JPL Publication **06-2**

Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies

Evaluation Number 15

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July 10, 2006

The research described in this publication was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

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ABSTRACT

This is the fifteenth in a series of evaluated sets of rate constants and photochemical cross sections compiled by the NASA Panel for Data Evaluation.

The data are used primarily to model stratospheric and upper tropospheric processes, with particular emphasis on the ozone layer and its possible perturbation by anthropogenic and natural phenomena.

Copies of this evaluation are available in electronic form and may be printed from the following Internet URL:

http://jpldataeval.jpl.nasa.gov/

TABLE OF CONTENTS

INTRODUCTION xv
- 1.1 Basis of the Recommendations xvii
- 1.2 Scope of the Evaluation xvii
- 1.3 Format of the Evaluation xviii
- 1.4 Computer Access xviii
- 1.5 Data Formats xviii
- 1.6 Units xviii
- 1.7 Noteworthy Changes in this Evaluation xviii
- 1.8 Acknowledgements xxi
- 1.9 References xxi

SECTION 1. BIOMOLECULAR REACTIONS 1-1
- 1.1 Introduction 1-1
- 1.2 Uncertainty Estimates 1-2
- 1.3 Notes to Table 1 1-33
- 1.4 References 1-119

SECTION 2. TERMOLECULAR REACTIONS 2-1
- 2.1 Introduction 2-1
- 2.2 Low-Pressure-Limiting Rate Constant $k^x_o(T)$ 2-2
- 2.3 Temperature Dependence of Low-Pressure Limiting Rate Constants: T^n 2-2
- 2.4 High-Pressure-Limit Rate Constants, $k_\infty(T)$ 2-3
- 2.5 Temperature Dependence of High-Pressure Limiting Rate Constants: T^m 2-3
- 2.6 Uncertainty Estimates 2-6
- 2.7 Notes to Table 2 2-8
- 2.8 References 2-19

SECTION 3. EQUILIBRIUM CONSTANTS 3-1
- 3.1 Format 3-1
- 3.2 Definitions 3-1
- 3.3 Notes to Table 3 3-3
- 3.4 References 3-6

SECTION 4. PHOTOCHEMICAL DATA 4-1
- 4.1 Format and Error Estimates 4-4
- 4.2 Halocarbon Absorption Cross Sections and Quantum Yields 4-5
- 4.3 Web Access to Recommended Data in Text and Graphical Formats 4-5
- 4.4 References 4-211

SECTION 5. HETEROGENEOUS CHEMISTRY 5-1
- 5.1 Introduction 5-1
- 5.2 Surface Types─Acid/Water, Liquids and Solids 5-2
- 5.3 Surface Types─Soot and Alumina 5-2
- 5.4 Surface Types─Solid Alkali Halide Salts and Aqueous Salt Solutions 5-3
- 5.5 Surface Composition and Morphology 5-4
- 5.6 Surface Porosity 5-6
- 5.7 Temperature Dependences of Parameters 5-5
- 5.8 Solubility Limitations 5-5
- 5.9 Data Organization 5-5
- 5.10 Parameter Definitions 5-5
- 5.11 Mass Accommodation Coefficients for Surfaces Other Than Soot 5-9
- 5.12 Notes to Table 5-1 5-12
- 5.13 Gas/Surface Reaction Probabilities for Surfaces Other Than Soot 5-21
- 5.14 Notes to Table 5-2 5-26
- 5.15 Soot Surface Uptake Coefficients 5-50
- 5.16 Notes to Table 5-3 5-50

5.17 Henry's Law Constants for Pure Water 5-53
5.18 Notes to Table 5-4 5-56
5.19 Ion-Specific Schumpe Parameters 5-61
5.20 Henry's Law Constants for Acids 5-62
5.21 Notes to Table 5-6 5-63
5.22 References 5-66

APPENDIX A. GAS-PHASE ENTROPY AND ENTHALPY VALUES
FOR SELECTED SPECIES AT 298.15 K AND 100 KPA A-1

TABLES

Table 1-1. Rate Constants for Second-Order Reactions 1-5

Table 2-1. Rate Constants for Termolecular Reactions 2-4

Table 3-1. Equilibrium Constants 3-2

Table 4-1. Photochemical Reactions 4-6
Table 4-2. Combined Uncertainties for Cross Sections and Quantum Yields 4-9
Table 4-3. Absorption Cross Sections of O_2 Between 205 and 240 nm 4-10
Table 4-4. Summary of O_3 Cross Section Measurements 4-11
Table 4-5. Absorption Cross Sections of O_3 at 218 and 293-298 K 4-15
Table 4-6. Parameters for the Calculation of $O(^1D)$ Quantum Yields 4-17
Table 4-7. Absorption Cross Sections of HO_2 4-18
Table 4-8. Absorption Cross Sections of H_2O Vapor 4-18
Table 4-9. Absorption Cross Sections of H_2O_2 Vapor 4-19
Table 4-10. Mathematical Expression for Absorption Cross Sections of H_2O_2 as a Function of Temperature 4-19
Table 4-11. Summary of NO_2 Cross Section Measurements 4-20
Table 4-12. Absorption Cross Sections of NO_2 at 220 and 294 K 4-23
Table 4-13. Quantum Yields for NO_2 Photolysis 4-24
Table 4-14. Summary of NO_3 Cross Section Measurements 4-25
Table 4-15. Absorption Cross Sections of NO_3 at 298 K 4-28
Table 4-16. Quantum Yields (multiplied by 1000) for the Product Channels $NO + O_2$ and $NO_2 + O(^3P)$ in the Photolysis of NO_3 at 298, 230 and 190 K 4-30
Table 4-17. Summary of N_2O Cross Section Measurements 4-31
Table 4-18. Absorption Cross Sections of N_2O at 298 K 4-32
Table 4-19. Mathematical Expression for Absorption Cross Sections of N_2O as a Function of Temperature 4-32
Table 4-20. Absorption Cross Sections of N_2O_4 at 220 K 4-33
Table 4-21. Absorption Cross Sections N_2O_5 at 195-300 K and Temperature Coefficients 4-35
Table 4-22. Quantum Yields from Photolysis of N_2O_5 4-36
Table 4-23. Summary of HONO Cross Section Measurements 4-36
Table 4-24. Absorption Cross Sections of HONO at 298 K 4-38
Table 4-25. Absorption Cross Sections at 298 K and Temperature Coefficients of HNO_3 Vapor 4-40
Table 4-26. Absorption Cross Sections at HO_2NO_2 at 296-298 K 4-41
Table 4-27. Quantum Yields of HO_2NO_2 4-42
Table 4-28. Photodissociation Band Strengths and Quantum Yields for Several Overtone and Combination Bands of HO_2NO_2 4-42
Table 4-29. Summary of CH_2O Cross Section Measurements 4-42
Table 4-30. Absorption Cross Sections of CH_2O at 298 K and Temperature Coefficients Averaged over 1-nm Intervals 4-45
Table 4-31. Absorption Cross Sections of CH_2O at 298 K and Temperature Coefficients Averaged over Intervals Used in Atmospheric Modeling 4-46
Table 4-32. Quantum Yields for Photolysis of CH_2O at 296-300 K 4-47
Table 4-33. Absorption Cross Sections of CH_3CHO at 298-300 K 4-49
Table 4-34. Recommended Quantum Yields for the Photolysis of CH_3CHO at 1 bar Total Pressure 4-50
Table 4-35. Absorption Cross Sections of C_2H_5CHO at 298-300K 4-51
Table 4-36. Absorption Cross Sections of CH_3O_2, $C_2H_5O_2$, and $CH_3C(O)O_2$ 4-52
Table 4-37. Absorption Cross Sections of CH_3OOH 4-53

Table 4-38. Absorption Cross Sections of $HOCH_2OOH$ 4-54
Table 4-39. Absorption Cross Sections of $CH_3C(O)O_2NO_2$ at 298 K, Temperature Coefficients B 4-55
Table 4-40. Absorption Cross Sections of $C_2H_5C(O)O_2NO_2$ at 296 K and Temperature Coefficients B 4-56
Table 4-41. Absorption Cross Sections of CH_2=CHCHO at 298 K 4-57
Table 4-42. Absorption Cross Sections of CH_2=C(CH_3)CHO at 298 K 4-58
Table 4-43. Absorption Cross Sections of CH_3(O)CH=CH_2 at 298 K 4-60
Table 4-44. Absorption Cross Sections of $HOCH_2CHO$ at 298 K 4-61
Table 4-45. Absorption Cross Sections of $CH_3C(O)CH_3$ at 298 K and Temperature Coefficients 4-64
Table 4-46. Quantum Yields for the Photolysis of Acetone 4-66
Table 4-47. Absorption Cross Sections of $CH_3C(O)CH_2OH$ at 298 K 4-67
Table 4-48. Absorption Cross Sections of CHOCHO at 296 K 4-69
Table 4-49. Absolute Quantum Yields in the Photolysis of CHOCHO 4-70
Table 4-50. Absorption Cross Sections of $CH_3COC(O)H$ at 295-298 K 4-71
Table 4-51. Absorption Cross Sections of HC(O)OH and $(HC(O)OH)_2$ at 302 K 4-74
Table 4-52. Absorption Cross Sections of $CH_3C(O)OH$ and $(CH_3C(O)OH)_2$ at 298 K 4-75
Table 4-53. Absorption Cross Sections of $CH_3C(O)OOH$ at 298 K 4-76
Table 4-54. Absorption Cross Sections of $CH_3C(O)C(O)OH$ at 298 K 4-77
Table 4-55. Absorption Cross Sections of $HC(O)OCH_3$ at 297-298 K 4-78
Table 4-56 Absorption Cross Sections of $HC(O)OC_2H_5$ at 297 K 4-78
Table 4-57. Absorption Cross Sections of FO_2 at 295 K 4-79
Table 4-58. Absorption Cross Sections of F_2O at 273 K 4-79
Table 4-59. Absorption Cross Sections of F_2O_2 at 193-195 and 273 K 4-80
Table 4-60. Absorption Cross Sections of FNO at 298 K 4-81
Table 4-61. Absorption Cross Sections of COF_2 at 298 K 4-82
Table 4-62. Absorption Cross Sections of COHF at 298 K 4-82
Table 4-63. Absorption Cross Sections of CF_3OOCF_3 at 298 K 4-83
Table 4-64. Absorption Cross Sections of $CF_3O_3CF_3$ at 298 K 4-84
Table 4-65. Absorption Cross Sections of CF_3CHO at 298 K 4-85
Table 4-66. Absorption Cross Sections of $CF_3C(O)F$ at 298 K 4-86
Table 4-67. Absorption Cross Sections of $CF_3C(O)Cl$ at 296-298 K 4-86
Table 4-68. Absorption Cross Sections of $CF_3(O)O_2NO_2$ at 298 K 4-87
Table 4-69. Absorption Cross Sections of CF_3CH_2CHO at 298 K 4-88
Table 4-70. Absorption Cross Sections of $CF_3C(O)OH$ at 296 K 4-89
Table 4-71. Absorption Cross Sections of $CH_3C(O)F$ at 296 K 4-89
Table 4-72. Absorption Cross Sections of CH_2=$CHCF_3$ at 295 K 4-90
Table 4-73. Absorption Cross Sections of CH_2=$CFCF_3$ at 295 K 4-90
Table 4-74. Absorption Cross Sections of CF_2=CF_2 at 295-298 K 4-91
Table 4-75. Absorption Cross Sections of CF_2=$CFCF_3$ at 295-298 K 4-92
Table 4-76. Absorption Cross Sections of Cl_2 at 298 K 4-93
Table 4-77. Absorption Cross Sections of ClO at 298 K 4-94
Table 4-78. Absorption Cross Sections of ClO at the band heads of the v′, v″ = 1,0 to 21,0 bands 4-95
Table 4-79. Absorption Cross Sections of ClOO 4-95
Table 4-80. Summary of Previous Measurements of OClO Cross Sections 4-96
Table 4-81. Absorption Cross Sections of OClO at 204 K (averages over 1-nm intervals) 4-97
Table 4-82. Absorption Cross Sections of OClO at the a(21) to a(3) Band Peaks at 213-293 K 4-98
Table 4-83. Absorption Cross Sections of OClO at the Band Peaks (after Wahner et al. [830]) 4-99
Table 4-84. Absorption Cross Sections of Cl_2O 4-101
Table 4-85. Absorption Cross Sections of ClOOCl at 195-265 K 4-102
Table 4-86. Absorption Cross Sections of Cl_2O_3 at 220-260 K 4-103
Table 4-87. Absorption Cross Sections of Cl_2O_4 at 298 K 4-104
Table 4-88. Absorption Cross Sections of Cl_2O_6 at 298 K 4-105
Table 4-89. Absorption Cross Sections of Cl_2O_7 at 298 K 4-105
Table 4-90. Absorption Cross Sections of $ClClO_2$ at 298 K 4-106
Table 4-91. Absorption Cross Sections of HCl and DCl at 298 K 4-107
Table 4-92. Absorption Cross Sections of HOCl 4-108
Table 4-93. Absorption Cross Sections of ClNO 4-109
Table 4-94. Absorption Cross Sections of $ClNO_2$ at 298 K 4-110
Table 4-95. Absorption Cross Sections of ClONO at 231 K 4-110
Table 4-96. Absorption Cross Sections and Temperature Coefficients of $ClONO_2$ 4-111
Table 4-97. Absorption Cross Sections of CCl_4 at 295-298 K 4-114

Table 4-98. Absorption Cross Sections of CH_3OCl 4-114
Table 4-99. Absorption Cross Sections of $CHCl_3$ at 295-298 K 4-115
Table 4-100. Absorption Cross Sections of CH_2Cl_2 at 295-298 K 4-116
Table 4-101. Absorption Cross Sections of CH_3Cl at 295-298 K 4-117
Table 4-102. Absorption Cross Sections of CH_3CCl_3 at 295-298 K 4-118
Table 4-103. Absorption Cross Sections of CH_3CH_2Cl at 298 K 4-118
Table 4-104. Absorption Cross Sections of $CH_3CHClCH_3$ at 295 K 4-118
Table 4-105. Absorption Cross Sections of $COCl_2$ at 294-298 K 4-120
Table 4-106. Absorption Cross Sections of COHCl at 298 K 4-121
Table 4-107. Absorption Cross Sections of COFCl at 296-298 K 4-123
Table 4-108. Absorption Cross Sections of $CFCl_3$ at 295-298 K 4-124
Table 4-109. Absorption Cross Sections of CF_2Cl_2 at 295-298 K 4-125
Table 4-110. Absorption Cross Sections of CF_3Cl at 295 K 4-125
Table 4-111. Absorption Cross Sections of $CF_2ClCFCl_2$ at 295-298 K 4-126
Table 4-112. Absorption Cross Sections of CF_2ClCF_2Cl at 295 K 4-127
Table 4-113. Absorption Cross Sections of CF_3CF_2Cl at 295-298 K 4-129
Table 4-114. Absorption Cross Sections of $CHFCl_2$ at 295-298 K 4-130
Table 4-115. Absorption Cross Sections of CHF_2Cl at 295-298 K 4-131
Table 4-116. Absorption Cross Sections of CH_2FCl at 298 K 4-131
Table 4-117. Absorption Cross Sections of CF_3CHCl_2 at 295 K 4-133
Table 4-118. Absorption Cross Sections of CF_3CHFCl at 295 K 4-134
Table 4-119. Absorption Cross Sections of CF_3CH_2Cl at 298 K 4-134
Table 4-120. Absorption Cross Sections of CH_3CFCl_2 at 295-298 K 4-135
Table 4-121. Absorption Cross Sections of CH_3CF_2Cl at 295-298 K 4-136
Table 4-122. Absorption Cross Sections of CH_2ClCHO at 298 K 4-137
Table 4-123. Absorption Cross Sections of $CHCl_2CHO$ at 298 K 4-138
Table 4-124. Absorption Cross Sections of CF_2ClCHO at 298 K and Temperature Coefficients 4-139
Table 4-125. Absorption Cross Sections of $CFCl_2CHO$ at 298 K and Temperature Coefficients 4-139
Table 4-126. Absorption Cross Sections of CCl_3CHO at 298 K and Temperature Coefficients 4-140
Table 4-127. Absorption Cross Sections of $CH_3C(O)Cl$ at 295-298 K 4-141
Table 4-128. Absorption Cross Sections of $CH_2ClC(O)Cl$ at 298 K 4-142
Table 4-129. Absorption Cross Sections of $CHCl_2C(O)Cl$ at 298 K 4-142
Table 4-130. Absorption Cross Sections of $CCl_3C(O)Cl$ at 295 K 4-143
Table 4-131. Absorption Cross Sections of $CF_3CF_2CHCl_2$ and CF_2ClCF_2CFCl at 298 K 4-144
Table 4-132. Absorption Cross Sections of $CH_3C(O)CH_2Cl$ at 296 K 4-145
Table 4-133. Summary of Cross Section Measurements of Br_2 4-146
Table 4-134. Absorption Cross Sections of Br_2 at 298 K 4-147
Table 4-135. Summary of Cross Section Measurements of HBr 4-147
Table 4-136. Absorption Cross Sections of HBr at 296-298 K 4-148
Table 4-137. Summary of Cross Section Measurements of BrO 4-148
Table 4-138. Absorption Cross Sections at the Vibrational Band Peaks in the A ← X Spectrum of BrO (0.4 nm resolution) 4-149
Table 4-139. Absorption Cross Sections of BrO at 298 K 4-150
Table 4-140. Peak Absorption Cross Sections of OBrO at 298 K 4-152
Table 4-141. Absorption Cross Sections of OBrO at 298 K 4-153
Table 4-142. Absorption Cross Sections of Br_2O at 298 K 4-154
Table 4-143. Absorption Cross Sections of HOBr 4-155
Table 4-144. Absorption Cross Sections of BrNO at 298 K 4-157
Table 4-145. Absorption Cross Sections of BrONO at 253 K 4-157
Table 4-146. Absorption Cross Sections of $BrONO_2$ at 296 K and Temperature Coefficients 4-159
Table 4-147. Absorption Cross Sections of BrCl at 298 K 4-161
Table 4-148. Absorption Cross Sections of BrOCl at 298 K 4-161
Table 4-149. Absorption Cross Sections of CH_3Br at 295-296 K 4-162
Table 4-150. Absorption Cross Sections of CH_2Br_2 at 295-298 K 4-164
Table 4-151. Absorption Cross Sections of $CHBr_3$ at 295-296 K 4-165
Table 4-152. Absorption Cross Sections of CH_2BrCH_2Br at 295 K 4-166
Table 4-153. Absorption Cross Sections of C_2H_5Br at 295 K 4-166
Table 4-154. Absorption Cross Sections of $COBr_2$ at 298 K 4-167
Table 4-155. Absorption Cross Sections of COHBr at 298 K 4-168
Table 4-156. Absorption Cross Sections of CH_2ClBr at 295 K 4-169

Table 4-157. Absorption Cross Sections of $CHClBr_2$ at 296 K 4-170
Table 4-158. Absorption Cross Sections of $CHCl_2Br$ at 298 K 4-171
Table 4-159. Absorption Cross Sections of CCl_3Br at 298 K 4-171
Table 4-160. Absorption Cross Sections of CHF_2Br at 298 K 4-172
Table 4-161. Absorption Cross Sections of CF_2Br_2 at 295-296 K 4-174
Table 4-162. Absorption Cross Sections of CF_2ClBr_2 at 295-298 K 4-177
Table 4-163. Absorption Cross Sections of CF_3Br at 295-298 K 4-179
Table 4-164. Absorption Cross Sections of CH_2=CHBr at 295 K 4-179
Table 4-165. Absorption Cross Sections of CHBr=CF_2 at 295 K 4-180
Table 4-166. Absorption Cross Sections of CFBr=CF_2 at 295 K 4-180
Table 4-167. Absorption Cross Sections of CH_2=$CBrCF_3$ at 295 K 4-181
Table 4-168. Absorption Cross Sections of CF_3CH_2Br at 295 K 4-181
Table 4-169. Absorption Cross Sections of $CF_3CHClBr$ at 295-298 K 4-182
Table 4-170. Absorption Cross Sections of CF_3CHFBr at 295 K 4-183
Table 4-171. Absorption Cross Sections of CF_2BrCF_2Br at 296 K 4-184
Table 4-172. Absorption Cross Sections of CF_3CF_2Br at 298 K 4-185
Table 4-173. Absorption Cross Sections of $CH_3CH_2CH_2Br$ and $CH_3CHBrCH_3$ at 295 K 4-185
Table 4-174. Absorption Cross Sections of $CH_3C(O)CH_2Br$ at 296 K 4-186
Table 4-175. Absorption Cross Sections of I_2 at 295 K 4-188
Table 4-176. Cross Sections at the Maxima and Minima of I_2 at 295 K 4-189
Table 4-177. Summary of Cross Section Measurements of IO 4-190
Table 4-178. Absorption Cross Sections of IO at 298 K 4-191
Table 4-179. Absorption Cross Sections of OIO at 295 K 4-193
Table 4-180. Absorption Cross Sections of HI at 298 K 4-195
Table 4-181. Absorption Cross Sections of HOI at 295-298 K 4-196
Table 4-182. Absorption Cross Sections of ICI at 298 K 4-197
Table 4-183. Absorption Cross Sections of IBr at 298 K 4-198
Table 4-184. Absorption Cross Sections of INO at 298 K 4-198
Table 4-185. Absorption Cross Sections of IONO at 298 K 4-199
Table 4-186. Absorption Cross Sections of $IONO_2$ at 298 K 4-199
Table 4-187. Absorption Cross Sections of CH_3I at 296-298 K and Temperature Coefficients 4-201
Table 4-188. Absorption Cross Sections of CH_2I_2 at 298 K 4-202
Table 4-189. Absorption Cross Sections of C_2H_5I at 298 K and Temperature Coefficients 4-203
Table 4-190. Absorption Cross Sections of CH_3CHI_2 at 298 K 4-203
Table 4-191. Absorption Cross Sections of C_3H_7I at 298 K and Temperature Coefficients 4-205
Table 4-192. Absorption Cross Sections of $(CH_3)_3CI$ at 298 K 4-206
Table 4-193. Absorption Cross Sections of CF_3I at 295-300 K 4-208
Table 4-194. Absorption Cross Sections of CF_2I_2 at 294 K 4-210
Table 4-195. Absorption Cross Sections of C_2F_5I at 323 K 4-210
Table 4-196. Absorption Cross Sections of 1-C_3F_7I at 295-298 K 4-211
Table 4-197. Absorption Cross Sections of CH_2ICI at 298 K and Temperature Coefficients 4-212
Table 4-198. Absorption Cross Sections of CH_2BrI at 298 K and Temperature Coefficients 4-212

Table 5-1. Mass Accommodation Coefficients (α)for Surfaces Other Than Soot 5-9
Table 5-2. Gas/Surface Reaction Probabilities (γ) for Surfaces Other Than Soot 5-21
Table 5-3. Soot Surface Uptake Coefficients 5-50
Table 5-4. Henry's Law Constants for Pure Water 5-53
Table 5-5. Ion-Specific Schumpe Parameters 5-61
Table 5-6. Henry's Law Constants for Acids 5-62

FIGURES

Figure 4-1. Absorption Spectrum of NO_3 4-31
Figure 4-2. Absorption Spectrum of ClO 4-94
Figure 4-3. Absorption Spectrum of OClO at 204 K (after Wahner et al. [830]) 4-99
Figure 4-4. Absorption Spectrum of BrO (after Wahher et al. [829]) 4-151
Figure 4-5. Absorption Spectrum of OBrO (after Knight et al. [413]) 4-154

Figure 5-1. Recommended Reactive Uptake Coefficients as a Function of Temperature for Key Stratospheric Heterogeneous Processes on Sulfuric Acid Aerosols 5-9

INTRODUCTION

This compilation of kinetic and photochemical data is an update to the 14th evaluation prepared by the NASA Panel for Data Evaluation. The Panel was established in 1977 by the NASA Upper Atmosphere Research Program Office for the purpose of providing a critical tabulation of the latest kinetic and photochemical data for use by modelers in computer simulations of atmospheric chemistry. Table I-1 lists this publication's editions:

Table I-1: Editions of this Publication

	Edition	Reference
1	NASA RP 1010, Chapter 1	Hudson et al. [1]
2	JPL Publication 79-27	DeMore et al. [12]
3	NASA RP 1049, Chapter 1	Hudson and Reed [2]
4	JPL Publication 81-3	DeMore et al. [10]
5	JPL Publication 82-57	DeMore et al. [8]
6	JPL Publication 83-62	DeMore et al. [9]
7	JPL Publication 85-37	DeMore et al. [3]
8	JPL Publication 87-41	DeMore et al. [4]
9	JPL Publication 90-1	DeMore et al. [5]
10	JPL Publication 92-20	DeMore et al. [6]
11	JPL Publication 94-26	DeMore et al. [7]
12	JPL Publication 97-4	DeMore et al. [11]
13	JPL Publication 00-3	Sander et al. [19]
14	JPL Publication 02-25	Sander et al. [18]
15	JPL Publication 06-2	Sander et al. [17]

In addition to the current edition, several previous editions are available for download from the website.

Panel members, and their major responsibilities for the current evaluation are listed in Table I-2.

Table I-2: Panel Members and their Major Responsibilities for the Current Evaluation

Panel Members	Responsibility
S. P. Sander, Chairman	Editorial Review, publication, website, ClO_x/BrO_x reactions, photochemistry
V. L. Orkin M. J. Kurylo	Cl reactions with halocarbons
D. M. Golden	Three-body reactions, equilibrium constants, editorial review
R. E. Huie	Aqueous chemistry, thermodynamics
C. E. Kolb B. J. Finlayson-Pitts M. J. Molina	Heterogeneous chemistry, Na chemistry
R. R. Friedl	HO_x reactions, OH + C_3 hydrocarbon reactions, photochemistry
A. R. Ravishankara	$O(^1D)$, $O_2(^1\Sigma)$, OH + hydrocarbon reactions, photochemistry
G. K. Moortgat H. Keller-Rudek	Photochemistry (O_3, HO_x, NO_x, carbonyls, FO_x, ClO_x, BrO_x, IO_x)
P. H. Wine	Sulfur chemistry

As shown above, each Panel member concentrates his efforts on a given area or type of data. Nevertheless, the Panel's final recommendations represent a consensus of the entire Panel. Each member reviews the basis for all recommendations, and is cognizant of the final decision in every case.

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I.1 Basis of the Recommendations

The recommended rate data and cross sections are based on laboratory measurements. In order to provide recommendations that are as up-to-date as possible, preprints and written private communications are accepted, but only when it is expected that they will appear as published journal articles. Under no circumstances are rate constants adjusted to fit observations of atmospheric concentrations. The Panel considers the question of consistency of data with expectations based on the theory of reaction kinetics, and when a discrepancy appears to exist this fact is pointed out in the accompanying note. The major use of theoretical extrapolation of data is in connection with three-body reactions, in which the required pressure or temperature dependence is sometimes unavailable from laboratory measurements, and can be estimated by use of appropriate theoretical treatment. In the case of important rate constants for which no experimental data are available, the panel may provide estimates of rate constant parameters based on analogy to similar reactions for which data are available.

I.2 Scope of the Evaluation

In the past (releases 1-12 of this evaluation) it has been the practice of the Panel to reevaluate the entire set of reactions with individual Panel members taking responsibility for specific chemical families or processes. In recent years, the upper troposphere and lower stratosphere (UT/LS) have become the primary areas of focus for model calculations and atmospheric measurements related to studies of ozone depletion and climate change. Because the UT/LS is a region of relatively high chemical and dynamical complexity, a different approach has been adopted for future releases of the evaluation. Specifically, the entire reaction set of the data evaluation will no longer be re-evaluated for each release. Instead, specific subsets will be chosen for re-evaluation, with several Panel members working to develop recommendations for a given area. This approach will make it possible to treat each subset in greater depth, and to expand the scope of the evaluation to new areas. It is the aim of the Panel to consider the entire set of kinetics, photochemical and thermodynamic parameters every three review cycles. Each release of the evaluation will contain not only the new evaluations, but also recommendations for every process that has been considered in the past. In this way, the tables for each release will constitute a complete set of recommendations.

It is recognized that important new laboratory data may be published that lie outside the specific subset chosen for re-evaluation. In order to ensure that these important data receive prompt consideration, each evaluation will also have a “special topics” category. Feedback from the atmospheric modeling community is solicited in the selection of reactions for this category.

For the current evaluation, the specific subsets include the following:

- Hydrocarbon chemistry of the upper troposphere (C_3 hydrocarbons and below).
- Reactions of Cl with halocarbon species.
- Reactions of sulfur compounds.
- Photochemistry of O_3, NOx, carbonyl compounds, FOx, ClOx, BrOx and IOx
- Heterogeneous processes on liquid water, water ice, alumina and solid alkali halide salts
- Gas-liquid solubility (Henry’s Law Constants and Schumpe Parameters)
- Thermodynamic parameters (entropy and enthalpy of formation)
- The special topics category includes several important reactions in atmospheric chemistry such as O+ClO, HO_2+HO_2, HO_2+BrO.

I.3 Format of the Evaluation

Changes or additions to the data tables are indicated by shading. A new entry is completely shaded, whereas a changed entry is shaded only where it has changed. In some cases only the note has been changed, in which case the corresponding note number in the table is shaded.

I.4 Computer Access

This document is available online in the form of individual chapters and as a complete document in Adobe PDF (Portable Data File) format. Files may be downloaded from http://jpldataeval.jpl.nasa.gov/. This document is not available in printed form from JPL.

The tables of recommended cross sections from this evaluation can be downloaded from the spectral atlas of the Max-Planck Institute for Chemistry at: http://www.atmosphere.mpg.de/enid/2295

To receive email notification concerning releases of new publications and errata, a mailing list is available. To subscribe, send a blank message to join-jpl-dataeval@list.jpl.nasa.gov with "Subscribe" (without quotes) in the subject line.

For more information, contact Stanley Sander (Stanley.Sander@jpl.nasa.gov).

I.5 Data Formats

In Table 1 (Rate Constants for Bimolecular Reactions) the reactions are grouped into the classes O_x, HO_x, NO_x, Organic Compounds, FOx, ClOx, BrOx, IOx, SOx and Metal Reactions. The data in Table 2 (Rate Constants for Association Reactions) are presented in the same order as the bimolecular reactions. The presentation of photochemical cross section data follows the same sequence.

I.6 Units

Rate constants are given in units of concentration expressed as molecules per cubic centimeter and time in seconds. That is, for first-, second-, and third-order reactions, units of k are s^{-1}, cm^3 $molecule^{-1}$ s^{-1}, and cm^6 $molecule^{-2}$ s^{-1}, respectively. Cross sections are expressed as cm^2 $molecule^{-1}$, base e.

I.7 Noteworthy Changes in this Evaluation

I.7.1 Bimolecular Reactions (Section 1)

The rate constants for the reactions of O(1D) with N_2, O_2, and H_2O have been revised and the uncertainties in their values greatly reduced in this evaluation. These reactions (in competition) exert a significant influence on the production of HO_x throughout most of the lower and middle atmosphere. There have been previous suggestions that the reaction of $O_2(1\Sigma)$ with H_2 could be a source of HO_x. The overall rate coefficient for this reaction along with the branching ratio for the production of the reaction to produce 2 OH has been evaluated; this reaction is unlikely to be a significant source of HO_x anywhere in the troposphere and the stratosphere.

The reaction of $O_2(1\Sigma)$ with N_2O, a suggested route for the formation of NO_x in the atmosphere, has been evaluated. As in the case of $O_2(1\Sigma)$ reaction with H_2, this reaction to produce NO_x is small and negligible.

The reaction of OH with aldehydes has been updated and expanded. The new recommendation for the OH + acetone reaction indicates that the reaction products are almost exclusively $CH_3C(O)CH_2$ and H_2O. (Since the evaluation was completed, there is a suggestion based on calculations that the reaction of HO_2 with acetone at low temperatures could be an important loss process for acetone in the upper troposphere and thus alter the production of HO_x from acetone. This process has not been evaluated here.)

A comprehensive review of the reactions of hydrogen, methane, ethane, propane, and industrial and naturally occurring halogenated hydrocarbons with chlorine atoms was conducted for this evaluation. In doing so, attempts were made to understand and reconcile apparent differences between the results of absolute and relative rate measurements for some of the reactions. Relative rate constants were "renormalized" using the revised recommendations for the reference reactions. Thus, the re-evaluation procedure was an iterative one, since relative rate studies themselves were often included as the basis for the rate constant recommendations of these very reference reactions. The recommendations were then checked for self-consistency by seeing if ratios of the recommended rate constants were in agreement with published relative rate measurements. In some cases, disparities may seem to exist. However, it should be recognized that the focus of this re-evaluation was generating recommended rate constants over the temperature range of atmospheric importance (i.e., below 300 K). Finally, uncertainty factors (f and g) were carefully reviewed in an attempt to reasonably narrow the rate constant uncertainties for modeling purposes. Previous uncertainty limits were overly conservative in some cases.

A number of reactions in the inorganic reactions in the ClO_x and BrO_x families were reviewed with particular attention to reactions of stratospheric interest (e.g. O + ClO, BrO + HO_2, Br + HO_2, BrO + BrO, OH + HBr). For the most part, changes to the database for these reactions have not influenced the recommended values. However, the uncertainties have been reduced in many cases, particularly at low temperatures.

The section on SO_x reactions has been updated for the first time in nearly a decade. All literature published before the end of 2004 and selected more recent publications have been examined. Recommendations for approximately 30 reactions that appeared in Table 1 of Evaluation 14 have been revised. Reactions of dimethyl sulfoxide ($CH_3S(O)CH_3$) and methane sulfinic acid ($CH_3S(O)OH$) are included in Table 1 for the first time, as are bimolecular reactions of the weakly bound adducts SCS−OH, $(CH_3)2S$−OH, SCS−Cl, $(CH_3)2S$−Cl, and $(CH_3)2(O)S$−Cl. Also included in Table 1 for the first time are recommendations for the reactions BrO + CH_3SSCH_3, $CH_3SCH_2O_2$ + $CH_3SCH_2O_2$, and SH + N_2O.

Reactions involving atomic sodium and its oxide, hydroxide, carbonate, bicarbonate, and chloride molecules are updated in Section 1, Bimolecular Reactions, and Section 4, Photochemical Data, of this report. Although there is some evidence that volcanic action can deposit sodium species in the stratosphere, the main source of upper atmospheric sodium species is believed to be ablation from meteorites in the upper mesosphere and lower thermosphere. Meteorite ablation also deposits gaseous K, Li, Ca, Mg, Al and Fe species at these altitudes, but the observed concentrations of Na and Fe and the computed concentrations of their gaseous compounds significantly exceed concentrations of other mesospheric metals. Atmospheric models of meteor metal ablation and subsequent atmospheric chemistry have recently been reviewed by McNeil et al. [14] and laboratory and ab initio studies of their chemical kinetics and photochemistry have been reviewed by Plane [15, 16]. Since the available laboratory data for kinetic and photochemical processes involving sodium and its compounds significantly exceed those for other meteor metals and since Na is believed to have the most vigorous and complex atmospheric chemistry, we have restricted our evaluation of meteor metal chemical kinetics to Na species. Those interested in the chemical kinetics of meteor metals other than Na should see Plane [15, 16]. The major deficiency in current models of atmospheric Na chemistry and other meteor metals is the lack of quantitative data to model the sink for gaseous compounds, which is believed to be condensation on ultrafine oxide particulates of meteor "smoke" present in the mesosphere and upper stratosphere [13, 16].

I.7.2 Termolecular Reactions and Equilibrium Constants (Sections 2 and 3)

A specific entry has been written for the reaction OH + NO_2 + M → HOONO + M. This pathway was called out in the note in the last evaluation, but is now explicitly entered in the table.

The reaction OH + CO has been moved from Table 1 to Table 2. It is shown with two entries, one each for the association reaction to form HOCO and one for the chemical activation process to form H+CO_2. It is important to note that the chemical activation process is calculated using the expression for these types of reactions that is delineated in the Introduction to Table 2.

In addition to the changes to which attention is called by the shading convention, it should be noted that several reactions of species containing sulfur have been added to the table.

The equilibrium constant for the process forming HOONO from OH and NO_2 has been added, as have some sulfur reactions.

I.7.3 Photochemical Data (Section 4)

The section dealing with photochemical data has been greatly expanded and revised for all the chemical families (with the exception of HO_x). In all, 78 new species were added. The evaluations for many other species were revised and expanded. Most of the new species are organics and halogen-substituted organics including carbonyl compounds (aldehydes and ketones, both saturated and unsaturated). We have also included a number of new inorganic halogens that are important in the troposphere and stratosphere including Br_2, OBrO, I_2, IO, OIO, HOI and $IONO_2$.

I.7.4 Heterogeneous Chemistry (Section 5)

New and/or updated heterogeneous kinetics evaluations in this document have focused on processes on liquid water, on water ice, on alumina, and on solid alkali halide salts and and their aqueous solutions. Uptake studies of volatile organic species (VOCs) on water ice surfaces have not been included in his evaluation. A few important uptake processes occurring on liquid sulfuric acid surfaces have also been added or updated. The compilation of Henrys law parameters for pure water has been extended and a procedure for estimating the effective Henrys law parameters for aqueous salt solutions has been added.

I.7.5 Thermodynamic Parameters (Appendix A)

The table in Appendix A contains selected entropy and enthalpy of formation values at 298 K for a number of atmospheric species. As much as possible, the values were taken from primary evaluations, that is, evaluations that develop a recommended value from the original studies. Otherwise, the values were selected from the original literature, which is referenced in the table. Often, the enthalpy of formation and the entropy values are taken from different sources, usually due to a more recent value for the enthalpy of formation. The cited error limits are from the original references and therefore reflect widely varying criteria. Some enthalpy values were corrected slightly to reflect the value of a reference compound selected for this table; these are indicated. Values that are calculated or estimated are also indicated in the table.

I.8 Acknowledgements

The Panel wishes to acknowledge the contributions of the following persons for their assistance in the preparation and review of this report: Kyle Bayes (JPL), Jim Burkholder (NOAA), Carissa Howard (Georgia Tech), Rachna Kamath (Georgia Tech) and Ranajit Talukdar (NOAA). We also gratefully acknowledge the expert typing and editing skills of Rose Kendall (CSC), Xuan Sabounchi (JPL), Kathy Thompson (CSC) and Tom Wilson (JPL). Financial support from the NASA Upper Atmosphere Research and Tropospheric Chemistry Programs is gratefully acknowledged.

SPS wishes to acknowledge Joan and Steven Sander, whose love and support made this report possible.

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