrace{\frac{4\pi}{\gamma-1}\int_0^{R(t)} Pr^2 dr}_{\text{thermal energy}} + \underbrace{2\pi\int_0^{R(t)} \rho u^2 r^2 dr}_{\text{kinetic energy}}. \tag{11.103}$$

We introduce variables from our similarity transformations next:

$$E = \frac{4\pi}{\gamma-1}\int_0^1 \underbrace{P_o R^{-3} f_1}_{P}\underbrace{R^2\eta^2}_{r^2}\underbrace{R d\eta}_{dr} + 2\pi\int_0^1 \underbrace{\rho_o\psi}_{\rho}\underbrace{R^{-3}\phi_1^2}_{u^2}\underbrace{R^2\eta^2}_{r^2}\underbrace{R d\eta}_{dr}, \tag{11.104}$$

$$= \frac{4\pi}{\gamma-1}\int_0^1 P_o f_1\eta^2 d\eta + 2\pi\int_0^1 \rho_o\psi\phi_1^2\eta^2 d\eta, \tag{11.105}$$

$$= \frac{4\pi}{\gamma-1}\int_0^1 \frac{P_o A^2}{c_o^2}f\eta^2 d\eta + 2\pi\int_0^1 \rho_o\psi A^2\phi^2\eta^2 d\eta, \tag{11.106}$$

$$= 4\pi A^2\left(\frac{P_o}{c_o^2(\gamma-1)}\int_0^1 f\eta^2 d\eta + \frac{\rho_o}{2}\int_0^1 \psi\phi^2\eta^2 d\eta\right), \tag{11.107}$$

$$= 4\pi A^2\rho_o\underbrace{\left(\frac{1}{\gamma(\gamma-1)}\int_0^1 f\eta^2 d\eta + \frac{1}{2}\int_0^1 \psi\phi^2\eta^2 d\eta\right)}_{\text{dependent on }\gamma\text{ only}}. \tag{11.108}$$

The term inside the parentheses is dependent on γ only. So, if we consider air with $\gamma = 7/5$, we can, using our knowledge of $f(\eta)$, $\psi(\eta)$, and $\phi(\eta)$, which only depend on γ, to calculate once and for all the value of the integrals. For $\gamma = 7/5$, we obtain via numerical quadrature

$$E = 4\pi A^2\rho_o\left(\frac{1}{(7/5)(2/5)}(0.185194) + \frac{1}{2}(0.185168)\right), \tag{11.109}$$

$$= 5.3192\rho_o A^2. \tag{11.110}$$

Now, from Eq. (11.17, 11.52,11.53, 11.110) with $\gamma = 7/5$, we get

$$P = P_o R^{-3} f\frac{A^2}{c_o^2}, \tag{11.111}$$

$$= P_o R^{-3} f\frac{\rho_o}{\gamma P_o}A^2, \tag{11.112}$$

$$= R^{-3} f\frac{1}{\gamma}\rho_o A^2, \tag{11.113}$$

$$= R^{-3} f \frac{1}{\frac{7}{5}} \frac{E}{5.3192}, \tag{11.114}$$

$$= 0.1343 R^{-3} E f, \tag{11.115}$$

$$P(r,t) = 0.1343 \frac{E}{R^3(t)} f\left(\frac{r}{R(t)}\right). \tag{11.116}$$

The peak pressure occurs at $\eta = 1$, where $r = R$, and where

$$f(\eta = 1) = \frac{2\gamma}{\gamma + 1} = \frac{2(1.4)}{1.4 + 1} = 1.167. \tag{11.117}$$

So, at $\eta = 1$, where $r = R$, we have

$$P = (0.1343)(1.167)R^{-3}E = 0.1567 \frac{E}{R^3}. \tag{11.118}$$

The peak pressure decays at a rate proportional to $1/R^3$ in the strong shock limit.

Now, from Eqs. (11.19,11.54,11.110) we get for u:

$$u = R^{-3/2} A \phi, \tag{11.119}$$

$$= R^{-3/2} \sqrt{\frac{E}{5.319 \rho_o}} \phi, \tag{11.120}$$

$$u(r,t) = \sqrt{\frac{E}{5.319 \rho_o}} \frac{1}{R^{3/2}(t)} \phi\left(\frac{r}{R(t)}\right). \tag{11.121}$$

Let us now explicitly solve for the shock position $R(t)$ and the shock velocity dR/dt. We have from Eqs. (11.20, 11.110) that

$$\frac{dR}{dt} = A R^{-3/2}, \tag{11.122}$$

$$= \sqrt{\frac{E}{5.319 \rho_o}} \frac{1}{R^{3/2}(t)}, \tag{11.123}$$

$$R^{3/2} dR = \sqrt{\frac{E}{5.319 \rho_o}} dt, \tag{11.124}$$

$$\frac{2}{5} R^{5/2} = \sqrt{\frac{E}{5.319 \rho_o}} t + C. \tag{11.125}$$

Now, since $R(0) = 0$, we get $C = 0$, so

$$\frac{2}{5} R^{5/2} = \sqrt{\frac{E}{5.319 \rho_o}} t, \tag{11.126}$$

$$t = \frac{2}{5} R^{5/2} \sqrt{5.319 \rho_o} E^{-1/2}, \tag{11.127}$$

$$= 0.9225 R^{5/2} \rho_o^{1/2} E^{-1/2}. \tag{11.128}$$

Equation (11.128) is T(38). Solving for R, we get

$$R^{5/2} = \frac{1}{0.9225} t \rho_o^{-1/2} E^{1/2}, \tag{11.129}$$

$$R(t) = 1.03279 \rho_o^{-1/5} E^{1/5} t^{2/5}. \tag{11.130}$$

Thus, we have a prediction for the shock location as a function of time t, as well as point source energy E. If we know the position as a function of time, we can easily get the shock velocity by direct differentiation:

$$\frac{dR}{dt} = 0.4131 \rho_o^{-1/5} E^{1/5} t^{-3/5}. \tag{11.131}$$

If we can make a measurement of the blast wave location R at a given known time t, and we know the ambient density ρ_o, we can estimate the point source energy E. Let us invert Eq. (11.130) to solve for E and get

$$E = \frac{\rho_o R^5}{(1.03279)^5 t^2}, \tag{11.132}$$

$$= 0.85102 \frac{\rho_o R^5}{t^2}. \tag{11.133}$$

11.6.2 Comparison with experimental data

Now, Taylor's Part II paper from 1950 gives data for the 19 July 1945 atomic explosion at the Trinity site in New Mexico. We choose one point from the photographic record which finds the shock from the blast to be located at $R = 185\ m$ when $t = 62\ ms$. Let us assume the ambient air has a density of $\rho_o = 1.161\ kg/m^3$. Then, we can estimate the energy of the device by Eq. (11.133) as

$$E = 0.85102 \frac{\left(1.161\ \frac{kg}{m^3}\right) (185\ m)^5}{(0.062\ s)^2}, \tag{11.134}$$

$$= 55.7 \times 10^{12}\ J. \tag{11.135}$$

Now, 1 *ton* of the high explosive TNT is known to contain $4.25 \times 10^9\ J$ of chemical energy. So, the estimated energy of the Trinity site device in terms of a TNT equivalent is

$$TNT_{equivalent} = \frac{55.7 \times 10^{12}\ J}{4.25 \times 10^9\ \frac{J}{ton}} = 13.1 \times 10^3\ ton. \tag{11.136}$$

In common parlance, the Trinity site device was a 13 *kiloton* bomb by this simple estimate. Taylor provides some nuanced corrections to this estimate. Modern estimates are now around 20 *kiloton*.

11.7   Contrast with acoustic limit

We saw in Eq. (11.118) that in the expansion associated with a strong shock, the pressure decays as $1/R^3$. Let us see how that compares with the decay of pressure in the limit of a weak shock.

Let us first rewrite the governing equations. Here, we 1) rewrite Eq. (11.1) in a conservative form, using the chain rule to absorb the source term inside the derivative, 2) repeat the linear momentum equation, Eq. (11.2), and 3) re-cast the energy equation for a calorically perfect ideal gas, Eq. (11.11) in terms of the full partial derivatives:

$$\frac{\partial \rho}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \rho u\right) = 0, \tag{11.137}$$

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial r} + \frac{1}{\rho}\frac{\partial P}{\partial r} = 0, \tag{11.138}$$

$$\frac{\partial P}{\partial t} + u\frac{\partial P}{\partial r} - \gamma\frac{P}{\rho}\left(\frac{\partial \rho}{\partial t} + u\frac{\partial \rho}{\partial r}\right) = 0. \tag{11.139}$$

Now, let us consider the acoustic limit, which corresponds to perturbations of a fluid at rest. Taking $0 < \epsilon \ll 1$, we recast the dependent variables ρ, P, and u as

$$\rho = \rho_o + \epsilon\rho_1 + \ldots, \tag{11.140}$$

$$P = P_o + \epsilon P_1 + \ldots, \tag{11.141}$$

$$u = \underbrace{u_o}_{=0} + \epsilon u_1 + \ldots. \tag{11.142}$$

Here, ρ_o and P_o are taken to be constants. The ambient velocity $u_o = 0$. Strictly speaking, we should non-dimensionalize the equations before we introduce an asymptotic expansion. However, so doing would not change the essence of the argument to be made.

We next introduce our expansions into the governing equations:

$$\frac{\partial}{\partial t}\left(\rho_o + \epsilon\rho_1\right) + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\left(\rho_o + \epsilon\rho_1\right)\left(\epsilon u_1\right)\right) = 0, \tag{11.143}$$

$$\frac{\partial}{\partial t}(\epsilon u_1) + (\epsilon u_1)\frac{\partial}{\partial r}(\epsilon u_1) + \frac{1}{\rho_o + \epsilon\rho_1}\frac{\partial}{\partial r}\left(P_o + \epsilon P_1\right) = 0, \tag{11.144}$$

$$\frac{\partial}{\partial t}\left(P_o + \epsilon P_1\right) + (\epsilon u_1)\frac{\partial}{\partial r}\left(P_o + \epsilon P_1\right)$$
$$-\gamma\frac{P_o + \epsilon P_1}{\rho_o + \epsilon\rho_1}\left(\frac{\partial}{\partial t}\left(\rho_o + \epsilon\rho_1\right) + (\epsilon u_1)\frac{\partial}{\partial r}\left(\rho_o + \epsilon\rho_1\right)\right) = 0. \tag{11.145}$$

Now, derivatives of constants are all zero, and so at leading order the constant state satisfies the governing equations. At $\mathcal{O}(\epsilon)$, the equations reduce to

$$\frac{\partial \rho_1}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\rho_o u_1) = 0, \tag{11.146}$$

$$\frac{\partial u_1}{\partial t} + \frac{1}{\rho_o}\frac{\partial P_1}{\partial r} = 0, \tag{11.147}$$

$$\frac{\partial P_1}{\partial t} - \gamma\frac{P_o}{\rho_o}\frac{\partial \rho_1}{\partial t} = 0. \tag{11.148}$$

Now, adopt as before $c_o^2 = \gamma P_o/\rho_o$, so the energy equation, Eq. (11.148), becomes

$$\frac{\partial P_1}{\partial t} = c_o^2\frac{\partial \rho_1}{\partial t}. \tag{11.149}$$

Now, substitute Eq. (11.149) into the mass equation, Eq. (11.146), to get

$$\frac{1}{c_o^2}\frac{\partial P_1}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\rho_o u_1) = 0. \tag{11.150}$$

We take the time derivative of Eq. (11.150) to get

$$\frac{1}{c_o^2}\frac{\partial^2 P_1}{\partial t^2} + \frac{\partial}{\partial t}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\rho_o u_1\right)\right) = 0, \tag{11.151}$$

$$\frac{1}{c_o^2}\frac{\partial^2 P_1}{\partial t^2} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\rho_o\frac{\partial u_1}{\partial t}\right) = 0. \tag{11.152}$$

We next use the momentum equation, Eq. (11.147), to eliminate $\partial u_1/\partial t$ in Eq. (11.152):

$$\frac{1}{c_o^2}\frac{\partial^2 P_1}{\partial t^2} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\rho_o\left(-\frac{1}{\rho_o}\frac{\partial P_1}{\partial r}\right)\right) = 0, \tag{11.153}$$

$$\frac{1}{c_o^2}\frac{\partial^2 P_1}{\partial t^2} - \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial P_1}{\partial r}\right) = 0, \tag{11.154}$$

$$\frac{1}{c_o^2}\frac{\partial^2 P_1}{\partial t^2} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial P_1}{\partial r}\right). \tag{11.155}$$

This second-order linear partial differential equation has a well-known solution of the D'Alembert form:

$$P_1 = \frac{1}{r}g\left(t - \frac{r}{c_o}\right) + \frac{1}{r}h\left(t + \frac{r}{c_o}\right). \tag{11.156}$$

Here, g and h are arbitrary functions which are chosen to match the initial conditions. Let us check this solution for g; the procedure can easily be repeated for h.

If $P_1 = (1/r)g(t - r/c_o)$, then

$$\frac{\partial P_1}{\partial t} = \frac{1}{r}g'\left(t - \frac{r}{c_o}\right), \tag{11.157}$$

$$\frac{\partial^2 P_1}{\partial t^2} = \frac{1}{r}g''\left(t - \frac{r}{c_o}\right), \tag{11.158}$$

and

$$\frac{\partial P_1}{\partial r} = -\frac{1}{c_o}\frac{1}{r}g'\left(t-\frac{r}{c_o}\right) - \frac{1}{r^2}g\left(t-\frac{r}{c_o}\right). \tag{11.159}$$

With these results, let us substitute into Eq. (11.155) to see if it is satisfied:

$$\frac{1}{c_o^2}\frac{1}{r}g''\left(t-\frac{r}{c_o}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\left(-\frac{1}{c_o}\frac{1}{r}g'\left(t-\frac{r}{c_o}\right) - \frac{1}{r^2}g\left(t-\frac{r}{c_o}\right)\right)\right), \tag{11.160}$$

$$= -\frac{1}{r^2}\frac{\partial}{\partial r}\left(\frac{r}{c_o}g'\left(t-\frac{r}{c_o}\right) + g\left(t-\frac{r}{c_o}\right)\right), \tag{11.161}$$

$$= -\frac{1}{r^2}\left(-\frac{r}{c_o^2}g''\left(t-\frac{r}{c_o}\right) + \frac{1}{c_o}g'\left(t-\frac{r}{c_o}\right) - \frac{1}{c_o}g'\left(t-\frac{r}{c_o}\right)\right), \tag{11.162}$$

$$= \frac{1}{r^2}\left(\frac{r}{c_o^2}g''\left(t-\frac{r}{c_o}\right)\right), \tag{11.163}$$

$$= \frac{1}{c_o^2}\frac{1}{r}g''\left(t-\frac{r}{c_o}\right). \tag{11.164}$$

Indeed, our form of $P_1(r,t)$ satisfies the governing partial differential equation. Moreover, we can see by inspection of Eq. (11.156) that the pressure decays as does $1/r$ in the limit of acoustic disturbances. This is a much slower rate of decay than for the blast wave, which goes as the inverse cube of radius.

Bibliography

Here, we give a summary of some of the major books relevant to these lecture notes. Specific journal articles are not cited, though the main text of the lecture notes occasionally draws on such articles where relevant. The emphasis is on combustion, physical chemistry, and thermodynamics, with some mathematics. Some general works of historic importance are also included. The list is by no means comprehensive.

M. M. Abbott and H. C. van Ness, 1972, *Thermodynamics*, Schaum's Outline Series in Engineering, McGraw-Hill, New York.

> This is written in the style of all the Schaum's series. It has extensive solved problems and a crisp rigorous style that is readable by undergraduate engineers. It has a chemical engineering emphasis, but is also useful for all engineers.

R. Aris, 1962, *Vectors, Tensors, and the Basic Equations of Fluid Mechanics*, Dover, New York.

> This book is a jewel of continuum mechanics theory. It is brief and incisive. While the focus is on the inert Navier-Stokes equations, there is a short, excellent chapter on the reactive Navier-Stokes equations. Highly recommended.

J. Bebernes and D. Eberly, 1989, *Mathematical Problems from Combustion Theory*, Springer, Berlin.

> This monograph focuses on mathematical analysis of combustion systems, focusing on blowup phenomena.

A. Bejan, 2006, *Advanced Engineering Thermodynamics*, Third Edition, John Wiley, Hoboken, New Jersey.

> This is an advanced undergraduate text. It gives a modern treatment of the science of classical thermodynamics. It does not confine its attention to traditional engineering problems, and considers applications across biology and earth sciences as well. The thermodynamics of irreversible processes are discussed in detail.

R. S. Berry, S. A. Rice, and J. Ross,, 2000, *Physical Chemistry*, Second Edition, Oxford University Press, Oxford.

> This is a rigorous general text in physical chemistry at a senior or first year graduate level. It has a full treatment of classical and statistical thermodynamics as well as quantum mechanics.

R. B. Bird, W. E. Stewart, and E. N. Lightfoot, 2006, *Transport Phenomena*, Second Edition, Wiley, New York.

This acknowledged classic of the chemical engineering literature does not focus on reaction, but has an exemplary treatment of mass, momentum, and energy advection-diffusion phenomena.

L. Boltzmann, 1995, *Lectures on Gas Theory*, Dover, New York.

This is a detailed monograph by the founding father of statistical thermodynamics.

C. Borgnakke, and R. E. Sonntag, 2009, *Fundamentals of Thermodynamics*, Seventh Edition, John Wiley, New York.

This classic and popular undergraduate mechanical engineering text has stood the test of time and has a full treatment of most classical problems.

R. Boyle, 2003, *The Sceptical Chymist*, Dover, New York.

This is the original work of the famous early figure of the scientific revolution.

J. D. Buckmaster and G. S. S. Ludford, 1983, *Lectures on Mathematical Combustion*, SIAM, Philadelphia.

This is set of lecture notes which serves as an excellent graduate-level introduction to some of the mathematical challenges of combustion.

J. D. Buckmaster and G. S. S. Ludford, 2008, *Theory of Laminar Flames*, Cambridge, Cambridge.

This seminal monograph, first published in 1982, highlights rigorous mathematical methods applied to laminar flames.

H. B. Callen, 1985, *Thermodynamics and an Introduction to Thermostatistics*, Second Edition, John Wiley, New York.

This advanced undergraduate text has an emphasis on classical physics applied to thermodynamics, with a few chapters devoted to quantum and statistical foundations.

S. Carnot, 2005, *Reflections on the Motive Power of Fire*, Dover, New York.

This is the original source of Carnot's foundational work on the heat engines. Also included is a paper of Clausius.

N. Chigier, 1981, *Energy, Combustion, and Environment*, McGraw-Hill, New York.

This advanced undergraduate text gives an integrated science-based discussion of the topic matter stated in its title.

R. Courant and K. O. Friedrichs, 1999, *Supersonic Flow and Shock Waves*, Springer, New York.

This seminal mathematical treatment of inviscid compressible flow gives an outstanding and rigorous discussion of the application of partial differential equations to fluid mechanics. There is only a small discussion of combustion, but the methods are of high relevance in high speed reactive flow.

S. R. de Groot and P. Mazur, 1984, *Non-Equilibrium Thermodynamics*, Dover, New York.

This is an influential monograph which summarizes much of the work of the famous Belgian school of thermodynamics. It is written at a graduate level and has a strong link to fluid mechanics and chemical reactions.

E. Fermi, 1936, *Thermodynamics*, Dover, New York.

This short classic clearly and efficiently summarizes the fundamentals of thermodynamics. It is based on a series of lectures given by this Nobel prize winner.

W. Fickett and W. C. Davis, 1979, *Detonation*, U. California, Berkeley.

This distinctive monograph has a rich and focused discussion on detonation science. It opens with the relevant physical chemistry, then gives detailed exposition on the theory of detonation. Careful discussion of experiment is also included.

I. Glassman and R. Yetter, 2008, *Combustion*, Fourth Edition, Academic Press, New York.

This well known monograph gives a good description of important combustion phenomena.

W. T. Grandy, 2008, *Entropy and the Time Evolution of Macroscopic Systems*, Oxford, Oxford.

This monograph gives an enlightening description, fully informed by both historical and modern interpretations, of entropy and its evolution in the context of both continuum and statistical theories.

J. F. Griffiths and J. A. Barnard, 1995, *Flame and Combustion*, Third Edition, Chapman and Hall, Glasgow.

This is a graduate level text in combustion.

E. P. Gyftopoulos and G. P. Beretta, 1991, *Thermodynamics: Foundations and Applications*, Macmillan, New York.

This beginning graduate text has a rigorous development of classical thermodynamics.

J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, 1954, *Molecular Theory of Gases and Liquids*, Wiley, New York.

This comprehensive tome is a valuable addition to any library of thermal science. Its wide ranging text covers equations of state, molecular collision theory, reactive hydrodynamics, reaction kinetics, and many other topics all from the point of view of careful physical chemistry. Much of the work remains original.

W. Hundsdorfer and J. G. Verwer, 2003, *Numerical Solution of Time-Dependent Advection-Diffusion-Reaction Equations*, Springer, Berlin.

> This nice graduate level monograph focuses on modern numerical techniques for paradigm reactive flow systems. The systems themselves are easy to pose which allows effective exposition of the key challenges in numerical modelling.

A. M. Kanury, 1975, *Introduction to Combustion Phenomena*, Gordon and Breach, Amsterdam.

> This introductory graduate level text gives practical problems and good discussion of combustion phenomena.

A. K. Kapila, 1983, *Asymptotic Treatment of Chemically Reacting Systems*, Pitman, Boston.

> This short introductory monograph gives lecture notes on asymptotic analysis as applied to combustion.

E. L. Keating, 2007, *Applied Combustion*, Second Edition, CRC Press, Boca Raton, FL.

> This book is an engineering text for seniors or first year graduate students with a general coverage of topics.

J. Kestin, 1966, *A Course in Thermodynamics*, Blaisdell, Waltham, Massachusetts.

> This is a foundational textbook that can be read on many levels. All first principles are reported in a readable fashion. In addition the author makes a great effort to expose the underlying mathematical foundations of thermodynamics.

R. J. Key, M. E. Coltrin, and P. Glarborg, 2003, *Chemically Reacting Flow: Theory and Practice*, John Wiley, New York.

> This comprehensive text gives an introductory graduate level discussion of fluid mechanics, thermochemistry, and finite rate chemical kinetics. The focus is on low Mach number flows, and there is significant discussion of how to achieve computational solutions.

C. Kittel and H. Kroemer, 1980, *Thermal Physics*, Second Edition, Freeman, San Francisco.

> This is a classic undergraduate text for physics students. It has a good introduction to statistical thermodynamics and a short effective chapter on classical thermodynamics.

D. Kondepudi and I. Prigogine, 1998, *Modern Thermodynamics: From Heat Engines to Dissipative Structures*, John Wiley, New York.

> Detailed modern exposition which exploits the authors' unique vision of thermodynamics with both a science and engineering flavor.

V. P. Korobeinikov, 1989, *Unsteady Interaction of Shock and Detonation Waves in Gases*, Taylor and Francis, New York.

> This is a graduate level monograph.

K. K. Kuo, 2005, *Principles of Combustion*, Second Edition, John Wiley, New York.

This is a readable graduate level engineering text for combustion fundamentals. It includes a full treatment of reacting thermodynamics as well as discussion of links to fluid mechanics.

K. J. Laidler, 1965, *Chemical Kinetics*, McGraw-Hill, New York.

This is a standard advanced undergraduate chemistry text on the dynamics of chemical reactions.

L. D. Landau and E. M. Lifshitz, 1987, *Fluid Mechanics*, Second Edition, Butterworh-Heinemann, Oxford.

This classic comprehensive text of fluid physics contains a small discussion of reactive flow.

B. H. Lavenda, 1978, *Thermodynamics of Irreversible Processes*, John Wiley, New York.

This is a lively and opinionated monograph describing and commenting on irreversible thermodynamics. The author is especially critical of the Prigogine school of thought on entropy production rate minimization.

A. Lavoisier, 1984, *Elements of Chemistry*, Dover, New York.

This is the classic treatise which gives the first explicit statement of mass conservation in chemical reactions.

C. K. Law, 2006, *Combustion Physics*, Cambridge, Cambridge.

This modern text is a comprehensive graduate level discussion of combustion theory.

J. H. S. Lee, 2008, *The Detonation Phenomenon*, Cambridge, Cambridge.

This is a graduate level monograph focusing on detonation.

B. Lewis and G. von Elbe, 1961, *Combustion, Flames and Explosions of Gases*, Academic Press, New York.

For many years this was the graduate text in combustion. It has a fine description of scientific combustion experiments and good discussion of the key mechanisms of combustion.

H. W. Liepmann and A. Roshko, 1957, *Elements of Gasdynamics*, John Wiley, New York.

This is an influential text in compressible aerodynamics that is appropriate for seniors or beginning graduate students. It has a strong treatment of the physics and thermodynamics of compressible flow along with elegant and efficient text. Its treatment of both experiment and the underlying theory is outstanding.

J. C. Maxwell, 2001, *Theory of Heat*, Dover, New York.

This is a short readable book by the 19th century master. Here, the mathematics is minimized in favor of more words of explanation.

M. J. Moran and H. N. Shapiro, 2010, *Fundamentals of Engineering Thermodynamics*, Seventh Edition, John Wiley, New York.

This is a standard undergraduate thermodynamics text, and one of the more popular. *Note: some examples in this set of notes have been adopted from the 1992 Second Edition of this text.*

I. Müller and T. Ruggeri, 1998, *Rational Extended Thermodynamics*, Springer-Verlag, New York.

This modern monograph gives a rigorous treatment of some of the key issues in modern continuum mechanics and classical thermodynamics.

I. Müller and W. Weiss, 2005, *Entropy and Energy*, Springer-Verlag, New York.

This is a unique treatise on fundamental concepts in thermodynamics. The author provide mathematical rigor, historical perspective, and examples from a diverse set of scientific fields.

I. Müller, 2007, *A History of Thermodynamics: The Doctrine of Energy and Entropy*, Springer-Verlag, New York.

The author gives a readable text at an undergraduate level which highlights some of the many controversies of thermodynamics, both ancient and modern.

E. S. Oran and J. P. Boris, 2001, *Numerical Simulation of Reactive Flow*, Second Edition, Cambridge, Cambridge.

This monograph by two of the leading figures of computational combustion gives a good discussion of numerical challenges as well as physically relevant problems.

W. Pauli, 2000, *Thermodynamics and the Kinetic Theory of Gases*, Dover, New York.

This is a monograph on thermodynamics by a well known physicist.

L. Perko, 2001, *Differential Equations and Dynamical Systems*, Third Edition, Springer, New York.

This monograph gives no explicit discussion of combustion but does give an outstanding treatment of dynamic systems theory.

M. Planck, 1945, *Treatise on Thermodynamics*, Dover, New York.

This brief book gives many unique insights from a great physicist.

T. Poinsot and D. Veynante, 2005, *Theoretical and Numerical Combustion*, Second Edition, Edwards, Flourtown, PA.

This is a useful graduate level introduction to combustion.

I. Prigogine, 1967, *Introduction to Thermodynamics of Irreversible Processes*, Third Edition, Interscience, New York.

This is a famous book that summarizes the essence of the work of the Belgian school for which the author was awarded the Nobel prize.

K. W. Ragland and K. M. Bryden, 2011, *Combustion Engineering*, Second Edition, CRC Press, Boca Raton.

This is a beginning graduate text in combustion engineering.

L. E. Reichl, 1998, *A Modern Course in Statistical Physics*, John Wiley, New York.

This full service graduate text has a good summary of key concepts of classical thermodynamics and a strong development of modern statistical thermodynamics.

W. C. Reynolds, 1968, *Thermodynamics*, Second Edition, McGraw-Hill, New York.

This is an unusually good undergraduate text written for mechanical engineers. The author has wonderful qualitative problems in addition to the usual topics in such texts. A good introduction to statistical mechanics is included as well. Highly recommended.

D. E. Rosner, 2000, *Transport Processes in Chemically Reacting Flow Systems*, Dover, New York.

This graduate level monograph gives a chemical engineering perspective on reaction engineering in fluid systems.

S. I. Sandler, 1998, *Chemical and Engineering Thermodynamics*, Third Edition, John Wiley, New York.

Advanced undergraduate text in thermodynamics from a chemical engineering perspective with a good mathematical treatment.

E. Schrodinger, 1989, *Statistical Thermodynamics*, Dover, New York.

This is a short monograph written by the one of the pioneers of quantum physics.

A. H. Shapiro, 1953, *The Dynamics and Thermodynamics of Compressible Fluid Flow*, Vols. I and II, John Wiley, New York.

This classic two volume set has a comprehensive treatment of the subject of its title. It has numerous worked example problems, and is written from an engineer's perspective.

J. M. Smith, H. C. van Ness, and M. Abbott, 2004, *Introduction to Chemical Engineering Thermodynamics*, Seventh Edition, McGraw-Hill, New York.

This is probably the most common undergraduate text in thermodynamics in chemical engineering. It is rigorous and has went through many revisions.

R. A. Strehlow, 1984, *Combustion Fundamentals*, McGraw-Hill, New York.

This graduate level text has a nice discussion of physical chemistry followed by good descriptions of the author's seminal work in detonation experiments, among other standard combustion topics.

K. Terao, 2007, *Irreversible Phenomena: Ignitions, Combustion, and Detonation Waves*, Springer, Berlin.

This unique monograph links irreversible thermodynamics with phase transition, ignition and detonation.

J. W. Tester and M. Modell, 1997, *Thermodynamics and Its Applications*, Third Edition, Prentice Hall, Upper Saddle River, New Jersey.

This entry level graduate text in thermodynamics is written from a chemical engineer's perspective. It has a strong mathematical development for both classical and statistical thermodynamics.

T.-Y. Toong, 1982, *Combustion Dynamics: The Dynamics of Chemically Reacting Fluids*, McGraw-Hill, New York.

This is an entry level graduate text on combustion science.

C. A. Truesdell, 1980, *The Tragicomic History of Thermodynamics, 1822-1854*, Springer Verlag, New York.

This idiosyncratic monograph has a lucid description of the history of nineteenth century thermal science. It is written in an erudite fashion and the reader who is willing to dive into a difficult subject will be rewarded for diligence by many new insights.

C. A. Truesdell, 1984, *Rational Thermodynamics*, Springer-Verlag, New York.

This is a modern update on the evolution of classical thermodynamics in the twentieth century. It is at a graduate level and contains several articles by some of the present leaders of the field.

S. R. Turns, 2011, *An Introduction to Combustion*, Third Edition, McGraw-Hill, Boston.

This is a popular senior-level undergraduate text on combustion which uses many notions from thermodynamics of mixtures.

H. C. van Ness, 1983, *Understanding Thermodynamics*, Dover, New York.

This is a short readable monograph from a chemical engineering perspective.

W. G. Vincenti and C. H. Kruger, 1965, *Introduction to Physical Gas Dynamics*, John Wiley, New York.

This graduate text on high speed non-equilibrium flows contains some nice descriptions of the interplay of classical and statistical mechanics. There is an emphasis on aerospace applications.

J. Warnatz, U. Maas, and R. W. Dibble, 2006, *Combustion*, Fourth Edition, Springer, New York.

This short graduate level text is nonetheless comprehensive and gives a good introduction to combustion science.

F. A. Williams, 1985, *Combustion Theory*, Benjamin-Cummings, Menlo Park, California.

> This influential monograph was first published in 1965. It was one of the first texts to give a comprehensive theoretical treatment of reactive fluid mechanics for model and practical systems.

L. C. Woods, 1975, *The Thermodynamics of Fluid Systems*, Clarendon, Oxford.

> This graduate text gives a good, detailed survey of the thermodynamics of irreversible processes, especially related to fluid systems in which convection and diffusion play important roles.

I. B. Zel'dovich and A. S. Kompaneets, 1960, *Theory of Detonation*, Academic Press, New York.

> This is a readable monograph whose first author is one of the founding fathers of modern detonation theory.

Ya. B. Zel'dovich and Yu. P. Raizer, 2002, *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena*, Dover, New York.

> This classic tome of the Russian school is a tour de force of reactive flow physics.