

# Modeling and Analysis of Chemical Kinetics for Hypersonic Flows in Air

A DISSERTATION  
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL  
OF THE UNIVERSITY OF MINNESOTA  
BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY

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November 2018

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# Acknowledgements

This is the acknowledgements.

*for Lyndsay*

## Abstract

This is the abstract. Work was completed.

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# Chapter 1

## Introduction

### 1.1 Motivation

Chemical reactions occur in the gas flow around vehicles traveling at hypersonic speeds, which is typically defined as at least five times faster than the speed of sound. The rate of these reactions is often comparable to the time scales of the flow and other relevant processes. Therefore, predictions of the chemical evolution of the flow must consider the finite rate at which chemical kinetics occur [1, 2].

Some example references:

- Articles were cited already [1, 2].
- Conference papers [3].
- Technical report, the authors are McBride and Gordon [4].
- Two books are Ref. [5, 6].
- Book chapters by specific authors are [7, 8].
- A Ph.D thesis is Bender [9].

### 1.2 Measurements of Oxygen Dissociation

Collect all rate parameters and uncertainties at the end in generic Arrhenius form, for example from Boyd and Schwartzentruber [6, p. 130],

$$k_d = CT^n \exp\left(-\frac{T_D}{T}\right) \quad (1.1)$$

**Table 1.1: Summary of oxygen dissociation shock tube experiments with partners O<sub>2</sub>, O, and N<sub>2</sub>. Equilibrium dissociation rate fit to Arrhenius form, Equation (1.1), is shown. For this table, 5 significant figures are provided for  $C$  and  $T_D$  regardless of estimated uncertainty.**

| Reference                      | Year | Method               | M              | Rate Parameters  |      |                     | Uncertainty [%] |       | Temp. Range [K]             |
|--------------------------------|------|----------------------|----------------|--|------|---------------------|-----------------|-------|-----------------------------|
|                                |      |                      |                | $C$ [cm <sup>3</sup> s <sup>-1</sup> K <sup>-n</sup> ] | n    | $T_D$ [K]           | lower           | upper |                             |
| Eckerman [10]                  | 1958 | Ballistics Range     | O <sub>2</sub> | $2.6782 \times 10^{-3}$                                | -1.5 | 59,396              | -               | -     | 4000 to 7000                |
| Matthews [11]                  | 1959 | Interferometry       | O <sub>2</sub> | $1.8857 \times 10^1$                                   | -2.5 | 59,380              | 37              | 32    | 3000 to 5000                |
| Byron [12]                     | 1959 | Interferometry       | O <sub>2</sub> | $3.1948 \times 10^{-3}$                                | -1.5 | 59,350              | 25              | 25    | 2800 to 5000                |
|                                |      |                      | O              | $1.8905 \times 10^{-6}$                                | -0.5 |                     |                 |       |                             |
| Camac and Vaughan [13]         | 1961 | UV absorption        | O <sub>2</sub> | $1.7745 \times 10^{-5}$                                | -1   | 59,369              | 99              | 0     | 6000 to 7000                |
|                                |      |                      | O              | 1.0535   | -2   |                     | 50              | 50    | 5000 to 7500                |
| Rink <i>et al.</i> [14]        | 1961 | x-ray absorption     | O <sub>2</sub> | $5.3030 \times 10^{-5}$                                | -1   | 59,578              | 20              | 20    | 3000 to 6000                |
|                                |      |                      | O              | $1.5909 \times 10^{-4}$                                |      |                     |                 |       |                             |
| Schexnayder and Evans [15]     | 1961 | UV absorption        | O <sub>2</sub> | $1.5073 \times 10^{-10}$                               | 0    | 37,378              | -               | -     | 3800 to 9000                |
| Generalov and Losev [16]*      | 1966 | UV absorption        | O <sub>2</sub> | $9.4965 \times 10^4$                                   | -3.5 | 59,380              | -               | -     | 2600 to 7000                |
|                                |      |                      | N <sub>2</sub> | $1.6800 \times 10^4$                                   |      |                     |                 |       | 2000 to 7000                |
| Shatalov [17]                  | 1973 | 2- $T$ UV absorption | O <sub>2</sub> | $1.8079 \times 10^1$                                   | -2.5 | 59,369 <sup>†</sup> | -               | -     | 3700 to 10,000              |
|                                |      |                      | O              | $1.8735 \times 10^{-6}$                                | -0.5 |                     |                 |       | 4900 to 10,000              |
| Jerig <i>et al.</i> [18]       | 1991 | UV absorption (O)    | N <sub>2</sub> | $5.6458 \times 10^{-5}$                                | -1   | 59,380              | 25              | 25    | 2463 to 3999                |
| Ibraguimova <i>et al.</i> [19] | 2013 | 2- $T$ UV absorption | O <sub>2</sub> | $6.4263 \times 10^3$                                   | -3.1 | 59,380              | 50              | 100   | 6000 to 11,000 <sup>‡</sup> |

\* Based on information in the translated abstract and Ref. [20]; no complete translation is available.

† Dissociation energy is not given directly, so the value from Generalov and Losev [16] is used.

‡ For low temperatures (2000 K to 6000 K), the fit by Ibraguimova *et al.* [21] was found to describe the data.

## Chapter 2

# Methodology

Probably you should write something here.

Maybe how the vibrational energy  $\varepsilon_{\text{vib}}$  is defined?

$$\varepsilon_{\text{vib}} = \varepsilon_{\text{int}} - \varepsilon_{\text{rot}} \tag{2.1}$$

Seems like a roundabout sort of definition.

## Chapter 3

# Results

### 3.1 Oxygen Dissociation in $O_2 + N_2$ and Aggregate Oxygen Dissociation

The oxygen dissociation rate with partners  $N_2$ ,  $O_2$ , and  $O$ , for the equilibrium and nonequilibrium test set, is shown in Figure 3.1. This is a standard side-by-side figure layout for the author. A standard single-figure layout is Figure 3.2.

For testing, here is a handful of pages filled with junk. How does the header look, on a page like this?

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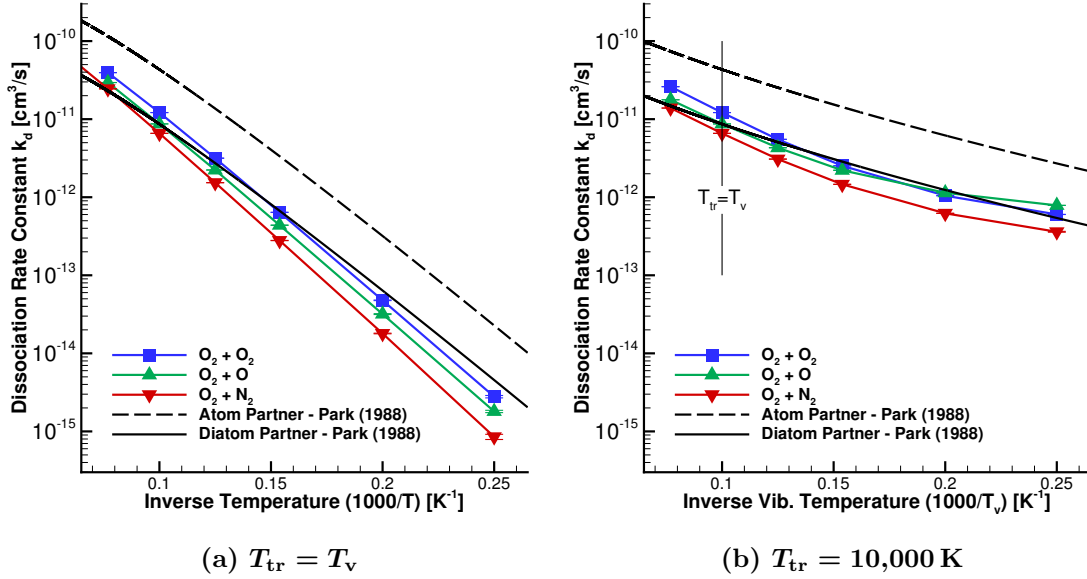


Figure 3.1: Oxygen dissociation rate with collision partners  $O_2$ ,  $O$ , and  $N_2$  for the equilibrium and nonequilibrium test set.

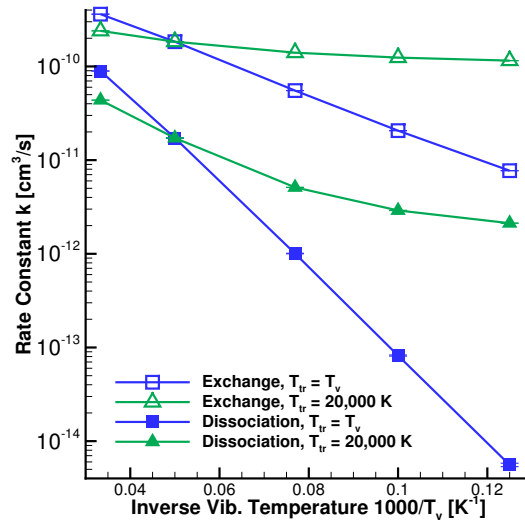


Figure 3.2: Reaction rate constants for exchange and dissociation in  $N_2 + N$ , for the equilibrium and nonequilibrium test set.

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## Chapter 4

# Conclusions

You should definitely have some of these. Don't write them at the last minute.



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## Appendix A

# Nomenclature and Acronyms

Several packages could be used for this, including `nomencl`<sup>1</sup> and `glossaries`<sup>2</sup>. However, I prefer to sort in my own order and include sub-headings, which I found cumbersome with those tools. Therefore, this nomenclature section just uses `longtable`. Feel free to customize as desired!

### A.1 Nomenclature

#### Latin

|     |  |
|-----|--|
| $b$ | Impact parameter, Å  |
| $T$ | Temperature, K   |
| $k$ | Rate constant, cm <sup>3</sup> /sec, OR<br>Some other constant, not confusing at all |
| $Z$ | Some duplicate entries to wrap   |
| $Z$ | Some duplicate entries to wrap   |
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| $Z$ | Some duplicate entries to wrap   |

#### Greek

|                            |  |
|----------------------------|--|
| $\varepsilon_{\text{vib}}$ | Vibrational energy, eV, Equation (2.1) |
|----------------------------|--|

#### Subscripts

|   |              |
|---|--------------|
| d | Dissociation |
| e | Exchange     |

---

<sup>1</sup><https://ctan.org/pkg/nomencl?lang=en>

<sup>2</sup><https://ctan.org/pkg/glossaries?lang=en>

---

|   |               |
|---|---------------|
| t | Translational |
| r | Rotational    |
| v | Vibrational   |

## **A.2 Acronyms**

|      |   |
|------|---|
| NASA | National Aeronautics and Space Administration |
| PES  | Potential Energy Surface                      |

## Appendix B

### Tables

This is some filler text. Here, there is no section title, so we set the section mark (for headers) using the command `\sectionmark{Tables for Nitrogen Dissociation}`. The section number is 0, though, which is a bit unfortunate but not a huge problem.

**Table B.1: Summary statistics for  $\text{N}_2 + \text{N}$ , equilibrium test set ( $T_{\text{tr}} = T_{\text{v}}$ ).**

| $T$ [K] | $\mathcal{N}$ [ $10^6$ ] | $k_{\text{d}}$ [ $\text{cm}^3/\text{sec}$ ] | $\langle \Delta \varepsilon_{\text{vib}} \rangle_{\text{d}}$ [eV] | $\langle \Delta \varepsilon_{\text{rot}} \rangle_{\text{d}}$ [eV] | $k_{\text{e}}$ [ $\text{cm}^3/\text{sec}$ ] | $\langle \Delta \varepsilon_{\text{vib}} \rangle_{\text{e}}$ [eV] | $\langle \Delta \varepsilon_{\text{rot}} \rangle_{\text{e}}$ [eV] |
|---------|--------------------------|---|---|---|---|---|---|
| 8000    | 240                      | $5.6(2) \times 10^{-15}$                    | -7.9(4)   | -1.60(9)  | $7.718(5) \times 10^{-12}$                  | $-3.0(7) \times 10^{-3}$  | $2.1(8) \times 10^{-3}$   |
| 10,000  | 150                      | $8.20(12) \times 10^{-14}$                  | -7.63(13)   | -1.82(4)  | $2.0638(11) \times 10^{-11}$                | $-4.6(7) \times 10^{-3}$  | $8.8(9) \times 10^{-3}$   |
| 13,000  | 60                       | $1.006(7) \times 10^{-12}$                  | -7.20(6)  | -2.20(2)  | $5.528(3) \times 10^{-11}$                  | $-5.2(10) \times 10^{-3}$   | 0.0104(13)  |
| 20,000  | 18                       | $1.722(6) \times 10^{-11}$                  | -6.52(3)  | -2.896(13)  | $1.8377(12) \times 10^{-10}$                | $-4.9(16) \times 10^{-3}$   | 0.014(2)  |
| 30,000  | 18                       | $8.939(14) \times 10^{-11}$                 | -5.930(11)  | -3.490(7)   | $3.6133(19) \times 10^{-10}$                | $-4.9(15) \times 10^{-3}$   | 0.018(2)  |

**Table B.2: Summary statistics for  $\text{N}_2 + \text{N}$ , nonequilibrium test set ( $T_{\text{tr}} = 20,000$  K).**

| $T_{\text{v}}$ [K] | $\mathcal{N}$ [ $10^6$ ] | $k_{\text{d}}$ [ $\text{cm}^3/\text{sec}$ ] | $\langle \Delta \varepsilon_{\text{vib}} \rangle_{\text{d}}$ [eV] | $\langle \Delta \varepsilon_{\text{rot}} \rangle_{\text{d}}$ [eV] | $k_{\text{e}}$ [ $\text{cm}^3/\text{sec}$ ] | $\langle \Delta \varepsilon_{\text{vib}} \rangle_{\text{e}}$ [eV] | $\langle \Delta \varepsilon_{\text{rot}} \rangle_{\text{e}}$ [eV] |
|--------------------|--------------------------|---|---|---|---|---|---|
| 8000               | 90                       | $2.122(7) \times 10^{-12}$                  | -1.333(8)   | -6.71(3)  | $1.1541(4) \times 10^{-10}$                 | 0.9139(7)   | -0.5638(11)   |
| 10,000             | 60                       | $2.903(11) \times 10^{-12}$                 | -2.292(14)  | -6.11(3)  | $1.2434(5) \times 10^{-10}$                 | 0.7583(9)   | -0.4785(13)   |
| 13,000             | 60                       | $5.118(15) \times 10^{-12}$                 | -4.011(17)  | -4.878(19)  | $1.4031(6) \times 10^{-10}$                 | 0.5136(9)   | -0.3338(13)   |
| 20,000             | 18                       | $1.722(6) \times 10^{-11}$                  | -6.52(3)  | -2.896(13)  | $1.8377(12) \times 10^{-10}$                | -0.0049(16)   | 0.014(2)  |
| 30,000             | 60                       | $4.371(5) \times 10^{-11}$                  | -7.565(10)  | -2.017(3)   | $2.3971(8) \times 10^{-10}$                 | -0.4721(9)  | 0.3574(11)  |