

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

Ross S. Chaudhry

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

Adviser: Graham V. Candler

November 2018

© Ross S. Chaudhry 2018
ALL RIGHTS RESERVED

Acknowledgements

This is the acknowledgements.

for Lyndsay

Abstract

This is the abstract. Work was completed.

Contents

Acknowledgements	i
Dedication	ii
Abstract	iii
List of Figures	v
List of Tables	vi
1 Introduction	1
1.1 Motivation	1
1.2 Measurements of Oxygen Dissociation	1
2 Methodology	3
3 Results	4
3.1 Oxygen Dissociation in $O_2 + N_2$ and Aggregate Oxygen Dissociation	4
4 Conclusions	8
Bibliography	9
Appendix A Nomenclature and Acronyms	11
A.1 Nomenclature	11
A.2 Acronyms	12
Appendix B Tables	13

List of Figures

3.1	Oxygen dissociation with various parameters	5
3.2	Exchange and dissociation rates in $N_2 + N$	5

List of Tables

1.1	O ₂ dissociation shock tube experiments	2
B.1	N ₂ + N, $T_{\text{tr}} = T_{\text{v}}$	14
B.2	N ₂ + N, $T_{\text{tr}} = 20,000 \text{ K}$	14

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_2 , O , and N_2 . 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 [$\text{cm}^3\text{s}^{-1}\text{K}^{-n}$]	n	T_D [K]	<i>lower</i>	<i>upper</i>	
Eckerman [10]	1958	Ballistics Range	O_2	2.6782×10^{-3}	-1.5	59,396	-	-	4000 to 7000
Matthews [11]	1959	Interferometry	O_2	1.8857×10^1	-2.5	59,380	37	32	3000 to 5000
Byron [12]	1959	Interferometry	O_2	3.1948×10^{-3}	-1.5	59,350	25	25	2800 to 5000
			O	1.8905×10^{-6}	-0.5				
Camac and Vaughan [13]	1961	UV absorption	O_2	1.7745×10^{-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_2	5.3030×10^{-5}	-1	59,578	20	20	3000 to 6000
			O	1.5909×10^{-4}					
Schexnayder and Evans [15]	1961	UV absorption	O_2	1.5073×10^{-10}	0	37,378	-	-	3800 to 9000
Generalov and Losev [16]*	1966	UV absorption	O_2	9.4965×10^4	-3.5	59,380	-	-	2600 to 7000
			N_2	1.6800×10^4					2000 to 7000
Shatalov [17]	1973	2- T UV absorption	O_2	1.8079×10^1	-2.5	59,369 [†]	-	-	3700 to 10,000
			O	1.8735×10^{-6}	-0.5				4900 to 10,000
Jerig <i>et al.</i> [18]	1991	UV absorption (O)	N_2	5.6458×10^{-5}	-1	59,380	25	25	2463 to 3999
Ibraguimova <i>et al.</i> [19]	2013	2- T UV absorption	O_2	6.4263×10^3	-3.1	59,380	50	100	6000 to 11,000 [‡]

* 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 ε_{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 $\text{O}_2 + \text{N}_2$ 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?

Lorem ipsum dolor sit amet, consectetur adipiscing elit. Ut purus elit, vestibulum ut, placerat ac, adipiscing vitae, felis. Curabitur dictum gravida mauris. Nam arcu libero, nonummy eget, consectetur id, vulputate a, magna. Donec vehicula augue eu neque. Pellentesque habitant morbi tristique senectus et netus et malesuada fames ac turpis egestas. Mauris ut leo. Cras viverra metus rhoncus sem. Nulla et lectus vestibulum urna fringilla ultrices. Phasellus eu tellus sit amet tortor gravida placerat. Integer sapien est, iaculis in, pretium quis, viverra ac, nunc. Praesent eget sem vel leo ultrices bibendum. Aenean faucibus. Morbi dolor nulla, malesuada eu, pulvinar at, mollis ac, nulla. Curabitur auctor semper nulla. Donec varius orci eget risus. Duis nibh mi, congue eu, accumsan eleifend, sagittis quis, diam. Duis eget orci sit amet orci dignissim rutrum.

Nam dui ligula, fringilla a, euismod sodales, sollicitudin vel, wisi. Morbi auctor lorem non justo. Nam lacus libero, pretium at, lobortis vitae, ultricies et, tellus. Donec aliquet, tortor sed accumsan bibendum, erat ligula aliquet magna, vitae ornare odio metus a mi. Morbi ac orci et nisl hendrerit mollis. Suspendisse ut massa. Cras nec ante. Pellentesque a nulla. Cum sociis natoque penatibus et magnis dis parturient montes, nascetur ridiculus mus. Aliquam tincidunt urna. Nulla ullamcorper vestibulum turpis. Pellentesque cursus luctus mauris.

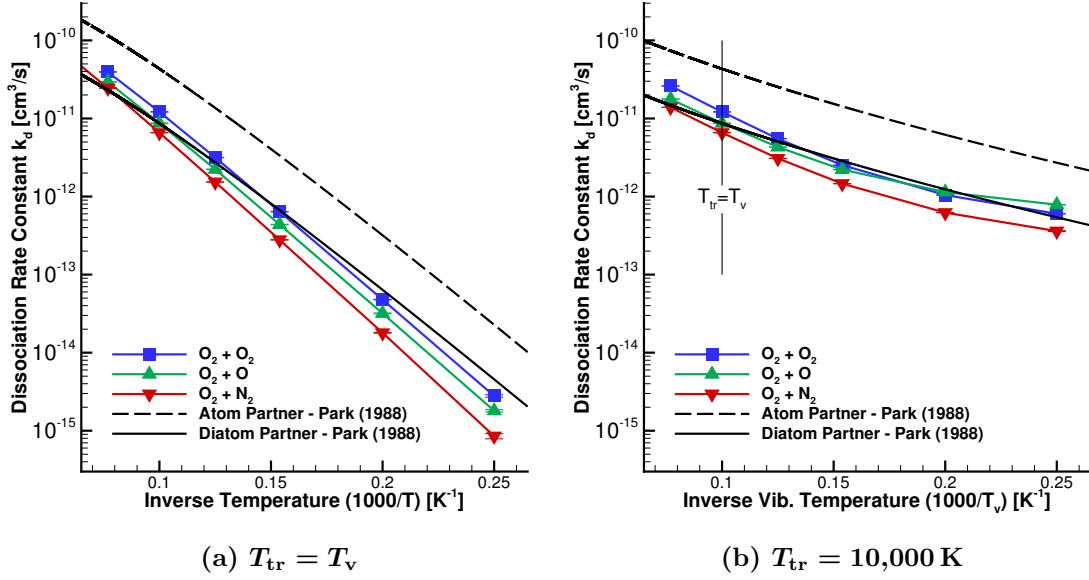


Figure 3.1: Oxygen dissociation rate with collision partners O_2 , O , and N_2 for the equilibrium and nonequilibrium test set.

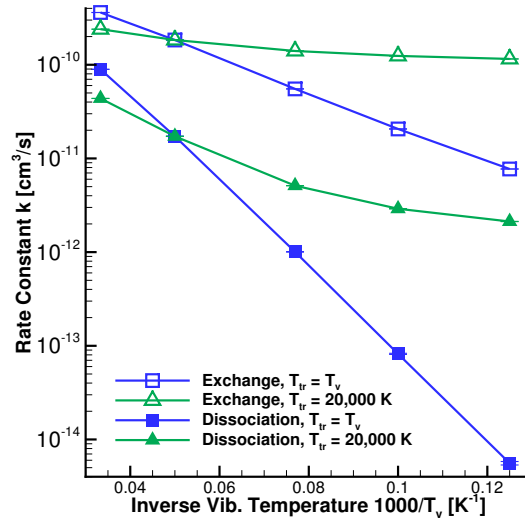


Figure 3.2: Reaction rate constants for exchange and dissociation in $N_2 + N$, for the equilibrium and nonequilibrium test set.

Nulla malesuada porttitor diam. Donec felis erat, congue non, volutpat at, tincidunt tristique, libero. Vivamus viverra fermentum felis. Donec nonummy pellentesque ante. Phasellus adipiscing semper elit. Proin fermentum massa ac quam. Sed diam turpis, molestie vitae, placerat a, molestie nec, leo. Maecenas lacinia. Nam ipsum ligula, eleifend at, accumsan nec, suscipit a, ipsum. Morbi blandit ligula feugiat magna. Nunc eleifend consequat lorem. Sed lacinia nulla vitae enim. Pellentesque tincidunt purus vel magna. Integer non enim. Praesent euismod nunc eu purus. Donec bibendum quam in tellus. Nullam cursus pulvinar lectus. Donec et mi. Nam vulputate metus eu enim. Vestibulum pellentesque felis eu massa.

Quisque ullamcorper placerat ipsum. Cras nibh. Morbi vel justo vitae lacus tincidunt ultrices. Lorem ipsum dolor sit amet, consectetur adipiscing elit. In hac habitasse platea dictumst. Integer tempus convallis augue. Etiam facilisis. Nunc elementum fermentum wisi. Aenean placerat. Ut imperdiet, enim sed gravida sollicitudin, felis odio placerat quam, ac pulvinar elit purus eget enim. Nunc vitae tortor. Proin tempus nibh sit amet nisl. Vivamus quis tortor vitae risus porta vehicula.

Fusce mauris. Vestibulum luctus nibh at lectus. Sed bibendum, nulla a faucibus semper, leo velit ultricies tellus, ac venenatis arcu wisi vel nisl. Vestibulum diam. Aliquam pellentesque, augue quis sagittis posuere, turpis lacus congue quam, in hendrerit risus eros eget felis. Maecenas eget erat in sapien mattis porttitor. Vestibulum porttitor. Nulla facilisi. Sed a turpis eu lacus commodo facilisis. Morbi fringilla, wisi in dignissim interdum, justo lectus sagittis dui, et vehicula libero dui cursus dui. Mauris tempor ligula sed lacus. Duis cursus enim ut augue. Cras ac magna. Cras nulla. Nulla egestas. Curabitur a leo. Quisque egestas wisi eget nunc. Nam feugiat lacus vel est. Curabitur consectetur.

Suspendisse vel felis. Ut lorem lorem, interdum eu, tincidunt sit amet, laoreet vitae, arcu. Aenean faucibus pede eu ante. Praesent enim elit, rutrum at, molestie non, nonummy vel, nisl. Ut lectus eros, malesuada sit amet, fermentum eu, sodales cursus, magna. Donec eu purus. Quisque vehicula, urna sed ultricies auctor, pede lorem egestas dui, et convallis elit erat sed nulla. Donec luctus. Curabitur et nunc. Aliquam dolor odio, commodo pretium, ultricies non, pharetra in, velit. Integer arcu est, nonummy in, fermentum faucibus, egestas vel, odio.

Sed commodo posuere pede. Mauris ut est. Ut quis purus. Sed ac odio. Sed vehicula hendrerit sem. Duis non odio. Morbi ut dui. Sed accumsan risus eget odio. In hac habitasse platea dictumst. Pellentesque non elit. Fusce sed justo eu urna porta tincidunt. Mauris felis odio, sollicitudin sed, volutpat a, ornare ac, erat. Morbi quis dolor. Donec pellentesque, erat ac sagittis semper, nunc dui lobortis purus, quis congue purus metus ultricies tellus. Proin et quam. Class aptent taciti sociosqu ad litora torquent per conubia nostra, per inceptos hymenaeos. Praesent sapien turpis, fermentum vel, eleifend faucibus, vehicula eu,

lacus.

Pellentesque habitant morbi tristique senectus et netus et malesuada fames ac turpis egestas. Donec odio elit, dictum in, hendrerit sit amet, egestas sed, leo. Praesent feugiat sapien aliquet odio. Integer vitae justo. Aliquam vestibulum fringilla lorem. Sed neque lectus, consectetur at, consectetur sed, eleifend ac, lectus. Nulla facilisi. Pellentesque eget lectus. Proin eu metus. Sed porttitor. In hac habitasse platea dictumst. Suspendisse eu lectus. Ut mi mi, lacinia sit amet, placerat et, mollis vitae, dui. Sed ante tellus, tristique ut, iaculis eu, malesuada ac, dui. Mauris nibh leo, facilisis non, adipiscing quis, ultrices a, dui.

Morbi luctus, wisi viverra faucibus pretium, nibh est placerat odio, nec commodo wisi enim eget quam. Quisque libero justo, consectetur a, feugiat vitae, porttitor eu, libero. Suspendisse sed mauris vitae elit sollicitudin malesuada. Maecenas ultricies eros sit amet ante. Ut venenatis velit. Maecenas sed mi eget dui varius euismod. Phasellus aliquet volutpat odio. Vestibulum ante ipsum primis in faucibus orci luctus et ultrices posuere cubilia Curae; Pellentesque sit amet pede ac sem eleifend consectetur. Nullam elementum, urna vel imperdiet sodales, elit ipsum pharetra ligula, ac pretium ante justo a nulla. Curabitur tristique arcu eu metus. Vestibulum lectus. Proin mauris. Proin eu nunc eu urna hendrerit faucibus. Aliquam auctor, pede consequat laoreet varius, eros tellus scelerisque quam, pellentesque hendrerit ipsum dolor sed augue. Nulla nec lacus.

Suspendisse vitae elit. Aliquam arcu neque, ornare in, ullamcorper quis, commodo eu, libero. Fusce sagittis erat at erat tristique mollis. Maecenas sapien libero, molestie et, lobortis in, sodales eget, dui. Morbi ultrices rutrum lorem. Nam elementum ullamcorper leo. Morbi dui. Aliquam sagittis. Nunc placerat. Pellentesque tristique sodales est. Maecenas imperdiet lacinia velit. Cras non urna. Morbi eros pede, suscipit ac, varius vel, egestas non, eros. Praesent malesuada, diam id pretium elementum, eros sem dictum tortor, vel consectetur odio sem sed wisi.

Chapter 4

Conclusions

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

Bibliography

- [1] Gnoffo, P. A., “Planetary-Entry Gas Dynamics,” *Annual Review of Fluid Mechanics*, Vol. 31, No. 1, 1999, pp. 459–494. doi:10.1146/annurev.fluid.31.1.459.
- [2] Candler, G. V., “Rate Effects in Hypersonic Flows,” *Annual Review of Fluid Mechanics*, Vol. 51, No. 1, 2019, p. null. doi:10.1146/annurev-fluid-010518-040258.
- [3] Chaudhry, R. S., Grover, M. S., Bender, J. D., Schwartzentruber, T. E., and Candler, G. V., “Quasiclassical Trajectory Analysis of Oxygen Dissociation via O_2 , O , and N_2 ,” *2018 AIAA Aerospace Sciences Meeting*, AIAA Paper 2018-0237, 2018. doi:10.2514/6.2018-0237.
- [4] McBride, B. J., and Gordon, S., “Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications, 2. Users Manual and Program Description,” Tech. Rep. RP-1331-2, NASA, June 1996.
- [5] Riley, K. F., Hobson, M. P., and Bence, S. J., *Mathematical Methods for Physics and Engineering*, 3rd ed., Cambridge University Press, Cambridge, UK, 2006.
- [6] Boyd, I. D., and Schwartzentruber, T. E., *Nonequilibrium Gas Dynamics and Molecular Simulation*, Cambridge Aerospace Series, Vol. 42, Cambridge University Press, Cambridge, UK, 2017.
- [7] Truhlar, D. G., and Muckerman, J. T., “Reactive Scattering Cross Sections III: Quasiclassical and Semiclassical Methods,” *Atom–Molecule Collision Theory: A Guide for the Experimentalist*, edited by R. B. Bernstein, Plenum Press, New York, 1979, Chap. 16, pp. 505 – 566.
- [8] Park, C., “Review of Finite-Rate Chemistry Models for Air Dissociation and Ionization,” *Molecular Physics and Hypersonic Flows*, NATO ASI Series (Series C: Mathematical and Physical Sciences), Vol. 482, edited by M. Capitelli, Kluwer Academic Publishers, Dordrecht, 1996, pp. 581–596. doi:10.1007/978-94-009-0267-1_39.
- [9] Bender, J. D., “Multiscale Computational Analysis of Nitrogen and Oxygen Gas-Phase Thermochemistry in Hypersonic Flows,” Ph.D. thesis, University of Minnesota, Minneapolis, MN, February 2016.
- [10] Eckerman, J., “The Measurement of the Rate of Dissociation of Oxygen at High Temperature,” Ph.D. thesis, The Catholic University of America, Washington, DC, 1958.

-
- [11] Matthews, D. L., "Interferometric Measurement in the Shock Tube of the Dissociation Rate of Oxygen," *The Physics of Fluids*, Vol. 2, No. 2, 1959, pp. 170–178. doi:10.1063/1.1705908.
- [12] Byron, S. R., "Measurement of the Rate of Dissociation of Oxygen," *The Journal of Chemical Physics*, Vol. 30, No. 6, 1959, pp. 1380–1392. doi:10.1063/1.1730209.
- [13] Camac, M., and Vaughan, A., "O₂ Dissociation Rates in O₂-Ar Mixtures," *The Journal of Chemical Physics*, Vol. 34, No. 2, 1961, pp. 460–470. doi:10.1063/1.4757209.
- [14] Rink, J. P., Knight, H. T., and Duff, R. E., "Shock Tube Determination of Dissociation Rates of Oxygen," *The Journal of Chemical Physics*, Vol. 34, No. 6, 1961, pp. 1942–1947. doi:10.1063/1.1731797.
- [15] Schexnayder, C. J., Jr., and Evans, J. S., "Measurements of the Dissociation Rate of Molecular Oxygen," Tech. Rep. TR R-108, NASA, 1961.
- [16] Generalov, N. A., and Losev, S. A., "Vibration, Excitation, and Molecular Dissociation of Gaseous Oxygen and Carbon Dioxide in a Shock Wave," *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 6, No. 1, 1966, pp. 101–125. doi:10.1016/0022-4073(66)90066-5.
- [17] Shatalov, O. P., "Molecular Dissociation of Oxygen in the Absence of Vibrational Equilibrium," *Combustion, Explosion and Shock Waves*, Vol. 9, No. 5, 1973, pp. 610–613. doi:10.1007/BF00742888.
- [18] Jerig, L., Thielen, K., and Roth, P., "High-Temperature Dissociation of Oxygen Diluted in Argon or Nitrogen," *AIAA Journal*, Vol. 29, No. 7, 1991, pp. 1136–1139. doi:10.2514/3.10714.
- [19] Ibraguimova, L. B., Sergievskaya, A. L., Levashov, V. Y., Shatalov, O. P., Tunik, Y. V., and Zabelinskii, I. E., "Investigation of Oxygen Dissociation and Vibrational Relaxation at Temperatures 4000–10800 K," *The Journal of Chemical Physics*, Vol. 139, No. 3, 2013, p. 034317. doi:10.1063/1.4813070.
- [20] Bortner, M. H., "A Review of Rate Constants of Selected Reactions of Interest in Re-Entry Flow Fields in the Atmosphere," Tech. Rep. NBTNA-484, National Bureau of Standards, May 1969.
- [21] Ibraguimova, L. B., Smekhov, G. D., and Shatalov, O. P., "Dissociation Rate Constants of Diatomic Molecules under Thermal Equilibrium Conditions," *Fluid Dynamics*, Vol. 34, No. 1, 1999, pp. 153 – 157. doi:10.1007/BF02698767.

Appendix A

Nomenclature and Acronyms

Several packages could be used for this, including `nomencl`¹ and `glossaries`². 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!

Includes a third column for where the variable/term is defined in the text.

A.1 Nomenclature

Latin

b	Impact parameter, Å	Chapter 1
T	Temperature, K	
k	Rate constant, cm ³ /sec, OR Some other constant, not confusing at all	Equation (1.1)
Z	Some duplicate entries to wrap	
Z	Some duplicate entries to wrap	
Z	Some duplicate entries to wrap	
Z	Some duplicate entries to wrap	
Z	Some duplicate entries to wrap	

Greek

ϵ_{vib}	Vibrational energy, eV, Equation (2.1)	Equation (2.1)
-------------------------	--	----------------

Subscripts

d	Dissociation
---	--------------

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

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

e	Exchange
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_{d} [cm^3/sec]	$\langle \Delta \varepsilon_{\text{vib}} \rangle_{\text{d}}$ [eV]	$\langle \Delta \varepsilon_{\text{rot}} \rangle_{\text{d}}$ [eV]	k_{e} [cm^3/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_{v} [K]	\mathcal{N} [10^6]	k_{d} [cm^3/sec]	$\langle \Delta \varepsilon_{\text{vib}} \rangle_{\text{d}}$ [eV]	$\langle \Delta \varepsilon_{\text{rot}} \rangle_{\text{d}}$ [eV]	k_{e} [cm^3/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)