Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions

Cite as: Journal of Physical and Chemical Reference Data 2, 25 (1973); https://doi.org/10.1063/1.3253112
Published Online: 29 October 2009

Keith Schofield

ARTICLES YOU MAY BE INTERESTED IN

Chemical Kinetic Data Base for Combustion Chemistry. Part I. Methane and Related Compounds
Journal of Physical and Chemical Reference Data 15, 1087 (1986); https://doi.org/10.1063/1.555759

Evaluated Kinetic Data for Combustion Modelling

Chemical Kinetic Data Sheets for High-Temperature Reactions. Part II
Journal of Physical and Chemical Reference Data 20, 1211 (1991); https://doi.org/10.1063/1.555901
Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions

Keith Schofield

Delco Electronics—Santa Barbara Operations, Division of General Motors, Goleta, California 93017

The available information, up to mid-1972, for the rate constants of a series of gas phase chemical reactions has been evaluated critically. For each reaction, relevant thermodynamic data are presented and values for the equilibrium constant expressed in mathematical form. Kinetic data are presented in tabular and graphical form together with a discussion of the pertinent details. Recommended rate constant values are presented wherever possible with suggested error limits. The reactions considered involve the species H, O, C, N, S, OH, HS, S, CS, SO, HSO, NH3, NH2, NO, N2O, N2O3, N2O5, N2, O3, H2, H2O, SO2, SO3, CS2, OCS, HS2, and CO. Particular emphasis is given to reactions involving sulfur chemistry. The best available data for these reactions have been summarized in a table at the end of the paper. An appendix discussing the available evaluations and review articles published since 1969 also has been included to publicize these sources of either evaluated data or of extensive reference bibliographies.

Key words: Activation energies; evaluation; gaseous reactions; radical reactions; rate constants; review; sulfur chemistry; tables.

Contents

1. Introduction ........................................ 25
2. Presentation of Data ................................. 26
3. Symbols and Conversion Factors .................... 27
4. Detailed Rate Constant Evaluations.............. 27
   4.1. O + H + M → OH + M .......................... 27
   4.2. CO + M → O + M ............................... 29
   4.3. CO + M → O + M ............................... 30
   4.4. N2O + M → N2 + O + M ....................... 32
   4.5. O + N2 + M → N2O + M ....................... 42
   4.6. N2O + M → NO + NO + M ..................... 43
   4.7. NH3 + M → NH2 + H + M ..................... 47
   4.8. NH3 + H + M → NH2 + M ..................... 49
   4.9. SO + O → SO2 + M ............................ 50
   4.10. SO + M → SO2 + M ............................ 50
   4.11. SO + O + M → SO2 + O ...................... 51
   4.12. SO + O + M → SO2 + M ...................... 53
   4.13. SO + O + M → SO3 + O ...................... 56
   4.14. SO + O + M → SO3 + S ...................... 57
   4.15. S + O + M → SO2 + O ....................... 58
   4.16. H + SO2 + M → HSO2 + M .................. 60
   4.17. O + CS2 → CS + SO .......................... 62
   4.18. O + OCS → CO + SO ......................... 64
   4.19. O + H2S → OH + HS .......................... 66
   4.20. H + HSO → H2 + SO ......................... 68
   4.21. H + HS + M → H2S + M ...................... 70
   4.22. HS + HS → H2S + S .......................... 71
   4.23. HS + HS → H2 + S ............................ 72
   4.24. H + HS → H2 + S ............................. 73
   4.25. S + HS → SO + H .............................. 74
   4.26. Miscellaneous Reactions ...................... 75
      O + H2 + M → H2O + M ......................... 75
      N + NO + M → N2O + M ......................... 75
      SO + O2 + M → SO2 + O ......................... 75

4. Detailed Rate Constant Evaluations—Con.
4.26. Miscellaneous Reactions—Con. .................. 75
      O + SO2 → SO + O2 .............................. 75
      SO + O2 → SO2 + O .............................. 75

5. Rate Constants—A Summary ......................... 79
6. Acknowledgments .................................... 80
Appendix ................................................ 80

1. Introduction

The available information on a series of gas phase chemical reactions has been carefully evaluated and tabulated. An effort has been made to include all pertinent references up to mid-1972. The aim of this publication is to provide a useful reference source of data against which new information can be compared and added at a later time. Also, it is hoped that it will better illustrate those areas of greatest uncertainty where further effort is needed and possibly dissuade researchers from repeating measurements of established values unless well justified.

A number of factors influenced the choice of reactions included in this review. They are frequently
encountered reactions that have not been evaluated elsewhere, and many of them are relevant to current research and development programs. The majority emphasize reactions of importance in the gas phase chemistry of sulfur compounds. Others were added to round off more completely the coverage of previously published evaluations. Nineteen related reactions for which very little information is available have been listed together in a miscellaneous reactions section. These frequently appear in chemical kinetic models. The extent and limit of our knowledge of their rate constants is outlined.

An evaluation of experimental data in chemical kinetics centers on various important facets. Judgments have to be made, based on present knowledge, as to whether the techniques used and the assumptions made were valid; whether it is necessary to reanalyze the primary experimental data using parameters that have since been improved on; and whether the reported rate constants actually refer to the reaction claimed. Assessments can only be fair if comparisons are truly valid. Frequently, it appears that only during the compilation of such tables does the opportunity arise to assess the available data carefully. To indulge in this time-consuming activity is not generally possible, and often is not of particular interest, to the average experimental investigator. Unfortunately, insufficient information still exists in many current publications, so that only a cursory evaluation can be made. Authors should be reminded that for others to judge their work, certain inclusions have to be made. For example, it is not unusual for an uncertainty to arise simply through the omission of the basic definition of the rate constant.

Inevitably, in spite of the strenuous efforts made to eliminate mistakes and omissions in such a collection of data, some may have occurred. The author hopes to be notified of any such findings.

2. Presentation of Data

The presentation of the available rate information, for the various chemical reactions considered, is based upon a style similar to that of the Leeds University Reports on High Temperature Reaction Rate Data by Baulch, et al. Each reaction is considered separately. A table of pertinent thermodynamic data is given, derived from the JANAF Thermochemical Tables.1

Where applicable, values of the equilibrium constants are given in both pressure (atm) and concentration (molecule cm⁻³) units. In addition, the equilibrium constant has been expressed in the mathematical form

\[ K = BE^n \exp \left( \frac{C}{RT} \right) \]

so that the rate constant for the reverse reaction can be calculated if required. The values for B, n, and C have been determined by taking the equilibrium constant data derived from the JANAF Tables at 100 K intervals over the range specified, and calculating a least squares fit. The temperature range has been restricted in some cases to minimize the deviation between the expression for K and the data points. The maximum deviation within the temperature range is specified.

The available rate data have been listed, and where possible original data points have been preferred. cm² molecule⁻¹ s⁻¹ and cm² molecule⁻² s⁻¹ units have been used throughout for bi- and termolecular rate constants, respectively. The experimental temperature range, a brief description of the method used with some experimental conditions, and brief comments are given. Occasionally, to facilitate comparison of data measured in similar temperature regimes, values for k have been calculated for a common temperature. Generally, the data have been plotted to better illustrate the extent of the scatter and the agreement between various studies. The values are then discussed in more detail and the reliability assessed. The data which form the basis for the recommended values are identified. The recommended value is listed separately with suggested error limits. It is based either on the most reliable single set of measurements or, where several sources of data are available, of similar uncertainty, an equally weighted least squares fit. Unreliable sources of data are not included in such an assessment. Error limits are approximately estimated as those which appear most reasonable considering the total available information. In instances where sufficient data permitted, standard deviations of the activation energy and the preexponential factor have been calculated.

The Arrhenius expression for the rate constants

\[ k = A \exp \left( \frac{-E}{RT} \right) \]

is used in most cases. The activation energy, E, is expressed in cal mol⁻¹. Occasionally, values have been expressed in the theoretical form

\[ k = \frac{Z}{(s-1)!} \left( \frac{\Delta E_v}{RT} \right)^{s-1} \exp \left( \frac{-\Delta E_v}{RT} \right) \]

where s represents the number of oscillator terms contributing to the dissociation process of unimolecular reactions.

---

1 Data were obtained from the JANAF Thermochemical Tables, PB 168370 (1968), vol. 1, 2, and 3 Addenda, PB 168371-1, 2, 3 (1966-1968). A revision of these tables has recently been published as JANAF Thermochemical Tables, 2nd Edition (NBS-NBS 37), D. R. Baulch and H. Prophet, Project Director. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. Catalog No. C 13-05-37, Price $0.25. The revisions do not significantly affect the thermodynamic data presented in this review.
Care has been taken to define the rate constant in a uniform way for reactions involving common species such as \( X + X \rightarrow Y + Z \), for which
\[
\frac{d[Y]}{dt} = -0.5 \frac{d[X]}{dt} = k[X]^2.
\]

Unimolecular reactions present certain problems in displaying the available data. The low pressure region where the chemistry is described by 2nd order kinetics and the high pressure 1st order regimes can be handled conventionally. It is the intermediate region where the chemistry is described by 2nd order displaying the available data. The low pressure can be handled conventionally. It is the intermediate region where the chemistry is described by 2nd order.

Where necessary, sensible guesses have been made for the temperature of certain measurements for which the investigator merely reported "room-temperature."

References pertaining to a particular reaction are listed at the end of each section.

3. Symbols and Conversion Factors

- \( K, K_e \): equilibrium constant
- \( K_p \): equilibrium constant in terms of partial pressures (atm)
- \( K_c \): equilibrium constant in terms of concentrations (molecule cm\(^{-3}\))
- \( k, k_{rX} \): reaction rate constant
- \( k_{A+B} \): rate constant for the reaction \( A + B \rightarrow M \)
- \( k_m \): rate constant with \( M \) as the chaperon third body
- \( k_u \): unimolecular rate constant (s\(^{-1}\)) at its infinite pressure limit
- \( [A] \): concentration of \( A \)
- \( A \): pre-exponential factor of a rate constant
- \( E \): activation energy of a reaction
- \( R \): gas constant, equal to 1.987 cal deg\(^{-1}\) mol\(^{-1}\)
- \( T \): temperature in Kelvin (K)

Avogadro's Number \( = 6.0225 \times 10^{23} \) particle mol\(^{-1}\)

- 1 cal = 4.184 joules
- 1 mm Hg = 1 torr = 1760 atm
- 1 millitorr = 10\(^{-2}\) torr
- 1 atm = 7.3355 \times 10\(^{9}\)/T particles cm\(^{-3}\) = 0.012187/T mol cm\(^{-3}\) = 1.01325 \times 10\(^{4}\) Newtons meter\(^{-2}\)
- 1 molecule cm\(^{-3}\) = 1.6604 \times 10^{-21} \) mol l\(^{-1}\)

1 cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) = 6.0225 \times 10^{20} \) cm\(^3\) mol\(^{-1}\) s\(^{-1}\) = 6.0225 \times 10^{20} \) mol\(^{-1}\) s\(^{-1}\)

1 cm\(^6\) molecule\(^{-3}\) s\(^{-1}\) = 3.6278 \times 10^{4} \) cm\(^3\) mol\(^{-2}\) s\(^{-1}\) = 3.6278 \times 10^{4} \) mol\(^{-1}\) s\(^{-1}\)

4. Detailed Rate Constant Evaluations

4.1. \( O + H + M \rightarrow OH + M \)

Thermodynamic data

<table>
<thead>
<tr>
<th>( TK )</th>
<th>( \Delta H^0 ) kcal mol(^{-1})</th>
<th>( \Delta S^0 ) cal deg(^{-1}) mol(^{-1})</th>
<th>( \log_{10} K_p ) atm(^{-1})</th>
<th>( \log_{10} K_c ) cm(^3) molecule(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>101.331</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>101.630</td>
<td>-18.705</td>
<td>218.012</td>
<td>198.146</td>
</tr>
<tr>
<td>200</td>
<td>101.797</td>
<td>-9.090</td>
<td>70.127</td>
<td>50.736</td>
</tr>
<tr>
<td>300</td>
<td>102.233</td>
<td>-21.999</td>
<td>69.665</td>
<td>50.277</td>
</tr>
<tr>
<td>400</td>
<td>102.836</td>
<td>-23.541</td>
<td>39.802</td>
<td>26.635</td>
</tr>
<tr>
<td>500</td>
<td>100.262</td>
<td>-25.322</td>
<td>17.206</td>
<td>-1.660</td>
</tr>
<tr>
<td>700</td>
<td>100.309</td>
<td>-27.031</td>
<td>5.715</td>
<td>-12.850</td>
</tr>
<tr>
<td>800</td>
<td>100.723</td>
<td>-27.399</td>
<td>3.383</td>
<td>-15.085</td>
</tr>
<tr>
<td>900</td>
<td>100.761</td>
<td>-27.603</td>
<td>1.817</td>
<td>-16.571</td>
</tr>
<tr>
<td>1000</td>
<td>100.372</td>
<td>-27.777</td>
<td>0.694</td>
<td>-17.628</td>
</tr>
<tr>
<td>1100</td>
<td>100.846</td>
<td>-27.916</td>
<td>0.155</td>
<td>-18.419</td>
</tr>
<tr>
<td>1200</td>
<td>100.937</td>
<td>-28.032</td>
<td>0.816</td>
<td>-19.028</td>
</tr>
<tr>
<td>1300</td>
<td>100.913</td>
<td>-28.132</td>
<td>-1.348</td>
<td>-19.515</td>
</tr>
<tr>
<td>1400</td>
<td>100.739</td>
<td>-28.221</td>
<td>-1.786</td>
<td>-19.911</td>
</tr>
<tr>
<td>1500</td>
<td>100.735</td>
<td>-28.300</td>
<td>-2.151</td>
<td>-20.288</td>
</tr>
</tbody>
</table>

Equilibrium Constant

- \( K_s = 0.313 T^{-1.481} \) exp(103.850/RT) atm\(^{-1}\)
- \( = 3.89 \times 10^{-2} T^{-0.808} \) exp(102.580/RT) atm\(^{-1}\)

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.4 percent (300–1000 K) and 0.6 percent (1000–3000 K).

Recommended Rate Constant

No reliable data are available for this reaction. A value \( k_u \approx 2 \times 10^{-32} \) cm\(^6\) molecule\(^{-3}\) s\(^{-1}\) for the 1000–3000 K temperature range with a possible error of a factor of 10 would be compatible with observations. No information has been published for the reverse reaction, the dissociation of OH.

Discussion

For several years now, in spite of the scant data available, this reaction has been included in performance calculations of supersonic combustors [Da-Riva, 1966], rocket and ramjet nozzle expansions [Boynton, 1964; Francis and Lezberg, 1963; Baulknight, 1965; Westenberg and Favin, 1963], hypersonic wake flow fields [Langan et al., 1965], and shock tube kinetic schemes [Duff, 1958; Schott, 1960]. Also, it has appeared in various
such a force

...original text...
It appears that the nine-reaction mechanism used is not sufficient to fully describe the system and additional reactions of HO, H₂O, and O₃ need to be considered.

From effects of composition Jenkins et al. (1967) conclude that H₂O and O₃ are equally efficient third bodies for this reaction.

References


The thermodynamic data for 7000 to 15,000 K have been calculated using the JANAF program.

Equilibrium Constant

\[ K_p = 2.18 \times 10^8 \ T^{-0.6} \ \text{exp} \left( -260,550 / RT \right) \ \text{atm} \]

(6000–14,000 K range).

This reproduces the 1000 K interval equilibrium data with deviations of up to 0.8 percent in the range specified.

Recommended Rate Constant

Fairbairn's work (1969) provides the only available data relating directly to this reaction (see discussion). It infers a value of \( \leq 5 \times 10^{-16} \text{ cm}^{-3} \text{ molecule}^{-1} \cdot s^{-1} \) at 8000 K, with a quoted uncertainty of ±50 percent. Further work is obviously necessary.

Third body efficiencies: \( k_d \sim k_f \).

No experimental data other than these are available for the reverse three body recombination reaction.

Discussion

The rate for the one-step reaction

\[ k_1 \]

\[ \text{CO} + \text{M} \rightarrow \text{C} + \text{O} + \text{M} \]

has not yet been satisfactorily measured. Fairbairn's (1968, 1969) observation of an induction period in the shock tube dissociation of CO, since confirmed...
by Appleton, Steinberg and Liquornik (1970), established that the dissociation mechanism cannot be described by such a one-stage process, but is rather a series of reactions involving an intermediate. Therefore, although the steady state dissociation rate after the induction period can be represented by the expression

\[ -\frac{d[CO]}{dt} = k[CO] \text{ [M]} \]

The rate constant so derived has only empirical meaning as it refers to the overall mechanism involved rather than \( k \).

Fairbairn (1969) reports that the reactions (2) to (4)

(2) \( \text{CO} + \text{M} \rightarrow \text{C} + \text{O} + \text{M} \),
(3) \( \text{C} + \text{CO} \rightarrow \text{C}_2 + \text{O} \),
(4) \( \text{C}_2 + \text{M} \rightarrow \text{C} + \text{O} + \text{M} \),

can account for the essential features of the dissociation process.

At 8000 K he has estimated constants for the rate constants which reproduce the observed \( C_2 \) and CO emission profiles. He reports a value of \( \leq 2 \times 10^{-24} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) for the reverse three-body recombination \( \text{C} + \text{O} + \text{M} \rightarrow \text{CO} + \text{M} \) which converts to the value of \( k_1 \leq 4.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) quoted here. However, the conclusions are based on limited data and it would be premature to accept this mechanism over others which invoke electronically excited CO state intermediates [Fairbairn, 1968; Appleton et al., 1970]. It must be regarded as approximate until further measurements are made.

He reports also, values derived from the initial reaction rate during the induction period of CO/Ne mixtures \( (9.2 \times 10^{-18} \text{ at } 8000 \text{ K}) \), but these are subject to an error of about a factor of four owing to the difficulties in the data reduction. Similar slow decays of CO during the induction period were not reported by Appleton et al. (1970).

Little difference was found between Ar or Ne as third bodies [Fairbairn, 1969].

References


4.3. CO+M/C+O+M

Values for the rate constant measured from the steady state dissociation of CO and defined by \( \frac{d[CO]}{dt} = -k[CO][M] \) but which are identified solely as values that relate to the overall mechanism.

Thermodynamic Data and Equilibrium Constant

Listed under the CO+M→C+O+M reaction.

**Recommended Rate Constant**

\[ k_M = 1.46 \times 10^6 T^{-1.52} \exp \left( -255,760/RT \right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]

Temperature range: 7000–15,000 K.

Suggested error limits:

\[ \pm 75 \text{ percent } (7000–10,000 \text{ K}), \]
\[ \pm 50 \text{ percent } (10,000–15,000 \text{ K}). \]

Third body efficiencies:

\[ k_C \leq 2k_A, \quad k_O = 15k_A. \]

The available rate constant data are shown in figure 1.
Discussion

Although the rate constants derived from the steady state dissociation of CO do not refer to the elementary step $\text{CO} + \text{M} \rightarrow \text{O} + \text{O} + \text{M}$ but rather to the overall process, which is also described by the expression $d(\text{CO})/dt = -k(\text{CO})[\text{M}]$, it may be of some use to evaluate the available data. Three shock tube studies constitute the sources of data and are in good agreement which is reassuring since different methods of monitoring the [CO] decay were used in each.

Davies (1964) monitored the infra-red fundamental band of CO at $4.65 \mu$ and also the emission at $6433 \AA$, which he claimed to be from the (3,0) triplet band of the CO $d\Delta \rightarrow a\Pi$ system. Fairbain (1989), more recently, looked unsuccessfully for this same triplet emission. Both emissions were found to decay similarly and postulating the establishment of a steady state non-equilibrium population in the CO $d\Delta (\nu' = 3)$ level proportional to the total CO concentration, he managed to obtain rate constants one 20-50 percent higher than those obtained from the $4.65 \mu$ measurements. However, owing to the assumptions involved, the $4.65 \mu$ data are considered the more reliable and are quoted here.

Presley, et al. (1966) express their dissociation rate in the form of the recombination coefficient, a practice unfortunately quite common in many shock tube studies of dissociation rates and one which should be dissuaded. They report $k_{\text{recon}} = 6.8 \times 10^{-15} T^{-1/2}$ for the temperature range studied. However, an error in their published expression for the equilibrium constant has made it preferable to read the data points directly off their plot of $k_{\text{dissociation}}$ rather than use this expression and an equilibrium constant.

Appleton, et al. (1970) conclude that CO and Ar have similar third body effects and show the high efficiency of O atoms as a collision partner. However, it
is surprising that such a large efficiency has not shown up as an autocatalytic effect in other CO/Ar studies.

Except for Davies’ high temperature results, all the rate expressions show nearly the same temperature dependence and appear to be independent of the nature of M. This tends to suggest a common mechanism independent of the nature of the collision partner.

Davies and Appleton, et al have fit their data to both an Arrhenius type expression and also to the theoretical form which allows for the participation of several classical harmonic oscillators and fixes the activation energy equal to the dissociation energy.

The recommended value for $k_{Ar}$ is based on the data of Davies (1964) and Appleton, Steinberg and Liqueurnik (1970) giving slightly more weight to the latter investigation. From the spread of the data it appears accurate to better than ±75 percent (<10,000 K) and ±50 percent (>10,000 K).

**References**


**4.4. N₂O+M→N₂+O+M**

<table>
<thead>
<tr>
<th>$T$ K</th>
<th>$\Delta H^0$ kcal mol⁻¹</th>
<th>$\Delta S^0$ cal deg⁻¹ mol⁻¹</th>
<th>log$_{10} K_p$ atm</th>
<th>log$_{10} K_p$ mole cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>38.59</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>100</td>
<td>39.076</td>
<td>26.648</td>
<td>—79.585</td>
<td>—59.719</td>
</tr>
<tr>
<td>298</td>
<td>39.949</td>
<td>31.692</td>
<td>—22.856</td>
<td>—22.365</td>
</tr>
<tr>
<td>300</td>
<td>39.954</td>
<td>31.711</td>
<td>—22.175</td>
<td>—22.797</td>
</tr>
<tr>
<td>500</td>
<td>40.330</td>
<td>32.758</td>
<td>—10.477</td>
<td>8.699</td>
</tr>
<tr>
<td>1000</td>
<td>40.477</td>
<td>32.983</td>
<td>—1.638</td>
<td>17.230</td>
</tr>
<tr>
<td>1500</td>
<td>40.222</td>
<td>32.791</td>
<td>1.306</td>
<td>19.996</td>
</tr>
<tr>
<td>2500</td>
<td>39.477</td>
<td>32.412</td>
<td>3.633</td>
<td>22.101</td>
</tr>
<tr>
<td>3000</td>
<td>39.083</td>
<td>32.270</td>
<td>4.205</td>
<td>22.593</td>
</tr>
<tr>
<td>3500</td>
<td>38.702</td>
<td>32.152</td>
<td>4.610</td>
<td>22.932</td>
</tr>
<tr>
<td>4000</td>
<td>38.347</td>
<td>32.057</td>
<td>4.911</td>
<td>23.175</td>
</tr>
<tr>
<td>4500</td>
<td>38.026</td>
<td>31.981</td>
<td>5.142</td>
<td>23.344</td>
</tr>
<tr>
<td>5000</td>
<td>37.744</td>
<td>31.922</td>
<td>5.327</td>
<td>23.494</td>
</tr>
<tr>
<td>5500</td>
<td>37.505</td>
<td>31.876</td>
<td>5.476</td>
<td>23.601</td>
</tr>
<tr>
<td>6000</td>
<td>37.308</td>
<td>31.842</td>
<td>5.600</td>
<td>23.657</td>
</tr>
</tbody>
</table>

**Equilibrium Constant**

$K_p=4.00\times10^7 T^{-0.489} \exp \left(-39,790/(RT)\right) \text{ atm} \quad (300-1000 \text{ K range}),$

$=2.68\times10^7 T^{-0.356} \exp \left(-41,240/(RT)\right) \quad (1000-3000 \text{ K range}).$

These expressions reproduce the 100 K interval data derived from the JANAF thermochemical tables with deviations of up to 1.6 percent (300–1000 K) and 0.4 percent (1000–3000 K).

**Recommended Rate Constant**

**Low Concentration Region** 2nd order kinetics

M=Ar $k=7.8\times10^{-16} \exp \left(-58,000/(RT)\right) \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1} \quad (1500–2500 \text{ K}).$

Concentration: <6×10⁻⁴ mol cm⁻³.

Suggested error limits: ±25 percent.

M=Ne $k=4.2\times10^{-11} \exp \left(-43,600/(RT)\right) \quad (1500–2600 \text{ K}).$

Concentration: <10⁻⁴ mol cm⁻³.

Suggested error limits: ±50 percent.

M=Kr $k=1.2\times10^{-11} \exp \left(-40,700/(RT)\right) \quad (1750–2800 \text{ K}).$

Concentration: <10⁻⁴ mol cm⁻³.

Suggested error limits: within a factor of 2 to 3.

**Intermediate Concentrations**

5×10⁻⁴ to 10⁻² mol cm⁻³. The plotted data of Olschewski, et al. (1965, 1966) (M=Ar, 1500–2100 K) and Johnston (1951) (M=N₂O, 888 K) are preferred.

**High Concentrations** 1st order kinetics

$k=1.4\times10^{12} \exp \left(-59,400/(RT)\right) \text{ s}^{-1} \quad (800–2100\text{K}).$

Concentration: >10⁻³ mol cm⁻³.

Suggested error limits: ±50 percent.

The available rate constant data are presented in six plots, figures 2 to 7, which illustrate the character of the dissociation in the various pressure regimes.

**Discussion**

That the chemistry of even simple systems can be complex is well illustrated by studies of the unimolecular decomposition of the N₂O linear tristatomic molecule. This dissociation became of considerable interest because of its simple molecular nature and the fact that the entire unimolecular fall-off region was experimentally accessible, making it attractive for testing various theories. However, the dissociation is not without complications and our quantitative understanding is still somewhat unsatisfactory in spite of a multitude of investigations spanning several generations of chemists.

Original studies were based on static thermal systems whereas emphasis, more recently, has centered on exploiting the high temperature shock tube techniques. Data have been collected over a four decade range of total concentration or pressure.

\[ (2\times10^{-7} - 2\times10^{-3} \text{ mol cm}^{-3})(0.01-300 \text{ atm}) \]
<table>
<thead>
<tr>
<th>Rate constant ( k ) (cm(^3) molecule(^{-1}) s(^{-1}))</th>
<th>M</th>
<th>Exp. temp. (K)</th>
<th>Pressure/Concentration (atm/mol cm(^{-3}))</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.2\times10^{-8} \ exp (-60,000/RT) )</td>
<td>Ar</td>
<td>1630-1820, 1640-1690</td>
<td>5.6-6.7/0.45\times10^{-4}</td>
<td>0.8 percent (higher pressures) and 1.8 percent (lower pressures) mole fraction of N(_2)O in Ar. Shock tube study, [N(_2)O] monitored by uv absorption at 2250-2400 Å behind reflected shock waves. Jost, Michel, Troe, and Wagner 1963.</td>
<td>Initial rates measured to avoid thermal effects. ( k ) taken as ( \frac{3}{2}k_{exp}). Appears bimolecular in this region.</td>
</tr>
<tr>
<td>( 1.7\times10^{-4} \ exp (-61,000/RT) )</td>
<td>Ar</td>
<td>1500-2500</td>
<td>2-20/(1.1-1.4)\times10^{-4}</td>
<td>0.5-3 percent N(_2)O/Ar mixtures studied by the shock tube method. [N(_2)O] and [NO] monitored behind reflected shock waves using uv absorption at 2300 and 2260 Å, respectively. Jost, Michel, Troe, and Wagner 1964.</td>
<td>Initial rates of decomposition measured. ( k ) taken as ( \frac{3}{2}k_{exp}). Bimolecular in this region.</td>
</tr>
<tr>
<td>( 7.8\times10^{-18} \ exp (-58,000/RT) )</td>
<td>Ar</td>
<td>1480-2550</td>
<td>0.8-12/(0.5-6)\times10^{-4}</td>
<td>Shock tube study of 0.02-1 percent N(_2)O/Ar mixtures. [N(_2)O] followed by IR emission at 4.5\mu; agrees with uv absorption measurements at 2300-2500Å. Both incident and reflected shock waves investigated. Olschewski, Troe, and Wagner 1966.</td>
<td>Low pressure region &lt;0.5 \times10^{-4} mol cm(^{-3}). Bimolecular kinetics. ( k ) taken as ( \frac{3}{2}k_{exp}). Incident and reflected shock wave results agree.</td>
</tr>
<tr>
<td>( 8.3\times10^{-12} )</td>
<td>Ar 1428</td>
<td>Low pressure region</td>
<td>Rapid adiabatic compression of 0.3% N(_2)O/Ar mixtures. [N(_2)O] followed by the 4.5\mu IR emission. Martinego, Troe, and Wagner 1966.</td>
<td>Bimolecular kinetics. Question as to whether ( k_{exp} ) represents ( k ) or ( \frac{1}{2}k ). ( k ) = ( \frac{1}{2}k_{exp} ) taken.</td>
<td></td>
</tr>
<tr>
<td>( 1.1\times10^{-14} \ exp (-51,400/RT) )</td>
<td>Ar</td>
<td>1728-2080</td>
<td>2.7-3.2/1.0 \times10^{-4}</td>
<td>Shock tube study of 2 percent N(_2)O/Ar mixtures. [N(_2)O] followed behind incident shock waves using IR emission at 2.3 and 4.5\mu; and absorption at 2590Å. Experiments also with reflected shock waves and some with 2 percent N(_2)O/O(_2) mixtures. Fishburne, et al. 1964.</td>
<td>Emission and absorption measurements in agreement. Reflected shock wave values slightly higher than those from incident shock waves. The rate constants for concentrations of 0.75 and 1.5 \times10^{-4} mol cm(^{-3}) fall below the others and lie in the intermediate pressure region. ( k = k_{exp} ) taken.</td>
</tr>
<tr>
<td>( 1.2\times10^{-14} \ exp (-52,400/RT) )</td>
<td>Ar</td>
<td>1748-2020</td>
<td>4.0-4.6/0.28 \times10^{-4}</td>
<td>( k_{exp} ) taken.</td>
<td></td>
</tr>
<tr>
<td>( 1.4\times10^{-18} \ exp (-55,000/RT) )</td>
<td>Ar</td>
<td>1728-2190</td>
<td>10.6-13.0/0.75 \times10^{-4}</td>
<td>( k_{exp} ) taken.</td>
<td></td>
</tr>
<tr>
<td>( 1.3\times10^{-18} \ exp (-55,700/RT) )</td>
<td>Ar</td>
<td>1640-2193</td>
<td>20.2-25.0/1.50 \times10^{-4}</td>
<td>( k_{exp} ) taken.</td>
<td></td>
</tr>
<tr>
<td>( 6.0\times10^{-11} \ exp (-45,200/RT) )</td>
<td>O(_2)</td>
<td>1550-2175</td>
<td>1.4-2.0/0.13 \times10^{-4}</td>
<td>( k_{exp} ) taken.</td>
<td></td>
</tr>
<tr>
<td>( 5.5\times10^{-11} \ exp (-50,000/RT) )</td>
<td>O(_2)</td>
<td>1545-2155</td>
<td>2.5-3.0/0.17 \times10^{-4}</td>
<td>( k_{exp} ) taken.</td>
<td></td>
</tr>
<tr>
<td>( k_{exp} \approx 1.5 k_{Ar} )</td>
<td></td>
<td>1000</td>
<td>2.5/0.14 \times10^{-4}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)

<table>
<thead>
<tr>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>M</th>
<th>Exp. temp. (K)</th>
<th>Pressure/Concentration (atm/mol cm$^{-3}$)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.1 \times 10^{-17} \exp (-60,000/RT)$</td>
<td>Ar</td>
<td>1877-2500</td>
<td>0.15 - 0.86/(0.8 - 4.5) $\times 10^{-4}$</td>
<td>Reflected shock waves in 4 percent N$_2$O/Ar mixtures sampled through an orifice on the end of the shock tube into a quadrupole mass filter. [N$_2$O], [O$_2$], [N$_2$], and [NO] monitored in different experiments. Gutman, Belford, Hay, and Pancirov 1966.</td>
<td>$E$ assumed to be 60 kcal mol$^{-1}$. Time resolution $= 10$ μsec. Values extrapolated to $t = 0$ to eliminate temperature and boundary layer effects. Steady state [O] rapidly established below 2500 K but some uncertainty concerning this at higher temperatures. $k = 1/2k_{exp}$ taken.</td>
</tr>
<tr>
<td>$2.7 \times 10^{-16} \exp (-60,000/RT)$</td>
<td>Ar</td>
<td>1877-3421</td>
<td>0.15 - 1.0/(0.8 - 4.5) $\times 10^{-6}$</td>
<td>Reflected shock waves in 0 percent N$_2$O/Ar mixtures. [N$_2$O] followed in absorption at 2590 Å. Drummond and Hiscock 1967.</td>
<td>$k = 1/2k_{exp}$ taken. Measurements made 14 and 75 mm from the reflecting end plate agree. Temperatures calculated from the flow parameters assuming no reaction (frozen equilibrium).</td>
</tr>
<tr>
<td>$5.2 \times 10^{-15}$ exp ($-56,800/RT$)</td>
<td>Ar</td>
<td>1665-1919</td>
<td>3.2 - 4.0/$\sim 2.4 \times 10^{-7}$</td>
<td>Shock tube study of reflected shock waves</td>
<td>20-50 μs time resolution. Since an allowance is made in the analysis for the subsequent reactions $k = k_{ref}$.</td>
</tr>
<tr>
<td>$3.15 \times 10^{-18}$</td>
<td>Ne</td>
<td>1815</td>
<td>0.55/3.7/$10^{-6}$</td>
<td>Reflected shock waves sampled with a nozzle and TOF mass analyzed for N$_2$O, N$_2$, O$_2$, NO. 2 percent N$_2$O/Ne mixtures studied (and one 5 percent mixture). Nonstationary solution of the kinetic equations. Borisov 1968.</td>
<td></td>
</tr>
<tr>
<td>$3.65 \times 10^{-18}$</td>
<td>Ne</td>
<td>1985</td>
<td>0.55/5.5/$10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$5.31 \times 10^{-18}$</td>
<td>Ne</td>
<td>2010</td>
<td>0.63/3.8/$10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.31 \times 10^{-15}$</td>
<td>Ne</td>
<td>2020</td>
<td>0.55/2.1/$10^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2.21 \times 10^{-15}$</td>
<td>Ne</td>
<td>2050</td>
<td>0.64/3.8/$10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$9.65 \times 10^{-18}$</td>
<td>Ne</td>
<td>2180</td>
<td>0.70/3.9/$10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2.74 \times 10^{-18}$</td>
<td>Ne</td>
<td>2350</td>
<td>0.76/4.0/$10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3.98 \times 10^{-18}$</td>
<td>Ne</td>
<td>1920-2350</td>
<td>0.47 - 0.58/$3 \times 10^{-6}$</td>
<td>Shock tube study of the reflected shock wave in 5 percent N$_2$O/Ne mixtures. Sampled with a conical orifice into a TOF mass spectrometer. Gay, Kistiakowsky, Michael, and Niki 1965.</td>
<td></td>
</tr>
<tr>
<td>$2.6 \times 10^{-14}$ exp ($-50,000/RT$)</td>
<td>Ne</td>
<td>1880-2360</td>
<td>0.31 - 0.39/$2 \times 10^{-6}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2.8 \times 10^{-15}$ exp ($-52,500/RT$)</td>
<td>Ne</td>
<td>1920-2350</td>
<td>0.47 - 0.58/$3 \times 10^{-6}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.69 \times 10^{-18}$</td>
<td>Ne</td>
<td>1820</td>
<td>$\sim 0.3/1.8 \times 10^{-4}$</td>
<td>Shock tube study of the reflected wave in 0.3-0.9 percent N$_2$O/Ne mixtures. Sampled by TOF mass spectrometer. Garnett, Kistiakowsky, and O'Grady 1969.</td>
<td></td>
</tr>
<tr>
<td>$1.64 \times 10^{-18}$</td>
<td>Ne</td>
<td>1925</td>
<td>$\sim 0.3/1.8 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.50 \times 10^{-18}$</td>
<td>Ne</td>
<td>2015</td>
<td>$\sim 0.3/1.8 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.50 \times 10^{-18}$</td>
<td>Ne</td>
<td>2150</td>
<td>$\sim 0.3/1.8 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.50 \times 10^{-18}$</td>
<td>Ne</td>
<td>2170</td>
<td>$\sim 0.3/1.8 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.50 \times 10^{-18}$</td>
<td>Ne</td>
<td>2205</td>
<td>$\sim 0.3/1.8 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3.64 \times 10^{-18}$</td>
<td>Ne</td>
<td>2350</td>
<td>$\sim 0.3/1.8 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3.77 \times 10^{-18}$</td>
<td>Ne</td>
<td>2370</td>
<td>$\sim 0.3/1.8 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$5.18 \times 10^{-18}$</td>
<td>Ne</td>
<td>2420</td>
<td>$\sim 0.3/1.8 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$5.86 \times 10^{-18}$</td>
<td>Ne</td>
<td>2580</td>
<td>$\sim 0.3/1.8 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$7.45 \times 10^{-18}$</td>
<td>Ne</td>
<td>2600</td>
<td>$\sim 0.3/1.8 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
KINETIC RATE CONSTANTS

2nd order rate constant—Continued

<table>
<thead>
<tr>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>M</th>
<th>Exp. temp. (K)</th>
<th>Pressure/Concentration (atm/mol cm$^{-3}$)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.0 \times 10^{-11} \exp (-41,000/RT)$</td>
<td>Ne</td>
<td>1600-2100</td>
<td>$\sim 0.3/2 \times 10^{-6}$</td>
<td>Shock tube study of the reflected wave in $\sim 1$ percent $N_2O/Ne$ mixtures containing small amounts of $SO_2$ and $O_2$. Sampled by TOF mass spectrometer. Clark, Garnett, and Kistiakowsky 1970.</td>
<td>Rate constant refers to initial reaction. $N_2O$ used as the source of $O$ atoms in a study of the $N_2+3SO_2$ reaction. [O] at the observed time period (400 μs).</td>
</tr>
<tr>
<td>$1.2 \times 10^{-11} \exp (-40,700/RT)$</td>
<td>Kr</td>
<td>1780-2780</td>
<td>$0.2-0.4/(1.4-1.8) \times 10^{-4}$</td>
<td>Shock tube study of the reflected shock wave in $2.1$ percent $N_2O/Kr$ mixtures. Sampled via orifice on the end plate into a TOF mass spectrometer. Analyzed for $N_2O$, $O_2$, $NO$, and $N_2$. Data fit to numerical solutions of the kinetic rate expressions. Barton and Dove 1969.</td>
<td></td>
</tr>
<tr>
<td>$4.7 \times 10^{-9} \exp (-50,400/RT)$</td>
<td>$N_2O$</td>
<td>841-1052</td>
<td>$\sim 0.02-0.08/(0.25-0.9) \times 10^{-6}$</td>
<td>Reanalysis and synopsis of five earlier studies by Nagasaki and Volmer (1930), Volmer and Froehlich (1932a), Musgrave and Hinshelwood (1932), Hunter (1934), Lewis and Hinshelwood (1938), of the thermal dissociation of pure $N_2O$ in static systems. The reaction was followed by measuring the pressure change resulting from the dissociation process. Data corrected for a 1st order contribution in the low pressure region. Rate constants conv. to 2nd order: $k=1/2k_{exp}$ taken. Bio- molecular region $&lt;1 \times 10^{-4}$ mol cm$^{-1}$ at 888 K ($\sim 55$ torr) $E\sim 60$ kcal mol$^{-1}$ for concentrations up to $5 \times 10^{-4}$ mol cm$^{-1}$. A particularly high value for the preexponential factor.</td>
<td></td>
</tr>
<tr>
<td>$1.27 \times 10^{-21}$</td>
<td>$N_2O$</td>
<td>993</td>
<td>$0.013/1.6 \times 10^{-7}$</td>
<td>Thermal dissociation of $10-1000$ Torr $N_2O$ in several reactions vessels. The reaction followed by monitoring the increase in pressure in the system. Lindars and Hinshelwood 1955.</td>
<td></td>
</tr>
<tr>
<td>$9.44 \times 10^{-22}$</td>
<td>$N_2O$</td>
<td></td>
<td>$0.026/7.2 \times 10^{-7}$</td>
<td>Thermal dissociation of $10-1000$ Torr $N_2O$ in several reactions vessels. The reaction followed by monitoring the increase in pressure in the system. Lindars and Hinshelwood 1955.</td>
<td></td>
</tr>
<tr>
<td>$7.21 \times 10^{-22}$</td>
<td>$N_2O$</td>
<td></td>
<td>$0.053/6.5 \times 10^{-7}$</td>
<td>Thermal dissociation of $10-1000$ Torr $N_2O$ in several reactions vessels. The reaction followed by monitoring the increase in pressure in the system. Lindars and Hinshelwood 1955.</td>
<td></td>
</tr>
<tr>
<td>$4.50 \times 10^{-22}$</td>
<td>$N_2O$</td>
<td></td>
<td>$0.13/1.6 \times 10^{-7}$</td>
<td>Thermal dissociation of $10-1000$ Torr $N_2O$ in several reactions vessels. The reaction followed by monitoring the increase in pressure in the system. Lindars and Hinshelwood 1955.</td>
<td></td>
</tr>
<tr>
<td>$3.77 \times 10^{-22}$</td>
<td>$N_2O$</td>
<td></td>
<td>$0.26/3.2 \times 10^{-7}$</td>
<td>Thermal dissociation of $10-1000$ Torr $N_2O$ in several reactions vessels. The reaction followed by monitoring the increase in pressure in the system. Lindars and Hinshelwood 1955.</td>
<td></td>
</tr>
<tr>
<td>$2.81 \times 10^{-22}$</td>
<td>$N_2O$</td>
<td></td>
<td>$0.39/4.8 \times 10^{-7}$</td>
<td>Thermal dissociation of $10-1000$ Torr $N_2O$ in several reactions vessels. The reaction followed by monitoring the increase in pressure in the system. Lindars and Hinshelwood 1955.</td>
<td></td>
</tr>
<tr>
<td>$2.57 \times 10^{-22}$</td>
<td>$N_2O$</td>
<td></td>
<td>$0.53/6.5 \times 10^{-7}$</td>
<td>Thermal dissociation of $10-1000$ Torr $N_2O$ in several reactions vessels. The reaction followed by monitoring the increase in pressure in the system. Lindars and Hinshelwood 1955.</td>
<td></td>
</tr>
<tr>
<td>$2.42 \times 10^{-22}$</td>
<td>$N_2O$</td>
<td></td>
<td>$0.66/8.1 \times 10^{-7}$</td>
<td>Thermal dissociation of $10-1000$ Torr $N_2O$ in several reactions vessels. The reaction followed by monitoring the increase in pressure in the system. Lindars and Hinshelwood 1955.</td>
<td></td>
</tr>
<tr>
<td>$2.12 \times 10^{-22}$</td>
<td>$N_2O$</td>
<td></td>
<td>$1.31/1.6 \times 10^{-7}$</td>
<td>Thermal dissociation of $10-1000$ Torr $N_2O$ in several reactions vessels. The reaction followed by monitoring the increase in pressure in the system. Lindars and Hinshelwood 1955.</td>
<td></td>
</tr>
</tbody>
</table>
36
KEITH SCHOFIELD

2nd order rate constant—Continued

<table>
<thead>
<tr>
<th>Rate constant (k) (em (^{-3}) molecule(^{-1}) 8-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_{O_2}: k_{N_2}: k_{CO_2}: k_{He}: k_{N_20} = 0.21: 0.26: 1.2: 1.0: 1.0)</td>
</tr>
</tbody>
</table>

| \(k_{Ne}: k_{Ar}: k_{Kr}: k_{Xe}: k_{N_20} = 0.44: 0.183: 0.236: 0.147: 1.0\) |

| \(k_{CO_2}: k_{F_4}: k_{S_0_2}: k_{N_20} = 0.46: 0.85: 0.59: 1.0\) |

| \(k_{He}: k_{Ne}: k_{Ar}: k_{Kr}: k_{Xe}: k_{N_20} = 0.488: 0.261: 0.149: 0.079: 0.176: 1.0\) |

**Method & reference**

| Thermal dissociation of \(N_20/M\) gas mixtures in a 0.7 liter quartz vessel. \(N_20\) condensed out and its concentration measured after reaction times of 10-30 min. Nagasako 1931. |
| Thermal dissociation of \(N_20/M\) mixtures in 0.7 liter quartz vessel. \(N_20\) condensed out and its concentration measured after reaction times of 12-34 min. Volmer and Froehlich 1932. |
| Thermal dissociation of about 33 percent, \(N_20/M\) mixtures. \(N_20\) condensed out and its concentration measured after reaction times of 16-30 min. Vohner and Bogdan 1933. |
| Thermal decomposition of 50 torr \(N_20/200\) torr \(\chi\) mixtures in 0.5 liter quartz vessel. Initial rates of \(N_20\) decomposition measured from the increase in pressure. Kaufman, Gerri, and Bowman 1956. |
| Homogeneous thermal dissociation studied in a 240 cm\(^3\) silica vessel. 50, 100 torr \(N_20\) in the presence of various third bodies. Initial rate of dissociation measured either by following the resulting pressure change or by analysis of the mixture after a certain reaction time. Bell, Robinson, and Trenwith 1957 and 1958. |

**Comments**

| Gas mixtures studied: 1 \(N_20: 0.8-3.3\) \(O_2\): 2.4-13 \(N_2\): 1-20 \(CO_2\): 0.7-4 \(He\): 0.7-10 \(Ar\) |
| Gas mixtures studied: 1 \(N_20: 10 O_2: 0.7-12\) \(He\): 0.7-10 \(Ar\) |

<table>
<thead>
<tr>
<th>Initial rates of decomposition: (M = [N_20]/dt) mm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>(He): 1.72</td>
</tr>
<tr>
<td>(Ar): 1.09</td>
</tr>
<tr>
<td>(N_2): 1.21</td>
</tr>
<tr>
<td>(O_2): 1.22</td>
</tr>
</tbody>
</table>

The rate of dissociation is fit to the empirical relationship:

\[-d[N_20]/dt = k'[N_20]^{0.55} + k''[N_20]^{0.55}[X]\]

where \(X\) represents a particular third body other than \(N_20\).
## KINETIC RATE CONSTANTS

### 1st order rate constant

<table>
<thead>
<tr>
<th>Rate constant $k_a$ (s$^{-1}$)</th>
<th>$k_a$ 1000 K</th>
<th>Exp. temp. (K)</th>
<th>Pressure/ concentration (atm/mol cm$^{-3}$)</th>
<th>Method &amp; reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.38 \times 10^{10} \exp (-59,500/RT)$</td>
<td>$1.37 \times 10^{-2}$</td>
<td>1410–2080</td>
<td>$115–300/10^{-3}–2 \times 10^{-2}$</td>
<td>Shock tube study of 0.02–0.2 percent $N_2O/Ar$ mixtures. $[N_2O]$ followed by IR emission at 4.5 μm. Both incident and reflected shock waves investigated. Olschewski, Troe, and Wagner 1965, 1966.</td>
<td>M = Ar High pressure region $&gt;10^{2}$ mol cm$^{-3}$, (140 atm). Unimolecular kinetics. $k$ taken as $\frac{1}{2}k_{exp}$.</td>
</tr>
<tr>
<td>$2.31 \times 10^{23} \exp (-60,600/RT)$</td>
<td>$1.32 \times 10^{-2}$</td>
<td>840–930</td>
<td>$40/\sim 5 \times 10^{-4}$</td>
<td>Reanalysis of an earlier study by Hunter (1934) of the thermal dissociation of pure $N_2O$ in a high pressure static system. The reaction was monitored by measuring the resulting pressure change. Johnston 1951.</td>
<td>A levelling off of the 1st order rate constant was noted at this high pressure. $k = \frac{1}{2}k_{exp}$ taken.</td>
</tr>
</tbody>
</table>

**Figure 2.** Experimental values of $k_{N_2O+Ar-\rightarrow N_2+O+Ar}$.  

**Figure 3.** Experimental values of $k_{N_2O+M \rightarrow N_2+O+M}$, $M = Ne$, Kr, and $O_2$, together with the recommended values for $k_{N_2O+Ar}$.  

Figure 4. Comparison of high and lower temperature values for $k_{\text{NO}+\text{M}}$.

Figure 5. 1st order data for $k_{\text{NO}+\text{M}}$ in the intermediate concentration/pressure region.

Figure 6. Low temperature 1st order experimental data for $k_{\text{NO}}$ in the intermediate concentration/pressure region.

Figure 7. 1st order values for $k_{\text{NO}+\text{M}}$ from high concentration/pressure studies.
at temperatures between 850-1050 and 1350-3400 K. Experimentally measured rate constants refer to the rate of disappearance of N\textsubscript{2}O and are reported as 1st or 2nd order constants.

\[ -d[N\textsubscript{2}O]/dt=k_{\text{exp}}[N\textsubscript{2}O][M] \text{ 2nd order,} \]
\[ =k_{\text{exp}}[N\textsubscript{2}O] \text{ 1st order.} \]

One complication of the dissociation results from the subsequent reactions (2) and (3) which immediately follow the primary dissociation process, reaction (1):

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) ( N\textsubscript{2}O + M \rightarrow N\textsubscript{2} + O + M )</td>
<td>( \Delta H_{\text{298}}^o = 39.9 \text{ kcal mol}^{-1} )</td>
</tr>
<tr>
<td>(2) ( O + N\textsubscript{2}O \rightarrow N\textsubscript{2} + O_2 )</td>
<td>( k_2 )</td>
</tr>
<tr>
<td>(3) ( O + N\textsubscript{2}O \rightarrow NO + NO )</td>
<td>( k_3 )</td>
</tr>
</tbody>
</table>

Owing to this possible loss of a second \( N\textsubscript{2}O \) molecule, the measured rate at low concentrations refers either to \( 2k_1 \) or \( k_1 \), according to whether the consecutive reactions are sufficiently fast or not to establish a steady state concentration of atomic oxygen before the observation period. This problem is aggravated by an uncertainty in the values of \( k_2 \) and \( k_3 \) (Baulch, et al., 1966). Olschewski, Troe, and Wagner (1966), in a shock tube study, report that at 2000 K and above, with a very dilute mixture of 0.02 percent \( N\textsubscript{2}O \) in argon that \( k_{\text{exp}} \) was a factor of two lower than its value for mixtures of 0.1 percent \( N\textsubscript{2}O/Ar \) and larger. It is possible that they observed \( k_1 \) directly at this very low mixture strength. Barton and Dove (1969) derived numerical solutions to the kinetic rate expressions for their shock tube experiments with \( N\textsubscript{2}O/Kr \) mixtures. Fenimore and Jones' (1962) values for \( k_{\text{He-N2O}} \) were more consistent with their data than those of Fishburne and Edse (1966). \( k_1 \) was found to be about (0.55-0.6) \( k_{\text{exp}} \) for their temperature range 1780-2790 K. Borisov (1968) obtained approximate analytical solutions to the non-linear differential kinetic equations describing the \( N\textsubscript{2}O/Ne \) dissociation. Using shock tube TOF mass spectrometric techniques to monitor \( [N\textsubscript{2}] \), \( [O_2] \), \( [NO] \), and \( [N\textsubscript{2}O] \) he derived values for \( k_1 \), \( k_2 \), and \( k_3 \). The values for the latter two lie between those of Fenimore and Jones (1962) and Fishburne and Edse (1966), [Baulch et al., 1969]. Gutman et al. (1966) also have reported that below 2000 K it appears that a steady state \( O \) atom concentration is rapidly established. However, Clark, Garnett, and Kistiakowsky (1970) and Garnett, Kistiakowsky, and O'Grady (1969) have calculated that the O atom concentration for \( N\textsubscript{2}O/Ne \) mixtures at \( \leq 2100 \) K can be described as a linear function of time, indicating insufficient time (~400 \( \mu \)s) for it to equilibrate. At lower temperatures the formation of NO is evidence for some contribution from reaction (3). Kaufman, Gerri, and Bowman (1956) found large amounts of NO formed in the initial stages of the dissociation. Up to about 60 percent of the dissociating \( N\textsubscript{2}O \) produced NO at \( 876-1031 \) K (10-780 torr \( N\textsubscript{2}O, 1.5 \times 10^{-2}-1.3 \times 10^{-2} \) mol cm\(^{-3}\)). Consequently the contribution from reactions (2) and (3) appears to be of some importance at all temperatures. Unless derived directly from analytical solutions of the rate expressions it has been assumed throughout this evaluation that the rate of disappearance of \( N\textsubscript{2}O \) is doubled as a result of these secondary reactions.

A second complicating feature that has been discussed occasionally and was studied in detail by Drummond and Hiscock (1967) pertains to shock tube studies of systems where the released enthalpy affects the shock wave parameters. Owing to the enthalpy changes in reactions (1) to (3) the overall reaction will be either endo- or exothermic according to the relative contributions of (2) and (3). Drummond and Hiscock (1967) discuss the difficulty in establishing the exact shock speed and temperature in a reacting system where the enthalpy changes are not negligible. In order to minimize the problem they recommended that observations be made as close to the reflecting end plate as possible so that the speed and temperature differ little from frozen equilibrium values. The fact that measurements at 14 mm and 75 mm from the end plate agreed for their relatively \( N\textsubscript{2}O \) rich mixtures (6% \( N\textsubscript{2}O/Ar \) tends to confirm Barton and Dove's calculation (1969) that the overall enthalpy change for the reaction is small. Jost, et al. (1963, 1964) and Olschewski, et al. (1966) collected their data \( 10 \) cm and 2.5 cm upstream from the end plate, respectively, and the data appeared not to have suffered from thermal effects at these positions. They also used dilute mixtures. The very good agreement between the 2nd order data of Olschewski, et al. (1966), Fishburne, et al. (1964), and Drummond and Hiscock (1967) for \( M=Ar \), figure 2, suggests that the data are not degraded by any such thermal problems.

The dissociation is a unimolecular process but the reaction kinetics appear quite complex. If the rate of dissociation is expressed in terms of a 1st order rate constant it varies with pressure according to an expression of the type:

\[ k(s^{-1}) = \sum A_i[M] / \left( 1 + B_i[M] \right) \]

To account for the changes in \( k(s^{-1}) \) over the full pressure range studied at least three separate terms have to be included. A simplistic scheme to illustrate such a general form is:

\[ N\textsubscript{2}O + M \stackrel{k_4}{\kappa} N\textsubscript{2}O* + M \]
\[ N\textsubscript{2}O* \rightarrow N\textsubscript{2} + O, \]
\[ O + N\textsubscript{2}O \rightarrow 2NO \text{ or } N\textsubscript{2} + O_2. \]
Making the usual steady state assumptions, this predicts a rate of dissociation given by

$$\frac{-d[N_2O]}{dt} = \frac{2k_2[N_2O][M]}{(1+k_2[M]/k_3)}$$

so that at low concentrations the rate tends to $2k_2[N_2O][M]$ and at the high concentration limit a 1st order expression $2k_2[N_2O]$. However, this scheme oversimplifies the decomposition since an allowance for its forbidden nature must be considered. Friedmann and Bigeleisen (1953) removed any doubts as to the dissociation products by showing that no N atoms were formed in the initial bond rupturing. Consequently two overall processes are possible

$$N_2O(\Sigma) \rightarrow N_2(\Sigma) + O(^3P) \Delta H_{\text{Diss}} = -39.9 \text{ kcal mol}^{-1},$$

$$N_2O(\Sigma) \rightarrow N_2(\Sigma) + O(^1D) \quad = -85.3.$$  

The former, although spin forbidden, now is generally accepted as the process. The mechanism depends on a transition from the $N_2O$ (\Sigma) ground electronic state to either one of the $^1\Pi$ or $^3\Sigma$ repulsive excited states which correlate to the observed dissociation products [Reuben and Linnett, 1959; Gill and Laidler, 1958]. A scheme involving the energization of $N_2O$, its transformation to these triplet states followed by their decomposition appears to fit the observed features of the dissociation [Reuben and Linnett, 1959]. It also suggests that since the cross-over point lies above the heat of dissociation of $N_2O$, that the dissociation products, particularly the O-atom, initially will contain a large fraction of the excess energy. However, no evidence for the presence of such "hot" O atoms has been reported.

**Low Pressures—2nd Order Data**

**M—Ar, N 2 0**

The data of five independent studies have been plotted in figure 2. The values of Jost, et al. (1963, 1964) and Olschewski, Troe, and Wagner (1966) are in very close agreement differing at the most by 25 percent over the temperature ranges studied. Because of this only their later data have been plotted [Olschewski, et al., 1966]. This refers also to lower total concentrations where the kinetics are bimolecular. The data of Fishburne, et al. (1964) shows a larger sensitivity to concentration and as seen in the 1st order plot, figure 5, has a more pronounced fall-off. Their five expressions almost parallel to one another when plotted as a function of $T^{-1}$. Values for $k$ cm$^3$ molecule$^{-1}$ s$^{-1}$ gradually decrease with increasing total concentration. Their lowest concentration data has been taken. The values of Martinengo, Troe, and Wagner (1966) appear too low at their lower temperatures. Drummond and Hiscock's data (1967) is in excellent agreement with that of Olschewski, et al. (1966) and Fishburne, et al. (1964). The higher temperature values of Gutman, et al. (1966) appear questionable.

Because of the observed agreement and since their data refers to very dilute mixtures of $N_2O$ Ar the values of Olschewski, et al. (1966) are recommended for $M$=Ar. However, values around 2500 K require confirmation. Earlier data by Modica (1965) and Bradley and Kistiakowsky (1961) have not been included since they constituted an evaluation and development of the shock tube-TOF mass spectrometer technique rather than a source of reliable values for $k_M$.

**M=N 2 0**

The data of Borisov (1968), Gay, Kistiakowsky, et al. (1965), Garnett, Kistiakowsky, et al. (1969), and Clark, Garnett, and Kistiakowsky (1970) are in good agreement as illustrated in figure 3. A line best fitting the four corresponds to a value

$$k_{N 2 0} = 4.1 \times 10^{-11} \exp (-43.600/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$  

This is considered accurate to within about 50 percent in the temperature range 1500–2600 K, and the activation energy should be within ±4 kcal mol$^{-1}$. Only the concentration range $\leq 6 \times 10^{-4}$ mol cm$^{-3}$ has been studied with neon. Clark, Garnett, and Kistiakowsky (1970) used $N_2O$ as a source of O atoms to study the $^{16}O+{^{32}}O_2$ exchange reaction. Olschewski, Troe, and Wagner's value for $k_N$ (1966) was not compatible with their observations and a much lower value for the activation energy of $k_{N 2 0}$ was clearly evident.

**Other Third Bodies**

Values are reported also for $k_{O_2}$, $k_{Kr}$, and $k_{Kr-O_2}$. The lower concentration data of Fishburne, et al. (1964) for $M$=O$_2$, values for $k_{Kr}$ [Barton and Dove, 1969] and the lower temperature studies of $k_{Kr-O_2}$ have been plotted in figures 3 and 4. The activation energy of the dissociation in the low concentration region appears to increase from Kr (40.7 kcal mol$^{-1}$) to Ne (43.8), O$_2$ (48.2), Ar (58), and $N_2O$ (59.4). Although these values may be in error to various extents the differences appear definitely significant.

Additional data for $M$=Kr and O$_2$ are required. Johnston's values for $M$=N$_2$O (1951) are probably reliable to within a factor of 2–3. The pre-exponential in their expression seems particularly high. Bell, Robinson, and Trenwith (1957) studied the effects of differing third bodies in a static system at 925–1025 K and with low concentrations. They noted that the activation energies for $M$=CO$_2$ or CF$_4$ were greater by about 3 kcal mol$^{-1}$ than for $M$=N$_2$O. Although in the 2000–2500 K region the rates for various third bodies (Ne, Ar,
Kr, O₂ do not differ by more than about a factor of two, at low temperatures the effects appear more pronounced. The available data, illustrated in table 2, shows discrepancies particularly for He, Kr, and CO₂.

### Table 2. Relative efficiencies of differing third bodies

<table>
<thead>
<tr>
<th>M</th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
<th>O₂</th>
<th>N₂</th>
<th>CO₂</th>
<th>N₂O</th>
<th>CF₄</th>
<th>SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volmer &amp; Kummerow (1930); Nagasako (1931)</td>
<td>*1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>*0.21</td>
<td>+0.20</td>
<td>*1.2</td>
<td>+1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volmer &amp; Froehlich (1932b)</td>
<td>1.0</td>
<td></td>
<td>0.1</td>
<td></td>
<td></td>
<td>0.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volmer &amp; Bogdan (1933)</td>
<td></td>
<td>*0.44</td>
<td></td>
<td>*0.18</td>
<td></td>
<td>*0.24</td>
<td>*0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bell, et al. (1957)</td>
<td></td>
<td>0.49</td>
<td>0.20</td>
<td>0.15</td>
<td>0.20</td>
<td>0.18</td>
<td></td>
<td>0.46</td>
<td>1.0</td>
<td>*0.85</td>
<td>*0.59</td>
</tr>
</tbody>
</table>

Kaufman, et al. (1956)

\[ k_{\text{He}} > k_{\text{Ne}} > k_{\text{Ar}} \]

\[ T = 895-1030 \text{ K} \]

*Preferred values.

At 1900 K, Fishburne, et al. (1964) report \( k_{\text{Ne}} = 1.4 k_{\text{Ar}} \), not too different from the ratio at lower temperatures. The fact that \( k_{\text{Kr}} > k_{\text{Ar}} \) (2000 K) makes Volmer and Bogdan’s (1933) higher value more appealing. Extrapolation of the high temperature rate constants down to 1000 K, figure 4, does not reflect the established third body effects at that temperature with the one exception of argon.

### Intermediate Pressures—Fall-Off Region

The available data in this region are expressed in 1st order form and shown in figure 5 as a function of the total concentration. The trend from 2nd to 1st order kinetics is clearly defined. The data of Jost, et al. (1963, 1964) appears bimolecular. Olschewski, et al. (1965, 1966) extended the studies of 0.1 percent \( \text{N}_2\text{O}/\text{Ar} \) mixtures to higher pressures (1-340 atm) and also obtained values for \( k_a \) which are shown for the two temperatures 1700 and 2000 K.

The data of Fishburne, et al. (1964) appear questionable since they do not tend to a 2nd order dependence at lower concentrations and values seem to be low. Johnston’s analysis (1961) involved correcting the older data for what was interpreted as a heterogeneous contribution. His reported values have also been plotted in figure 6 with those of Lindars and Hinshelwood (1955). The latter established that the reaction was homogeneous and that the variation of the 1st order rate constant at low concentrations was a definite feature of the N₂O dissociation. Consequently there are certain doubts as to the validity of Johnston’s corrections and whether at low concentrations, \(< 3 \times 10^{-4} \text{ mol cm}^{-3} \) (\(< 200 \text{ torr at 1000 K} \)), the kinetics do approximate to a 2nd order dependence.

At present the data of Olschewski, et al. (1965, 1966) and Johnston (1961) are preferred in this intermediate region.

### High Pressures—1st Order Data

Olschewski, et al. (1965, 1966) have obtained what appears to be reliable data up to 300 atm (2 \( \times 10^{-4} \) \text{ mol cm}^{-3} \). The only other high pressure study was by Hunter (1954) at 40 atm pressure (5 \( \times 10^{-4} \) mol cm^{-3}); later reanalyzed by Johnston (1951). This borders on the fall-off region and consequently values are expected to be slightly low. The agreement between the two sets of data acquired for different temperature regimes is extremely good as seen in figure 7 and suggests that some reliability can be placed on the values given by Olschewski, et al. (1965, 1966). Their values are recommended for the 800-2100 K range with a suggested uncertainty of \( \pm 50 \) percent. \( k_a \) should of course be independent of the nature of M. The low pre-exponential factor is considered a reflection of the forbidden nature of the dissociation process.

Olschewski, et al. (1965) studied the \( \text{N}_2\text{O} \) dissociation over a wide range of concentrations and reported no significant change in the activation energy (M = Ar) from 1.4 \( \times 10^{-4} \) to 1.9 \( \times 10^{-3} \) \text{ mol cm}^{-3}. Although Fishburne, et al. (1964) did find a sensitivity to concentrations their data are questionable for various reasons. Consequently we see that the activation energies for \( k_{\text{N}_2\text{O}}, k_{\text{Ar}}, \) and \( k_a \) are all about 58-59.5 kcal mol⁻¹ while those for \( k_{\text{He}}, k_{\text{Ne}}, \) and \( k_{\text{Kr}} \) appear significantly lower.

### References


4.5. O + N₂ + M —→ N₂O + M

Thermodynamic Data and Equilibrium Constant

Listed under the reverse dissociation reaction.

Recommended Rate Constant

The reaction appears to be slow as may be expected. It is not possible to recommend a rate because of insufficient data.

Discussion

(1) O²⁺(D) + N₂(²Σ) + M —→ N₂O(²Σ) + M,

(2) O²⁺(D) + N₂(²Σ) + M —→ N₂O(²Σ) + M.

The ground electronic state of N₂O correlates to O²⁺(D) and so based on spin correlation considerations reaction (1) is forbidden and (2) allowed. In Harteck and Dondes’ experiment (1954, 1957) only a trace of N₂O was detected, corresponding to about a 10⁻⁴ conversion of O₃ to N₂O. At the low temperature used, the approximate value that can be derived from their results refers to reaction (1). Recently, Stuhl and Niki (1971) also were able to place an upper limit on the room temperature value for k₉₀₇₅₋₅₂. Their value confirms the earlier estimate. Since the reverse reaction, the dissociation of N₂O has an activation energy in excess of the enthalpy change, the slowness of reaction (1) is not unexpected.

Groth and Schierholz (1957) photolysed a mixture of 7 torr O₃ and 419 torr N₂ at room temperature with 1295 and 1470 Å radiation. About 10⁻³ to 10⁻⁴ of the O atoms formed were converted to N₂O. The O²⁺(D) formed at these wavelengths either reacts
to produce N₂O or is lost by predominant collisional quenching, reaction (3)

\( \text{(3)} \quad \text{O}(^1\text{D}) + \text{M} = \text{O}(^3\text{P}) + \text{M} \quad k_{\text{on, N}_2} \approx 6 \times 10^{-11} \) cm³ molecule⁻¹ s⁻¹

\[ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

[Noxon, 1970; Gilpin, et al., 1971; Biedenkapp and Bair, 1970].

From their results, \( k_2 \) can be estimated by setting the relative rates of reaction and quenching equal to the observed factor.

\[ \frac{k_2 [\text{O}(^3\text{P})][\text{N}_2][\text{M}]}{k_2 [\text{O}(^1\text{D})][\text{M}]} = 10^4 \]

This gives a value for \( k_2 \) of about \( 4 \times 10^{-24} \) cm⁶ molecule⁻² s⁻¹.

Simonatis et al. (1972) find no evidence for N₂O formation on photolyzing 6–12 torr O₃ at 2537 Å for 12–24 hours with 42–115 torr O₂ and 870–900 torr N₂. They estimate an upper limit \( k_2 [\text{M}] \leq 2.5 \times 10^{-28} \) which infers a value for \( k_2 < 5 \times 10^{-28} \), two orders of magnitude lower than the estimate had from Groth and Schierholz’s work.

Any contribution from reaction (2) will always be overshadowed by the rapid quenching. It could only become important at extremely high pressures. The dominance of the quenching reaction was also noted by DeMore and Raper (1962, 1963) studying the interaction of O(1D) and N₂ in the liquid phase. They photolyzed a solution of O₃ in liquid N₂ at several wavelengths (2480–3340 Å) and liquid O₂/N₂ mixtures (1849, 2537 Å). The spin forbidden quenching of O(1D) to O(3P) by N₂ was about 75 times faster than the formation of N₂O and had a zero or low activation energy. The low efficiency of N₂O formation results from a feature of the potential energy surfaces which allow the vibrationally excited N₂O intermediate to predissociate predominantly. The transition probability for a cross over between the vibrationally excited \( ^1\Sigma \) state and the \( ^3\Pi \) or \( ^3\Sigma \) repulsive states of N₂O must be relatively high.

### References


### 4.6. N₂O + M = NO₂ + NO + M

#### Thermodynamic data

<table>
<thead>
<tr>
<th>TK</th>
<th>( \Delta H ) kcal mol⁻¹</th>
<th>( \Delta S ) cal deg⁻¹ mol⁻¹</th>
<th>( \log_{10} K_p ) atm</th>
<th>( \log_{10} K_p ) molecule cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.699</td>
<td>22.2</td>
<td>-20.474</td>
<td>-0.608</td>
</tr>
<tr>
<td>100</td>
<td>13.333</td>
<td>39.636</td>
<td>-20.474</td>
<td>-0.608</td>
</tr>
<tr>
<td>200</td>
<td>13.635</td>
<td>41.871</td>
<td>-5.747</td>
<td>13.518</td>
</tr>
<tr>
<td>288</td>
<td>13.650</td>
<td>41.962</td>
<td>-0.835</td>
<td>18.536</td>
</tr>
<tr>
<td>300</td>
<td>13.649</td>
<td>41.958</td>
<td>-0.773</td>
<td>18.615</td>
</tr>
<tr>
<td>400</td>
<td>13.505</td>
<td>41.550</td>
<td>1.702</td>
<td>20.966</td>
</tr>
<tr>
<td>500</td>
<td>13.274</td>
<td>41.040</td>
<td>3.167</td>
<td>22.334</td>
</tr>
</tbody>
</table>

Equilibrium Constant

\[ K_p = 1.08 \times 10^{33} \, T^{-1.104} \exp (-14,520/R) \, \text{atm} \]

(300-900 K range).

This expression reproduces the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.0 percent in this temperature range.

Recommended Rate Constant

The rate and rate constant are defined by

\[ \frac{d[N_2O_4]}{dt} = 0.5 \frac{d[N_2O]}{dt} = k[N_2O][N_2O_4] \]

2nd order, \( k \) = 1st order.

1st order rate constant

<table>
<thead>
<tr>
<th>Rate constant ( k ) (s(^{-1}))</th>
<th>Exp. temp. (K)</th>
<th>Pressure/concentration (atm/mol cm(^{-3}))</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.8 \times 10^9</td>
<td>303</td>
<td>0.45/1.4 \times 10^{-8}</td>
<td>Velocity of sound in ( N_2O_4 ), measured using a tube type CW sonic interferometer (9-451 kc s(^{-1})).</td>
<td></td>
</tr>
<tr>
<td>6.9 \times 10^9</td>
<td>298</td>
<td>0.34/1.4 \times 10^{-8}</td>
<td>Richards and Reid 1933a.</td>
<td></td>
</tr>
<tr>
<td>5.3 \times 10^9</td>
<td>298</td>
<td>0.31/1.2 \times 10^{-8}</td>
<td>This lower limit value of ( k ), measured using a tube type CW sonic interferometer (9-451 kc s(^{-1})), is questionable.</td>
<td></td>
</tr>
<tr>
<td>6.6 \times 10^9</td>
<td>298</td>
<td>0.88/3.6 \times 10^{-8}</td>
<td>This lower limit value of ( k ), measured using a tube type CW sonic interferometer (9-451 kc s(^{-1})), is questionable.</td>
<td></td>
</tr>
<tr>
<td>5.3 \times 10^9</td>
<td>298</td>
<td>0.84/1.4 \times 10^{-8}</td>
<td>This lower limit value of ( k ), measured using a tube type CW sonic interferometer (9-451 kc s(^{-1})), is questionable.</td>
<td></td>
</tr>
<tr>
<td>4.9 \times 10^9</td>
<td>298</td>
<td>0.21/8.7 \times 10^{-8}</td>
<td>This lower limit value of ( k ), measured using a tube type CW sonic interferometer (9-451 kc s(^{-1})), is questionable.</td>
<td></td>
</tr>
<tr>
<td>2.8 \times 10^9</td>
<td>234</td>
<td>0.34/1.4 \times 10^{-5}</td>
<td>This lower limit value of ( k ), measured using a tube type CW sonic interferometer (9-451 kc s(^{-1})), is questionable.</td>
<td></td>
</tr>
<tr>
<td>6.9 \times 10^9</td>
<td>274</td>
<td>0.34/1.5 \times 10^{-5}</td>
<td>This lower limit value of ( k ), measured using a tube type CW sonic interferometer (9-451 kc s(^{-1})), is questionable.</td>
<td></td>
</tr>
<tr>
<td>4.6 \times 10^9</td>
<td>274</td>
<td>0.20/9.1 \times 10^{-5}</td>
<td>This lower limit value of ( k ), measured using a tube type CW sonic interferometer (9-451 kc s(^{-1})), is questionable.</td>
<td></td>
</tr>
<tr>
<td>3.7 \times 10^9</td>
<td>274</td>
<td>0.17/7.7 \times 10^{-5}</td>
<td>This lower limit value of ( k ), measured using a tube type CW sonic interferometer (9-451 kc s(^{-1})), is questionable.</td>
<td></td>
</tr>
</tbody>
</table>

**At high concentrations** >4 \times 10^{-4} mol cm\(^{-3}\) (10 atm, 298 K) no data yet are available for this pressure region where the decomposition tends to unimolecular kinetics. Only approximate assessments of \( k_N \) have been made.

**Intermediate concentrations** (0.5-4) \times 10^{-4} mol cm\(^{-3}\) (1-10 atm, 298 K). The plotted data of Carrington and Davidson (1953) are the only available information. They are probably reliable to \pm 50 percent considering the accuracy of their lower concentration studies.

**Low concentrations** <5 \times 10^{-5} mol cm\(^{-3}\) (1 atm, 298 K) the kinetics are 2nd order. \( k_N = 3.3 \times 10^{-7} \)

**KINETIC RATE CONSTANTS**

<table>
<thead>
<tr>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>M</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$7.1 \times 10^{-14}$</td>
<td>NO$_2$+N$_2$O$_4$</td>
<td>303</td>
<td>Velocity of sound in N$_2$O$_4$, measured using tube type CW sonic interferometer (9-451 km$^{-1}$ max. and at 132-668 mtorr pressure). Richards and Reid 1938a.</td>
<td>Rate constants have been increased by 9 percent (Richards and Reid 1938b) and interpreted as 2nd order constants.</td>
</tr>
<tr>
<td>$8.3 \times 10^{-14}$</td>
<td>NO$_2$+N$_2$O$_4$</td>
<td>303</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$7.1 \times 10^{-14}$</td>
<td>NO$_2$+N$_2$O$_4$</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3.0 \times 10^{-14}$</td>
<td>NO$_2$+N$_2$O$_4$</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$6.3 \times 10^{-14}$</td>
<td>NO$_2$+N$_2$O$_4$</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$9.3 \times 10^{-14}$</td>
<td>NO$_2$+N$_2$O$_4$</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3.2 \times 10^{-13}$</td>
<td>NO$_2$+N$_2$O$_4$</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$7.5 \times 10^{-14}$</td>
<td>NO$_2$+N$_2$O$_4$</td>
<td>274</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$8.4 \times 10^{-14}$</td>
<td>NO$_2$+N$_2$O$_4$</td>
<td>274</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$7.9 \times 10^{-14}$</td>
<td>NO$_2$+N$_2$O$_4$</td>
<td>274</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$3.3 \times 10^{-7} \exp (-11,000/RT)$ or $8.81 \times 10^{-12}T^{7/2}/(12,700)^{1.64} \exp (-12,700/RT)$

$258-301$ kg$^{-1}$ molecule$^{-1}$ s$^{-1}$. Temperature range: 250$-$350 K. Suggested error limits: ±40 percent.

**Discussion**

The N$_2$O$_4$ dissociation typifies a unimolecular process that has been observed only in its low or intermediate pressure regions where the kinetics tend towards a 2nd order dependence. If the mechanism is described by the simple scheme

N$_2$O$_4$+M $\xrightarrow{k_1} N_2O_3$+M, $K_1$=$k_2/k_1$,

N$_2$O$_3$+M $\xrightarrow{k_2} 2$NO$_2$,

the rate of decomposition is given by

$$-d[N_2O_3]/dt=k_1[M][N_2O_4]/(k_2 [M]+1).$$

In the two pressure extremes, that is when the pressure tends to either zero or infinity, this reduces to the two limits

$$-d[N_2O_3]/dt=k_1[M][N_2O_4]/[M] or K_1[M]/k_2 [N_2O_4],$$

Carrington and Davidson (1953) found that in N$_2$ at pressures below about 1.2 atm the dissociation was 2nd order. However, at higher pressure the rate fell below that predicted from 2nd order kinetics. No investigations yet have been carried out at a sufficiently high pressure to observe the 1st order dependence. Except for this study (1953) all others have been in the low pressure region and rates are more appropriately described by 2nd order kinetics. The experimental values were expressed invariably in 1st order form and have been plotted in the 1st order rate constant graph, figure 8.
Below about 1.2 atm total pressure the rate of dissociation of \( \text{N}_2\text{O}_4 \) is described by 2nd order kinetics. Based on this, the acoustic measurements of Cher (1962), Blend (1970), Richards and Reid (1933a), and Sessler (1960) have been reinterpreted and the resulting values compared for \( M=\text{N}_2 \) in figure 9, assuming that

\[
k_{\text{N}_2\text{O}_4}: k_{\text{NO}_2}: k_{\text{N}_2}=1.0: 1.0 : 0.5,
\]

from Cher (1962). Over the observed temperature range, 253–350 K there is reasonably good agreement among the six independent studies.

Values quoted in the work of Wegener (1958, 1959, 1960) and Bauer and Gustavson (1954) have not been considered here since these involve highly sophisticated aerodynamic flow techniques which at best can only serve to confirm the values obtained from simpler systems.

The various efficiencies of differing third bodies have been reported in several studies. Carrington and Davidson (1953) give \( k_{\text{N}_2}=1.3 k_{\text{AT}} \) and Cher (1962),

\[
k_{\text{N}_2\text{O}_4}: k_{\text{NO}_2}: k_{\text{CO}_2}: k_{\text{N}_2}=1.0: 1.0 : 0.5 : 0.3,
\]

which differ slightly from the others.

It appears that the activation energy is less than the dissociation energy. The data conceivably can be fit to a slope corresponding to the dissociation energy but the trend and particularly the studies of Carrington and Davidson (1953), and Richards and
Reid (1933a) suggest a lower value. This predicts a negative activation energy for the reverse recombination reaction.

Carrington and Davidson’s value is recommended for the 250–250 K temperature range for pressures <1.2 atm and is considered accurate to about ±0 percent. The reaction has a very high preexponential factor.

According to the classical coupled oscillator model of a unimolecular reaction, their value for the 2nd order rate constant can be expressed in the form

$$k = \frac{1}{11.38} \times 10^{-11} T^{1/7} \left(\frac{12,700}{RT}\right)^{4.8} \exp (-12,700/RT),$$

which suggests the participation of four and a half oscillators in the dissociation process. If this expression is coupled with the equilibrium constant (molecule cm⁻³ units) it predicts the following value for the recombination reaction

$$k_{NO+NO+M} = 1.7 \times 10^{-40} T^{0.58} \exp (1820/RT) \text{ cm}^6 \text{ molecule}^{-2} \text{s}^{-1}.$$

References


Table: Kinetic Rate Constants

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔH° (kcal mol⁻¹)</th>
<th>ΔS° (cal deg⁻¹ mol⁻¹)</th>
<th>log₁₀ Kp atm</th>
<th>log₁₀ Kp molecule cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>101.690</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>100</td>
<td>102.186</td>
<td>22.547</td>
<td>—128.390</td>
<td>—198.524</td>
</tr>
<tr>
<td>200</td>
<td>103.140</td>
<td>27.847</td>
<td>—99.514</td>
<td>—50.123</td>
</tr>
<tr>
<td>300</td>
<td>103.148</td>
<td>27.876</td>
<td>—99.514</td>
<td>—50.123</td>
</tr>
<tr>
<td>400</td>
<td>103.153</td>
<td>27.941</td>
<td>—38.891</td>
<td>—9.124</td>
</tr>
<tr>
<td>500</td>
<td>105.162</td>
<td>31.680</td>
<td>—16.059</td>
<td>2.807</td>
</tr>
<tr>
<td>600</td>
<td>105.727</td>
<td>32.154</td>
<td>—8.376</td>
<td>10.814</td>
</tr>
<tr>
<td>700</td>
<td>105.903</td>
<td>32.297</td>
<td>—4.522</td>
<td>14.045</td>
</tr>
<tr>
<td>800</td>
<td>105.835</td>
<td>32.295</td>
<td>—2.298</td>
<td>16.210</td>
</tr>
<tr>
<td>900</td>
<td>105.511</td>
<td>32.112</td>
<td>—0.668</td>
<td>17.720</td>
</tr>
<tr>
<td>1000</td>
<td>104.972</td>
<td>31.947</td>
<td>0.427</td>
<td>18.749</td>
</tr>
<tr>
<td>1100</td>
<td>104.235</td>
<td>31.751</td>
<td>1.24d</td>
<td>19.109</td>
</tr>
<tr>
<td>1200</td>
<td>103.290</td>
<td>31.529</td>
<td>1.875</td>
<td>20.057</td>
</tr>
<tr>
<td>1300</td>
<td>102.134</td>
<td>31.286</td>
<td>2.373</td>
<td>20.340</td>
</tr>
<tr>
<td>1400</td>
<td>101.272</td>
<td>31.026</td>
<td>2.776</td>
<td>20.501</td>
</tr>
</tbody>
</table>

Equilibrium Constant

$$K_p = 34.4 \ T^{1.89} \ exp (-102,290/RT) \text{ atm}$$

0 (300–1000 K range)

$$= 2.45 \times 10^6 T^{0.93} \ exp (-105,110/RT)$$

(1000–3000 K range).

These expressions reproduce the 100 K interval data derived from the JANAF Thermochiempical tables with deviations of up to 1.4 percent (300–1000 K) and 0.9 percent (1000–3000 K).

Recommended Rate Constant

$$k_{AR} = 7.2 \times 10^{-6} \ exp (-79,500/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$  

Temperature range: 1800–3200 K.

Suggested error limits: within a factor of 2.5 in this range.

$$\log_{10} A = 9.86 \pm 0.22 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$  

$$E = 79,500 \pm 2000 \text{ kcal}.$$  

Discussion

The thermal decomposition of NH₃, even at temperatures as high as 1000 °C, is heterogeneous [Swarc, 1949]. Successful measurements of the homogeneous gas phase dissociation rate have been obtained only in shock tube studies in the 2000–3000 K range. Four such studies have provided data in reasonable accord, differing at the most by a factor of about 5 and all yield similar activation energies, 20–30 kcal mol⁻¹ below the NH₂–H bond strength. Experimental conditions vary from pressures of 0.08 to 20 atm and in this region the 2nd order nature of the dissociation appears predominant. The [NH₃] decay has been followed in both emission and absorption. Jacobs' earlier work (1960) was in error possibly because of gas contamination. His more reliable experiments (1963) differ from those of Michel and Wagner (1966) and Bradley, Butlin,

Reported rate constants

<table>
<thead>
<tr>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$k_{\text{exp}}$</th>
<th>Exp. temp. (K)</th>
<th>Pressure/concentration (atm/mol cm$^{-3}$)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(4.2-12.2) \times 10^{-4}$ exp($-77,700/RT$) †</td>
<td>$6.7 \times 10^{-15}$</td>
<td>2100-3100</td>
<td>$2.7-3.3/6 \times 10^{-4}$</td>
<td>Shock tube study of 1 and 8 percent NH$_3$/Ar mixtures. [NH$_3$] followed in absorption at 2300-2500 Å behind incident and reflected shock waves. Michel and Wagner 1965.</td>
<td>†Recalculated assuming $d[NH_3]/dt = k[NH_3]^4[Ar]$.</td>
</tr>
<tr>
<td>$7.2 \times 10^{-4}$ exp($-79,500/RT$) M = Ar</td>
<td>$8.1 \times 10^{-18}$</td>
<td>2100-2940</td>
<td>$\sim 2-20/(1.2-10.0) \times 10^{-4}$</td>
<td>Shock tube study of 10 percent NH$_3$/Ar mixtures. [NH$_3$] decay followed in absorption at 2300-2500 Å behind incident and reflected shock waves. Michel and Wagner 1965.</td>
<td>1st order dependence on [NH$_3$] and [Ar].</td>
</tr>
<tr>
<td>$3.8 \times 10^{-4}$ exp($-71,100/RT$) M = Ar</td>
<td>$2.3 \times 10^{-10}$</td>
<td>2450-2970</td>
<td>$\sim 7-3 \times 10^{-2}$</td>
<td>Shock tube study of 10 percent NH$_3$ in Ar. [NH$_3$] followed in absorption at 2245 Å. Initial rate of decomposition measured. No induction period observed at these temperatures. Takeyama and Miyama 1966.</td>
<td>Assume 1st order dependence on [NH$_3$] and [Ar].</td>
</tr>
<tr>
<td>$6.6 \times 10^{-6}$ exp($-83,000/RT$) M = Ar</td>
<td>$3.7 \times 10^{-18}$</td>
<td>1925-2960</td>
<td>$0.08-0.53/(4.7-20.8) \times 10^{-7}$</td>
<td>Shock tube study of 5, 10, and 20 percent NH$_3$/Ar mixtures. [NH$_3$] monitored in emission at 3a and [NH] in absorption at 3360 Å. Bradley, Butlin, and Lewis 1967.</td>
<td>Decomposition 1st order in [NH$_3$] and [Ar].</td>
</tr>
</tbody>
</table>

and Lewis (1967) in that the data appeared better fit to the rate expression


All four studies clearly refer to the same dissociation mechanism and differ only in their interpretation. As to why Jacobs observed a different dependence still is not quite clear. Mechanisms can be invoked as suggested by Bradley, et al. (1967) which predict such a relationship and which also satisfactorily explain the NH behavior and the low activation energy observed. For example,

$$\text{NH}_3 + M \rightarrow \text{NH}_2 + \text{H} + M,$$

$$\text{NH}_3 + \text{NH}_3 \rightarrow \text{N}_2\text{H}_2 + \text{H}_2,$$

$$\text{N}_2\text{H}_2 \rightarrow \text{NH} + \text{NH}_2,$$

$$\text{NH}_2 + \text{NH}_2 \rightarrow \text{products}.$$ 

More work is required in this area to resolve the problem. Recalculation of Jacobs' data (1963) assuming a 1st order dependence on [NH$_3$] and [Ar] leads to values in very good agreement with the other studies.

![Figure 10. Experimental values of $k_{\text{NH}_3+\text{Ar} \rightarrow \text{NH}+\text{H}+\text{Ar}}$](https://example.com/image.png)
All the data refer to \( M = \text{Ar} \) and no information on the effect of different third bodies is available.

Takeyama and Miyama (1966) have noted a temperature dependent induction period below 2400 K when the rate of decomposition is quite slow.

It appears that the values of Michel and Wagner (1965) provide a good mean value to the available data. Their value is recommended. From the spread of the other data it is expected to be accurate to within a factor of 2–2.5 in this temperature range.

References


4.8. \( \text{NH}_3+\text{H}+\text{M} \rightarrow \text{NH}_2+\text{M} \)

Thermodynamic Data and Equilibrium Constants

Listed under the reverse dissociation reaction.

Recommended Rate Constant

Owing to the limited data available no recommendation can be presented for this reaction.

Discussion

Rather limited data are available at present for this recombination reaction. Two radiolysis studies of pure ammonia provide room temperature values which must be regarded as approximate, until confirmed, owing to the technique used and the assumptions made in the analyses.

The value of \( k_{\text{H}+\text{H}+\text{NH}_3} = 0.8 \times 10^{-36} \) for \( k_{\text{NH}_2+\text{H}} \) used in the analysis of Gordon, Mulac, and Nangia (1971) is probably too low by an order of magnitude. Although information on the behavior of \( \text{NH}_3 \) as a third body is sparse and no information is available for its effect on the recombination of \( \text{H} \) atoms, typical room temperature values for polyatomic reactants are \( k_{\text{H}+\text{H}+\text{NH}_3} = 1.2 \times 10^{-31} \) (Eberius, et al., 1969), \( k_{\text{H}+\text{H}+\text{NH}_3} = 1.4 \times 10^{-32} \) [Ham, et al., 1970; Bennett and Blackmore, 1970]. However, it is true that the analysis is not particularly sensitive to its value.

The analysis of Boyd, et al. (1971) is rather involved and depends on the mechanism assumed and on the value for \( k_{\text{H}+\text{H}+\text{NH}_3} \). Both studies refer to \( M = \text{NH}_3 \). A lack of data for the dissociation of \( \text{NH}_3 \) at low temperatures eliminates the possibility of an estimate via the equilibrium constant.

References


<table>
<thead>
<tr>
<th>Rate constant ( k )</th>
<th>Exp. temp. ( T )</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 8 \times 10^{-14} ) ( M = \text{NH}_3 )</td>
<td>298</td>
<td>Radiolysis of pure ( \text{NH}_3 ) at 200–1500 torr in a 360 cm³ cell with a 30–50 ns pulse of 2 MeV electrons. ( \text{[NH}_3 ) and ( \text{[NH}_2 ) monitored in absorption at 3876 and 3880 Å respectively. Gordon, Mulac, and Nangia 1971.</td>
<td>The ( \text{[NH}_3 ) decay was fit to a 2 reaction loss mechanism. ( \text{NH}_3 + \text{H} + \text{M} \rightarrow \text{NH}<em>2 + \text{H} + \text{M} ). A value of ( k</em>{\text{H}+\text{H}+\text{NH}_3} = 0.8 \times 10^{-36} ) was used in the analysis.</td>
</tr>
<tr>
<td>( 1.8 \times 10^{-28} ) ( M = \text{NH}_3 )</td>
<td>298</td>
<td>Radiolysis of pure ( \text{NH}_3 ) at 700 torr using a Femtosecond 60 ns pulse. The numerical integration of the rate expressions for the proposed simple mechanism is compared with the measured yields of ( \text{NH}_3 ), ( \text{H}_2 ) and ( \text{N}_2 ) and the rate constants adjusted for a best fit. The yield of ( \text{N}_2 ) is mainly dependent on the ( \text{NH}_3 + \text{NH}_3 + \text{H} ) recombination reactions. Boyd, Willis, and Miller 1971.</td>
<td>Used a value of ( k_{\text{H}+\text{H}+\text{NH}_3} = 1.1 \times 10^{-32} ) in the analysis. The major reaction is the recombination of ( \text{H} + \text{NH}_3 ) to reform ( \text{NH}<em>3 ). Assumption ( k</em>{\text{H}+\text{H}+\text{NH}_3} = 2 \times 10^{-32} ) cm molecule⁻¹ s⁻¹.</td>
</tr>
</tbody>
</table>
### Thermodynamic Data

<table>
<thead>
<tr>
<th>TK</th>
<th>$\Delta H^o$ kcal mol$^{-1}$</th>
<th>$\Delta S^o$ cal deg$^{-1}$ mol$^{-1}$</th>
<th>$\log K_p$ atm$^{-1}$</th>
<th>$\log K_p$ cm$^3$ molecule$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-130.970</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>-131.399</td>
<td>-27.900</td>
<td>281.061</td>
<td>261.195</td>
</tr>
<tr>
<td>200</td>
<td>-132.146</td>
<td>-32.191</td>
<td>80.826</td>
<td>70.435</td>
</tr>
<tr>
<td>300</td>
<td>-132.151</td>
<td>-32.210</td>
<td>89.228</td>
<td>69.840</td>
</tr>
<tr>
<td>400</td>
<td>-133.613</td>
<td>-33.411</td>
<td>50.661</td>
<td>31.494</td>
</tr>
<tr>
<td>500</td>
<td>-134.143</td>
<td>-34.196</td>
<td>21.624</td>
<td>2.758</td>
</tr>
<tr>
<td>600</td>
<td>-134.219</td>
<td>-34.084</td>
<td>11.503</td>
<td>1.028</td>
</tr>
<tr>
<td>700</td>
<td>-134.333</td>
<td>-33.975</td>
<td>6.772</td>
<td>0.228</td>
</tr>
<tr>
<td>800</td>
<td>-134.400</td>
<td>-33.865</td>
<td>-6.772</td>
<td>-1.028</td>
</tr>
</tbody>
</table>

#### Equilibrium Constant

$K_p = 1.87 \times 10^{-5} \exp (131.740/RT)$ atm$^{-1}$

$= 2.35 \times 10^{-5} \exp (133.410/RT)$

(1000–6000 K range).

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.3 percent (300–1000 K) and 1.2 percent (1000–6000 K).

### Recommended Rate Constant

Only one value at room temperature is available. This requires confirmation.

### Discussion

This is the only published value unearthed and was measured at only one temperature. Data are not sufficiently firm to allow a value to be calculated from the equilibrium constant and the rate constant for the dissociation of SO$_2$ studied at higher temperatures.

### References


### 4.10. SO$_2$ + M → SO + O + M

#### Thermodynamic Data and Equilibrium Constant

Listed under the reverse recombination reaction.

#### Recommended Rate Constant

With some reservation the following value may be recommended as being the most appropriate at present for this reaction in the temperature range 4500–7500 K, M = Ar (see discussion).

$4.2 \times 10^{-10} \exp (-110,000/RT)$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

Further work is needed to confirm this sole determination which may be reliable to within a factor of two.

### 4.9. Reported rate constants

<table>
<thead>
<tr>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>M</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8.8 \times 10^{-31}$</td>
<td>Ar</td>
<td>300</td>
<td>Low power RF discharge in flowing SO$_2$/Ar mixtures. [O] and [SO] monitored by the intensities of the air and SO$_2$ afterglows. Halstead and Thrush 1966.</td>
<td></td>
</tr>
</tbody>
</table>

### 4.10. Reported rate constants

<table>
<thead>
<tr>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Exp. temp. (K)</th>
<th>Pressure/concentration (atm/mol cm$^{-2}$)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4.17 \times 10^{-18} \exp (-110,000/RT)$ or $1.8 \times 10^{-21} \exp (-130,970/RT)$</td>
<td>4500–7500</td>
<td>~5–40/(1.5–7.0) × 10$^{-4}$</td>
<td>Shock tube study of mixtures of 0.05–1 percent SO$_2$ in Ar. [SO] and [SO$_2$] monitored behind reflected shock waves. Gieschkewski, Troe, and Wagner 1965.</td>
<td>Requires a low concentration of SO$_2$ and a high temperature and pressure to observe this reaction. Appears to be in the 2nd order &quot;low pressure&quot; regime of a unimolecular decomposition.</td>
</tr>
</tbody>
</table>
Discussion

Using very low SO₂ concentrations, high temperatures, and a total pressure in the range of about 5–40 atm, Olszewski et al. (1965) obtained a rate constant for the dissociation of SO₂ which most probably refers to this reaction.

Although the observed activation energy falls below the known bond strength of (SO₂-O) this is not uncommon and by invoking the participation of about three classical harmonic oscillator terms the rate can be expressed in the usual form

\[ Z \left( \frac{\Delta E_a}{RT} \right)^{s-1} (s-1)^{-1} \exp \left( -\frac{\Delta E_a}{RT} \right). \]

At temperatures below 4500 K and with higher concentrations of SO₂ in an Ar mixture and lower total pressures (1 atm or less) the kinetics of the dissociation become more involved as inferred by a decrease in the activation energy to about 56–75 kcal mol⁻¹ (Gaydon, Kimball, and Palmer, 1963; Levitt and Sheen, 1967; Olszewski, et al., 1965). Explanations based on the participation of electronically excited states of SO₂ seem the most probable and a scheme of the following type is envisioned.

\begin{align*}
(1) & \quad \text{SO}_2 + \text{Ar} \rightarrow \text{SO} + \text{O} + \text{Ar}, \\
(2) & \quad \text{SO} + \text{Ar} \rightarrow \text{SO}_2 + \text{Ar}, \\
(3) & \quad \text{SO}_2 + \text{SO}_2 \rightarrow \text{SO}_3 + \text{SO}_2, \\
(4) & \quad \text{SO}_2 + \text{SO}_2 \rightarrow \text{SO}_3 + \text{SO}_2, \\
(5) & \quad \text{SO}_2 + \text{Ar} \rightarrow \text{SO}_2 + \text{O} + \text{Ar}.
\end{align*}

Reactions (2) and/or (3) become rate determining and explain the lower activation energies observed. Gaydon, Kimball, and Palmer (1963) studied SO₂ dissociation by shock heating 4–32 percent SO₂/Ar mixtures at total pressures around 1 atm and at temperatures of 3000–4000 K. They monitored [SO] in absorption and proposed reaction (4) for its formation. Olszewski, et al. (1965), using 0.36–1 percent SO₂/Ar mixtures at 5000–4000 K and a lower pressure, and Levitt and Sheen (1957) using 1–40 percent SO₂/Ar mixtures at 3000–5000 K and a total pressure of about 1 atm obtained similar results. Levitt and Sheen (1967) observed an induction period for the dissociation. A certain build up of SO or O may be necessary before the dissociation can proceed at the measured rate. Obviously the dissociation of SO₂ is complicated and dependent on SO₂ concentration, total pressure, and the temperature. The system is still far from understood.

References


KINETIC RATE CONSTANTS

4.11. SO + O₂ → SO₂ + O

<table>
<thead>
<tr>
<th>Tk</th>
<th>(\Delta H^0) kcal mol⁻¹</th>
<th>(\Delta S^0) cal deg⁻¹ mol⁻¹</th>
<th>(\log K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-12.992</td>
<td>-4.363</td>
<td>27.601</td>
</tr>
<tr>
<td>100</td>
<td>-13.079</td>
<td>-4.259</td>
<td>8.618</td>
</tr>
<tr>
<td>298</td>
<td>-13.028</td>
<td>-4.255</td>
<td>8.560</td>
</tr>
<tr>
<td>300</td>
<td>-13.027</td>
<td>-3.871</td>
<td>4.781</td>
</tr>
<tr>
<td>500</td>
<td>-12.873</td>
<td>-3.150</td>
<td>2.010</td>
</tr>
<tr>
<td>1000</td>
<td>-12.349</td>
<td>-2.717</td>
<td>1.128</td>
</tr>
<tr>
<td>1500</td>
<td>-11.818</td>
<td>-2.434</td>
<td>0.706</td>
</tr>
<tr>
<td>2000</td>
<td>-11.327</td>
<td>-2.064</td>
<td>0.198</td>
</tr>
<tr>
<td>2500</td>
<td>-10.905</td>
<td>-2.120</td>
<td>0.367</td>
</tr>
<tr>
<td>3000</td>
<td>-10.563</td>
<td>-2.246</td>
<td>0.463</td>
</tr>
<tr>
<td>3500</td>
<td>-10.285</td>
<td>-2.034</td>
<td>0.188</td>
</tr>
<tr>
<td>4000</td>
<td>-10.049</td>
<td>-2.071</td>
<td>0.118</td>
</tr>
<tr>
<td>4500</td>
<td>-9.832</td>
<td>-1.920</td>
<td>0.058</td>
</tr>
<tr>
<td>5000</td>
<td>-9.614</td>
<td>-1.874</td>
<td>0.011</td>
</tr>
<tr>
<td>5500</td>
<td>-9.379</td>
<td>-1.830</td>
<td>-0.027</td>
</tr>
<tr>
<td>6000</td>
<td>-9.122</td>
<td>-1.785</td>
<td>-0.058</td>
</tr>
</tbody>
</table>

Equilibrium Constant

\[ K = 3.60 \times 10^{4} T^{0.61} \exp \left( \frac{13.370}{RT} \right) \]

This expression, obtained from a least squares fit to the 100 K interval data derived from the JANAF Thermochemical tables, reproduces the data with deviations of up to 0.7 percent in this temperature range.

Recommended Rate Constant

\[ k = 3.0 \times 10^{-38} \exp \left( -\frac{5600}{RT} \right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Temperature range: 400–2500 K.

Suggested error limits: factor of 2 in this range.

\[ \log_{10} A = 13.47 \pm 0.20 \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1} \]

Discussion

As observed from a comparison of the various studies of this reaction, a large discrepancy exists as to its activation energy. The absolute values for the rate constant are in somewhat better agreement however, as seen in figure 11, and suggest a value of about 5600 cal mol⁻¹ based on the values of Sheen (1970), Homann, et al. (1968), and Williams (1968).

The latter’s repetition of Halstead and Thrush’s measurement (1966) but at slightly higher temperatures provides evidence for a low activation energy. Oxygen was added to a heated flow system containing only the reactive species SO (free of atomic oxygen). The observation of the SO₂ afterglow and the air afterglow if a trace of NO was added establishes the formation of O atoms. The SO + O₂ reaction appears the only likely explanation.

The low activation energy is supported most closely by the work of Homann, Krome, and Wagner (1968) where analysis was by mass spectrometer rather than by optical spectroscopy. There is no obvious expla-
<table>
<thead>
<tr>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2×10$^{-12}$</td>
<td>1255</td>
<td>H$_2$S/O$_2$/N$_2$ or Ar atm pressure flames sampled by microprobe, analysed by wet chemistry and by mass spectrometer. Difficulty in measuring SO and SO$_2$ concentrations. This reaction assumed to be the major source of SO$_2$ in the flame. Levy and Merryman 1965.</td>
<td></td>
</tr>
<tr>
<td>4.7, 10.8×10$^{-12}$</td>
<td>1260</td>
<td></td>
<td>Values must be regarded as only very approximate owing to the difficulties encountered in measuring SO and SO$_2$ concentrations.</td>
</tr>
<tr>
<td>9.3, 34.0×10$^{-12}$</td>
<td>1350</td>
<td></td>
<td>Values must be regarded as being very approximate owing to the uncertainties in the [SO] measurements.</td>
</tr>
<tr>
<td>$8.6×10^{-13}$ exp ($-19,300/RT$)</td>
<td>840–1123</td>
<td>Lean H$_2$S/O$_2$/N$_2$ flames burnt at 0.1 and 0.05 atm pressure. Sampled by microprobe and analysed by mass spectrometer and by wet chemistry. [SO$_2$] and [SO] monitored but the latter values are questionable. This reaction assumed to be the major source of SO$_2$ in the flame. Merryman and Levy 1967.</td>
<td></td>
</tr>
<tr>
<td>3.4×10$^{-14}$</td>
<td>840</td>
<td></td>
<td>No SO–O afterglow observed when O$_2$ added at a point in a flow tube where SO present in the absence of O. SO formed from RF discharge in SO$_2$/Ar mixtures. Halstead and Thrush 1966.</td>
</tr>
<tr>
<td>1.3</td>
<td>847</td>
<td></td>
<td>SO formed from excess OCS and atomic oxygen (from N/NO titration) in a mixture highly diluted with Ar. Mixed with excess O$_2$/Ar in a heated flow tube at 1.8–24 torr, sampled with a probe and SO$_2$, CO, OCS, O, SO, and O$_2$ concentrations analysed with a TOF mass spectrometer. [SO] calibrated by titration with NO$_2$. Homann, Krome, and Wagner 1968.</td>
</tr>
<tr>
<td>1.4</td>
<td>855</td>
<td></td>
<td>Dependent on rates of removal of O atoms by other processes. Wall recombination and removal by SO$_2$ measured in subsequent experiments with the same equipment.</td>
</tr>
<tr>
<td>1.5</td>
<td>895</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>990</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>990</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.5</td>
<td>1055</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.6×10$^{-13}$ exp ($-6500/RT$)</td>
<td>1055</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1095</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.9</td>
<td>1123</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$&lt;3×10^{-16}$</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$5.8×10^{-13}$ exp ($-6500/RT$)</td>
<td>580–1145</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3.3×10^{-11}$ exp ($-10,000/RT$)</td>
<td>440–530</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.6×10^{-16}$ exp ($-29,000/RT$)</td>
<td>1600–2100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$&lt;8×10^{-17}$</td>
<td>297</td>
<td></td>
<td>Reaction occurs only to negligibly small extent.</td>
</tr>
</tbody>
</table>
nation as to why the shock tube measurements [Sheen, 1970] gave a high value. However the CS₂/O₂ system is complicated and additional reactions should have been included in his analysis.

The results of Levy and Merryman (1965) and Merryman and Levy (1967) are of little value since they encountered great difficulty in monitoring SO and SO₂ concentrations by their microprobe/analysis method. The results are probably no better than to an order of magnitude.

The recommended value is based on the data of Sheen (1970), Homann, Krome, and Wagner (1968) and Williams (1968), weighted equally. It will be noted that the reaction appears to have a particularly low preexponential factor.

References

Brekenridge, W. H., and T. A. Miller, "Kinetic study by EPR of the production and decay of SO₂(4A) in the reaction of O₂(3Σg⁻) with SO (2Σg⁻)," J. Chem. Phys. 56, 465 (1972).


4.12. SO₂ + O + M → SO₃ + M

Thermodynamic data

<table>
<thead>
<tr>
<th>TK</th>
<th>ΔH° kcal mol⁻¹</th>
<th>ΔS° cal deg⁻¹ mol⁻¹</th>
<th>log⁡Kₗ atm⁻¹</th>
<th>log⁡Kᵡ cm³ molecule⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-81.865</td>
<td>-31.665</td>
<td>173.146</td>
<td>153.280</td>
</tr>
<tr>
<td>100</td>
<td>-82.395</td>
<td>-36.422</td>
<td>53.026</td>
<td>33.635</td>
</tr>
<tr>
<td>300</td>
<td>-83.207</td>
<td>-36.439</td>
<td>52.650</td>
<td>33.262</td>
</tr>
<tr>
<td>500</td>
<td>-83.566</td>
<td>-37.587</td>
<td>26.831</td>
<td>16.178</td>
</tr>
<tr>
<td>1000</td>
<td>-83.735</td>
<td>-37.672</td>
<td>10.966</td>
<td>8.800</td>
</tr>
<tr>
<td>1500</td>
<td>-83.576</td>
<td>-37.547</td>
<td>3.971</td>
<td>3.971</td>
</tr>
<tr>
<td>2000</td>
<td>-83.335</td>
<td>-37.411</td>
<td>0.930</td>
<td>0.930</td>
</tr>
<tr>
<td>2500</td>
<td>-83.061</td>
<td>-37.299</td>
<td>-0.888</td>
<td>-1.635</td>
</tr>
<tr>
<td>3000</td>
<td>-82.861</td>
<td>-37.217</td>
<td>-2.098</td>
<td>-20.486</td>
</tr>
<tr>
<td>3500</td>
<td>-82.669</td>
<td>-37.157</td>
<td>-2.958</td>
<td>-21.280</td>
</tr>
<tr>
<td>4000</td>
<td>-82.527</td>
<td>-37.118</td>
<td>-2.958</td>
<td>-21.280</td>
</tr>
<tr>
<td>4500</td>
<td>-82.443</td>
<td>-37.090</td>
<td>-4.104</td>
<td>-22.316</td>
</tr>
<tr>
<td>5000</td>
<td>-82.422</td>
<td>-37.094</td>
<td>-4.504</td>
<td>-22.671</td>
</tr>
<tr>
<td>5500</td>
<td>-82.466</td>
<td>-37.102</td>
<td>-4.822</td>
<td>-22.957</td>
</tr>
<tr>
<td>6000</td>
<td>-82.571</td>
<td>-37.121</td>
<td>-5.104</td>
<td>-23.101</td>
</tr>
</tbody>
</table>

Equilibrium Constant

\[ K_p = 2.18 \times 10^{-7} T^{-0.473} \exp (83,030 / RT) \ atm^{-1} \]

\( (300-1000 \text{ K range}) \)

\[ K_p = 0.55 \times 10^{-9} T^{0.215} \exp (84,190 / RT) \]

\( (1000-3000 \text{ K range}) \)

These expressions reproduce the 100 K interval data derived from the JANAF thermochemical tables with deviations of up to 1.2 percent (300-1000 K) and 3 percent (1000-3000 K).

Recommended Rate Constants

\[ k = 1 \times 10^{-31} \exp (+100/R T) \] for \( M = Ar, \text{O}_2, \text{N}_2, \text{He} \).

Temperature range: 250-1000 K.

This recommendation must be regarded as very tentative and is accurate to no better than a factor of two at room temperature. Until the activation energy is measured, a larger uncertainty will exist at other temperatures.

Very approximate third body efficiencies:

\[ k_{\text{Ar}}: k_{\text{O}_2}: k_{\text{N}_2} = 1:(6-40). \]

Discussion

The data for this reaction have all been obtained from room temperature studies and, if nothing else, do show a general trend of \( k_{\text{Ar}} > k_{\text{N}_2} > k_{\text{O}_2} \) for \( M = \text{Ar, He} \).

Discharge flow systems, stirred reactor, and static photolysis techniques have been used but the data are still full of inconsistencies and discrepancies such that \( k \) is not confidently known to be better than a factor of 3 to 4.
Reported rate constants

<table>
<thead>
<tr>
<th>Rate constant ( k )</th>
<th>M</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.3 \times 10^{-32} )</td>
<td>( \text{O}_2 )</td>
<td>298</td>
<td>O atoms produced from N/NO titration (O(_2) free) or from a microwave discharge in ( \text{O}_2 ) or an ( \text{O}_2/\text{Ar} ) mixture. Decay followed in flow tube by air afterglow intensity. ( \text{SO}_3 ) concentration measured gas chromatographically at various points. Allen and Cadle 1965. Cadle and Powers 1966.</td>
<td>Activation energy zero or very small. 3rd order reaction kinetics established.</td>
</tr>
<tr>
<td>( 1.2 \times 10^{-32} )</td>
<td>( \text{N}_2 )</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 1.3 \times 10^{-32} )</td>
<td>( \text{Ar} )</td>
<td>298</td>
<td>RF discharge of ( \text{O}_2 ) or 1-2 percent ( \text{O}_2/\text{Ar} ) mixtures; trace of NO added and the O-atom decay followed in a flow tube by the intensity of the air afterglow. Excess ( \text{SO}_2 ) added at either of two entry ports past the discharge. Halstead and Thrush 1966.</td>
<td>( k_{\text{Ar}} = k_{\text{O}_2} )</td>
</tr>
<tr>
<td>( 3.9 \times 10^{-32} )</td>
<td>( \text{SO}_4^+\text{NO}_2^- )</td>
<td>300</td>
<td>( 3860 \ \text{Å} ) photolysis of 3-10 torr ( \text{NO}_2 ) in the presence of 4-740 torr ( \text{SO}_3 ). [( \text{NO}_3 ) followed spectrophotometrically. Quantum yields for loss of ( \text{NO}_2 ) measured as a function of ( \text{SO}_2 ) pressure. Jaffe and Klein 1966.</td>
<td>Based on a comparison of the photolysis of ( \text{NO}_3 ) with and without ( \text{SO}_2 ). Value based on ([\text{SO}_2]+[\text{NO}_3]=2 ) torr data.</td>
</tr>
<tr>
<td>( 7.4 \times 10^{-32} )</td>
<td>( \text{O}_2 )</td>
<td>299</td>
<td>Microwave discharge in ( \text{O}_2 ) or 2 percent ( \text{O}_2/\text{Ar} ) mixtures. Products mixed with ( \text{SO}_2 ) in a 285 ( \text{cm}^3 ) stirred flow reactor at total pressures of 0.7 to 3.0 torr. [O] monitored by ESR at the inlet and outlet of the reactor. [( \text{SO}_2 )/[( \text{O}_2 )]( \approx 5-1000 ). Surface aged to give reproducible results. Mulcahy, Steven, and Ward 1967.</td>
<td>Efficiencies: ( k_{\text{Ar}}:k_{\text{O}<em>2}:k</em>{\text{SO}_2}=1.0:1.1:4.2 )</td>
</tr>
<tr>
<td>( 6.6 \times 10^{-32} )</td>
<td>( \text{Ar} )</td>
<td>299</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2.7 \times 10^{-35} )</td>
<td>( \text{SO}_2 )</td>
<td>299</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 3.8 \times 10^{-35} )</td>
<td>( \text{Ar} )</td>
<td>300</td>
<td>O atoms generated by a microwave discharge in 1.5 percent ( \text{O}_2/\text{Ar} ) and mixed with ( \text{SO}_2 ) in a 290 ( \text{cm}^3 ) stirred pyrex reactor. Total pressures about 2 torr. [O] at inlet and outlet monitored by ESR detection.</td>
<td>Relative efficiencies ( k_{\text{Ar}}:k_{\text{SO}_2}=1:6 ) assumed in the analysis. This is most consistent with the data.</td>
</tr>
<tr>
<td>( 2.7 \times 10^{-38} )</td>
<td>( \text{Ar} )</td>
<td>300</td>
<td>O atoms generated by a microwave discharge in 0.015-0.1 percent ( \text{O}_2/\text{Ar} ) mixtures. [O] at inlet and outlet of a 2234 ( \text{cm}^3 ) Teflon coated reactor measured by comparing air afterglow intensities resulting from addition of a trace of NO. Total pressures about 6 torr. Mulcahy, Steven, Ward, and Williams 1969.</td>
<td>Contribution of ( \text{SO}_2 ) to M is negligible in this case.</td>
</tr>
<tr>
<td>( 1.1 \times 10^{-38} )</td>
<td>( \text{SO}_2 )</td>
<td>298</td>
<td>Electrodeless discharge of 1 percent or less ( \text{O}_2 ) in ( \text{He} ) or ( \text{Ar} ) at 3.4-4.1 torr in a flow system. 0.09-0.28 torr ( \text{SO}_2 ) added after the discharge through movable inlet. [O] measured by ESR as a function of inlet position. [( \text{SO}_2 )/[( \text{O}_2 )]( \approx 6-24 ). Timmons, Lefevre, and Hollinden 1969.</td>
<td>Third body effects of both ( \text{SO}<em>2 ) and ( \text{He} ) or ( \text{Ar} ) considered in the analysis owing to the higher value of ( k</em>{\text{SO}<em>2} ). ( k</em>{\text{SO}<em>2}:k</em>{\text{Ar}}:k_{\text{He}}=41:0.8:1 )</td>
</tr>
<tr>
<td>( 2.2 \times 10^{-38} )</td>
<td>( \text{He} )</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2.7 \times 10^{-38} )</td>
<td>( \text{Ar} )</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E=3400 \text{ cal} )</td>
<td>( \text{SO}_2+\text{He} )</td>
<td>205-298</td>
<td></td>
<td>Determination of ( E ) assumes ( E_{\text{SO}<em>2}=E</em>{\text{He}} ). Positive ( E ) value reported.</td>
</tr>
<tr>
<td>Rate constant ( k ) (cm(^3) molecule(^{-1}) sec(^{-1}))</td>
<td>M</td>
<td>Exp. temp. (K)</td>
<td>Method &amp; reference</td>
<td>Comments</td>
</tr>
<tr>
<td>----------------</td>
<td>--------</td>
<td>---------------</td>
<td>-------------------</td>
<td>---------</td>
</tr>
<tr>
<td>(~1 \times 10^{-31})</td>
<td>( \text{N}_2\text{O} )</td>
<td>298</td>
<td>O atoms generated by the Hg photosensitized decomposition ((\geq 2200 \text{ A})) of 100-481 torr ( \text{N}_2\text{O} ) in the presence of 1.2-52 torr OCS. Absorbed intensity varied by a factor of 156 and the extent of the conversion by a factor of 13. [CO] [N(_2)]. analyzed gas chromatographically. Heicklen, Wood, Obayya, and Chelminik 1969.</td>
<td>The ratio ( \frac{k_{\text{O}+\text{O}+\text{N}^0}}{k_{\text{O}^3\text{S}02}} \approx 8 \times 10^{-13} ) cm(^3) molecule(^{-1}) determined. A very crude estimate however since it is very sensitive to the accuracy of the [CO] [N(<em>2)] measurement from which it is determined. Values fell in the range (3.1 \times 10^{-13}) to (2.5 \times 10^{-12}). A value of (k</em>{\text{O}+\text{O}+\text{N}^0} = 1.3 \times 10^{-11}) has been taken here (q.v.). The measurement can only be considered accurate to within a factor of 2-3.</td>
</tr>
<tr>
<td>(E\sim 2000) cal</td>
<td>( \text{O}_3 + \text{SO}_2 )</td>
<td>440-530</td>
<td>Decay of O atoms in ( \text{O}_3 ) mixtures containing ( \text{SO}_2 ) in a heated flow tube. Followed by chemiluminescent emission. Williams 1969.</td>
<td>Negative activation energy reported.</td>
</tr>
<tr>
<td>(8.3 \times 10^{-8})</td>
<td>( \text{O}_3 )</td>
<td>295</td>
<td>High-power microwave discharge in ( \text{O}_3 ) mixed with 4 percent NO and ( \text{SO}_2 ) in a flow tube. O-atom decay followed by intensity of the air afterglow and calibrated with ( \text{NO}_2 ) titration method. Kaufman 1958.</td>
<td>Approximate value. From room temperature measurements the ( \text{O} + \text{SO}_2 ) reaction appears to have an activation energy greater than 7 kcal mol(^{-1}).</td>
</tr>
<tr>
<td>(\geq 10^{-11})</td>
<td>( \text{H}_2 )</td>
<td>784</td>
<td>( \text{SO}_2 ) inhibition of the ( \text{H}_2/\text{O}_2 ) second pressure limit of explosion in KCl coated vessels. Webster and Walsh 1965.</td>
<td>An involved analysis, should be treated with some reserve.</td>
</tr>
</tbody>
</table>

Hasteed and Thrush (1966), Allen and Cadle (1965), and Cadle and Powers (1966) have obtained similar values for \(k_{\text{O}_2}, k_{\text{O}_3}\), and \(k_{\text{SO}_2}\) using flow tube methods at room temperature. However, they give few details of the experimental conditions and a larger than expected contribution from \(k_{\text{SO}_2}\) may have been overlooked in their analyses. Their values may be too high.

The reaction of \( \text{O} + \text{SO}_2 \) (q.v.) is negligible at room temperature, having an activation energy \( \geq 7 \) kcal mol\(^{-1}\). Consequently, no correction is necessary for this in the work of Mulcahy, et al. (1967, 1969) or in the other low temperature studies. Mulcahy, et al. (1969) found that wall effects in the stirred-flow reactor were of major importance since the efficiency of recombination on the walls varied with the gas phase composition. Their gas phase and wall effects were not independent variables and the data had to be extrapolated to zero [O] in order to obtain values for the three body gas phase recombination. However, since their values for this fall above the general trend of other available room temperature data, some doubt as to the reliability of their \(k_{\text{O}_2+\text{O}+\text{N}^0}\) values has to be expressed. They did attempt to separate the relative contributions of \(k_{\text{O}_2}, k_{\text{O}_3}\), and \(k_{\text{SO}_2}\).

The discharge flow study of Timmons, et al. (1969) has not clarified the picture. They report a very high ratio for \(k_{\text{SO}_2}:k_{\text{Re}, A}\), and a positive activation energy of \(3.4\) kcal mol\(^{-1}\) which would seem highly questionable for such a three body recombination. Williams (1968) gave a value of \(-2\) kcal mol\(^{-1}\) while Allen and Cadle (1965), and Cadle and Powers (1966) reported it as small or zero. Further studies at different temperatures are obviously needed to remove this severe discrepancy. A very tentative value of \(-1\) kcal mol\(^{-1}\) is recommended but this is based more on intuition than actual data.

Heicklen, et al. (1969) have obtained a very approximate value by estimating the ratio

\[
k_{\text{O}+\text{O}+\text{N}^0}/k_{\text{O}^3\text{S}02}
\]

from a photolysis study. This is uncertain by at least a factor of 2-3 but even so it appears that \(k_{\text{N}^0}\) may be quite similar in value to \(k_{\text{SO}_2}\).

The study of Jaffe and Klein (1966) is an involved photolysis based on previous knowledge of the \(\text{NO}_2\)
photolysis. Addition of SO₂ makes it a rather complicated system from which to extract data for specific reactions. Their values may only be approximate.

Several other investigations have been reported in the literature which invoke this reaction but are not considered as contributing any further information as to its rate constant value. Webster and Walsh (1965) interpreted the inhibiting effect of small amounts of SO₂ on the H₂/O₂ second pressure limit explosion as resulting from the removal of H atoms by the H+SO₂ + M reaction. For larger amounts of SO₂ they also had to invoke a mechanism for removing O atoms and proposed this reaction. Netleton and Stirling (1969) burned CH₄/O₂/SO₂ mixtures diluted with N₂ in an atmospheric pressure flow reactor. SO₂ and SO₃ concentrations were measured in the burnt gases by probe sampling followed by wet analysis. Values for [O] had to be assumed from the work of others. It appeared from the study that the effects of the reaction O+SO₂→SO₃+O₂ had to be considered at 2150 K and using reasonable values for this and the three body recombination of O+SO₂+M they could explain their results in a semi-quantitative manner. No independent value can be obtained from their work. Similarly, Levy and Merryman (1965) attempted to extract a value from H₂S/O₂/N₂ or Ar atmospheric pressure flames sampled with a microprobe and analysed by wet chemistry or mass spectrometrically. They had difficulty measuring [SO₃] absolutely and had to assume [O] based on certain flame equilibria. Because of this and the complexity of such flames no reliance can be placed on their values.

Kaufman's early study of this reaction (1958) now is considered to be only approximate.

Although none of the data can be recommended at present, a very tentative value for K_Ar_ONeNe has been quoted. This is based on those values plotted in figure 12.

**References**


4.13 SO₂+M→SO₃+O+M

**Thermodynamic Data and Equilibrium Constant**

Listed under the reverse recombination reaction.

**Recommended Rate Constant**

The available information for this reaction is too limited and too speculative for any recommendation to be made at present.
in nature. The shock tube experiments were analysed based on many assumptions, the main one being of mol-1 below the

tion found for this reaction and are highly speculative

The analysis of the flame reactor experiments assuming this to be the decomposition mechanism.

...from studies of the reverse recombination process

...that this reaction is responsible for the equilibration of SO2 and SO3 in the burnt gases of flames.

...the reaction violates the spin correlation rule

SO4(1A) → SO2(1A) + O(3P_2);

but from studies of the reverse recombination process it does not appear that spin reversal is rate determining in this case.

...indicaL, Nettleton and its equilibrium value.

This expression reproduces the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.8 percent in this temperature range.

The only available data are upper limit estimates

...rate constant and rate constant are defined by

\[ \log_{10} K = k[S02] = -0.5 \frac{d[S02]}{dt}. \]

...Reactor (The Combustion Institute, Pittsburgh, Pennsylvania 1969) p. 635.


4.14. SO+SO→SO2+S

<table>
<thead>
<tr>
<th>T K</th>
<th>ΔH^e kcal mol^-1</th>
<th>ΔS^e cal deg^-1 mol^-1</th>
<th>log_{10} K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-7.459</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>190</td>
<td>-7.580</td>
<td>-6.673</td>
<td>15.106</td>
</tr>
<tr>
<td>298</td>
<td>-7.547</td>
<td>-6.658</td>
<td>4.076</td>
</tr>
<tr>
<td>300</td>
<td>-7.546</td>
<td>-6.654</td>
<td>4.043</td>
</tr>
<tr>
<td>500</td>
<td>-7.376</td>
<td>-6.221</td>
<td>1.865</td>
</tr>
<tr>
<td>1000</td>
<td>-6.920</td>
<td>-5.593</td>
<td>0.289</td>
</tr>
</tbody>
</table>

Equilibrium Constant

\[ K = 1.38 \times 10^{-27} T^{-4.71} \exp \left( \frac{7850}{RT} \right) \]

(300-2600 K range.)

\[ S+O \rightarrow SO. \]

\[ S+2O \rightarrow S_2+O. \]

\[ S+2O \rightarrow S_2 + \text{O}_2. \]

\[ S+O=SO+M. \]

They obtained an upper limit estimate by taking an approximate value for the extinction coefficient of $S_O$.

$k_{SO2SO}$ appears to be $<3\times10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K and $<2\times10^{-12}$ at 1000 K. Exact values may be considerably below these upper limits.

References

Breckenridge, W. H., and T. A. Miller, "Kinetic study by EPR of the production and decay of SO($\lambda$) in the reaction of $O_2$($\lambda$) with SO ('SO')", J. Chem. Phys. 56, 465 (1972).


4.15. S$+$O$\rightarrow$SO$+$O

Thermodynamic data

<table>
<thead>
<tr>
<th>TK</th>
<th>$\Delta H^0$ kcal mol$^{-1}$</th>
<th>$\Delta S^0$ cal deg$^{-1}$ mol$^{-1}$</th>
<th>log$_{10}K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$-5.513$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>10</td>
<td>$-5.499$</td>
<td>2.310</td>
<td>12.495</td>
</tr>
<tr>
<td>298</td>
<td>$-5.481$</td>
<td>2.399</td>
<td>4.542</td>
</tr>
<tr>
<td>300</td>
<td>$-5.481$</td>
<td>2.399</td>
<td>4.517</td>
</tr>
<tr>
<td>350</td>
<td>$-5.497$</td>
<td>2.350</td>
<td>2.916</td>
</tr>
<tr>
<td>1000</td>
<td>$-5.429$</td>
<td>2.443</td>
<td>1.721</td>
</tr>
<tr>
<td>1500</td>
<td>$-5.389$</td>
<td>2.477</td>
<td>1.326</td>
</tr>
</tbody>
</table>
**Kinetic Rate Constants**

<table>
<thead>
<tr>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.7 \times 10^{-11}$ exp ($-50000$) $RT$</td>
<td>897-1129</td>
<td>Heated flow tube, sulfur vapor $S_2$/Ar mixture in excess reacted with O atoms (from N/NO titration) to form S atoms at low total pressure. $O_2$/Ar mix added downstream.</td>
<td>Data from the two sources of S atoms in agreement. Extrapolation to 298 K gives $k=1.3 \times 10^{-11}$. Values appear very questionable at this time.</td>
</tr>
<tr>
<td>$2 \times 10^{-11}$</td>
<td>298</td>
<td>Heat flow tube, sulfur vapor $S_2$/Ar mixture in excess reacted with O atoms (from N/NO titration) to form S atoms at low total pressure. $O_2$/Ar mix added downstream.</td>
<td>The observed $S(2P_3/2)$ decays were 1st order in $[S]$ and $[O_2]$. $k$ independent of flash energy over a 3-fold change and also for the different pressures studied. If OCS pressure increased to 0.3 torr $SO$ observed weakly in absorption.</td>
</tr>
<tr>
<td>$2.8 \times 10^{-12}$</td>
<td>298</td>
<td>Flash photolysis (1900-2600 Â) of mixtures of 0.1 torr OCS/0.06-0.29 torr $O_2$ with either 60, 100, or 200 torr of CO$_2$ or a 2.4 Ar:CO$_2$ mix at 100 or 200 torr. S($2P_3/2$) followed in absorption at 1807 and 1820 Â. Qualitative measurements also made on the weaker 1826 Â ($2P_3/2$) line. $[O_2]$ assumed constant since &lt;5% percent consumed. Fair and Thrush 1972.</td>
<td></td>
</tr>
<tr>
<td>$1.7 \times 10^{-12}$</td>
<td>295</td>
<td>Flash photolysis of 0.03 torr OCS/0.003-0.015 torr $O_2$/112.5 torr Ar or N$_2$ mixtures. $[O_2] \sim$ 9-64 fold $[S]$. $[S]$ monitored by atomic absorption at 1820 Â of the $3P_1$ state. Donovan and Little 1972.</td>
<td>96 percent of the $S(2D)$ initially formed will be quenched to $S(2P)$ during the flash period under these conditions.</td>
</tr>
<tr>
<td>$2.24 \times 10^{-12}$ exp ($-0/RT$)</td>
<td>252-423</td>
<td>Flash photolysis, $&gt;1650$ Â, of 0.06-0.10 torr OCS, 25 torr CO$_2$ and 0.004-0.040 torr $O_2$ mixtures. $[S]$ and $[O]$ monitored by resonance fluorescence following a 200 Â delay. $[S] \sim 10^6-10^7$ atoms/cm$^2$. Data also obtained for 0.100 torr OCS, 20 and 200 torr H$_2$, and 0.011-0.021 torr $O_2$ mixtures. Davis, Klemm, and Pilling 1972.</td>
<td>$[S]$ decay follows 1st order kinetics. $S(2D)$, $S(2D')$ quenched before data collection. No indication of any pressure dependence. CO$_2$ data appears uncomplicated by any side reactions.</td>
</tr>
</tbody>
</table>

---

Equilibrium Constant

$K=2.53 \times 10^{-0.07} \exp\left(-5520/RT\right)$ (300–2500 K range).

This expression reproduces the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.6 percent in this temperature range.

Recommanded Rate Constant

$k=2.2 \times 10^{-12}$ exp ($-0/RT$) cm$^3$ molecule$^{-1}$ s$^{-1}$.

Temperature range: 250–450 K.

Suggested error limits: ±30 percent.

$\log_{10}A=12.34 \pm 0.06$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $E=0 \pm 100$ cal.

Discussion

The agreement between the low temperature values of Fair and Thrush (1969), Fair, Van Roooelpaar, and Strausz (1971), Donovan and Little (1972), and Davis, Klemm, and Pilling (1972) casts grave doubts on the reliability of the higher temperature measurements of Homann, Krome, and Wagner (1968). Although it is desirable to obtain further values at elevated temperatures it appears now that the reaction proceeds with a near zero activation energy. Fair and Thrush (1969) produced S atoms via the reactions

$H+H_2S\rightarrow HS+H_2$, $H+HS\rightarrow H_2+S$. 

---

and followed the interaction with O₂ spectroscopically. This method for the formation of S atoms has been confirmed by Cupitt and Glass (1971) who used ESR detection to establish that, indeed, for conditions where H atoms are in excess, H₂S is converted almost quantitatively into S atoms and can be pumped through a flow system with little loss.

Fair, et al. (1971), Donovan and Little (1972), and Davis, et al. (1972) flash photolysed highly diluted mixtures containing OCS. Under their experimental conditions the S(1D/2S) initially formed in the photodissociation is rapidly quenched to ground state S(3P) to provide a clean source of S atoms. Davis, et al. (1972) prefer their data utilizing CO₂ as inert diluent. That with helium may have been slightly complicated by formation of some S₂ since in this case S(1D/2S) quenching may be partially via reaction with OCS. Even so, the values are scarcely outside their quoted error and are well within the ±30 percent error limits suggested here. They also found that values derived from the rate of appearance of [O] were in good agreement with [S] decay data. Based on this and the other values, a confidence level of ±30 percent seems quite appropriate particularly since three different monitoring techniques were used; chemiluminescence, atomic absorption and atomic fluorescence. The value of Davis, et al. (1972) is recommended.

Homann, et al. (1968) used both the reaction S₂+O→SO+S, and a discharge through sulfur vapor as separate methods of producing S atoms. The species were monitored with a TOF mass spectrometer. As to how the discrepancy arises in their results is not clear. No reliance can be placed on their values at this time.

It may be noted that Cupitt and Glass (1971) have observed that at room temperatures when [O₂]>[H]>[H₂S], all of the H₂S is converted to SO. This is explained by a reasonably fast rate of reaction between S and O₂ and is further confirmation of the low temperature values.

References


4.16. H₂SO₃+M→HSO₃⁻+M

Thermodynamic Data

The thermodynamic properties of the HSO₃ radical still are unknown.

Recommended Rate Constant

The systems in which this reaction is thought to participate have not been sufficiently well characterized to enable reliable values to be recommended for this rate constant.

Discussion

Webster and Walsh (1965) found that the effect of small amounts of SO₃ on the second pressure limit of explosion for H₂/O₂ mixtures could be satisfactorily explained if this reaction was included in the kinetic scheme. Its rate constant was derived relative to that for the H+O₂+M reaction, the value for which here has been taken as 3×10⁻¹² cm⁶ molecule⁻¹ s⁻¹ (784 K). This is based on the values of 2.8×10⁻¹³ obtained from the ratio of the rate constant for H₂O₂ to H₂O₂+M=22.5 mm Hg (784 K)=2.8×10⁻¹³ molecule cm⁻³ [Baldwin, et al., 1967] using kH₂O₂=7.7×10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ [Baulch, et al., 1969] and 3.1×10⁻²² obtained by Kurzis (1964) at this temperature.

Fenimore and Jones (1965) determined the heat release profile in low pressure flames with and without the presence of small amounts of SO₂. The difference was associated with the extra heat released by a catalytic recombination mechanism

\[
\begin{align*}
H₂SO₃+M &→ HSO₃⁻+M, \\
H₂O₂ &→ H₂+SO₂, \\
OH &→ H₂O₂+SO₂.
\end{align*}
\]

This value sets an upper limit since additional heat release processes not considered may occur. Kallend (1967) confirmed this mechanism and found the rate of catalytic recombination to have a first order dependence on [H], the case if the first reaction is rate determining. However, Halstead and Jenkins (1969), using higher temperature flames, found it to be a second order dependence on [H], since con-
### Kinetic Rate Constants

#### Reported rate constants

<table>
<thead>
<tr>
<th>Rate constant $k$ (^{(cm^3 \text{ molecule}^{-2} \text{ s}^{-1})})</th>
<th>M</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6 \times 10^{-21}$</td>
<td>H(_2)</td>
<td>784</td>
<td>SO(_2) inhibition of H(_2)/O(_2) second explosive limit in KCl coated vessels. Webster and Walsh 1965.</td>
<td>$k_{\text{H}_2+\text{SO}_2+\text{H}<em>2} = 2.0$ obtained. This has been coupled with a value of $k</em>{\text{H}_2+\text{O}_2+\text{H}_2} = 3 \times 10^{-32}$ (784K).</td>
</tr>
<tr>
<td>$\leq 2 \times 10^{-21}$</td>
<td>Burnt flame gases = 1 Ar: 0.7H(_2): 0.6H(_2)O</td>
<td>1480–1660</td>
<td>Fuel rich H(_2)/O(_2)/Ar/SO(_2) or H(_2)S flames burnt at 50–100 torr. Sampled by microprobe-mass spectrometric analysis. [H] measured from HD formation on adding a trace of D(_2)O to unburnt gases. Heat release profile calculated from temperature measurements. Fenimore and Jones 1965.</td>
<td>Upper limit value. Obtained by assuming no additional reactions but this contribute to the heat release profile.</td>
</tr>
<tr>
<td>$2 \times 10^{-21}$</td>
<td>H(_2)+N(_2)+H(_2)O</td>
<td>1047</td>
<td>Fuel rich atm pressure H(_2)/O(_2)/N(_2) flames with addition of up to 1.5 percent SO(_2). Microprobe sampler established the SO(_2) dominance in the flames over other S compounds. [H] measured from intensity of 4280 Å CuH band.</td>
<td>1st order dependence on [H]. This reaction appears to be the rate determining step.</td>
</tr>
<tr>
<td>$1.1 \times 10^{-31}$</td>
<td>0.68N(_2)+0.15H(_2)O +0.08CO(_2)+0.06CO</td>
<td>2080</td>
<td>Small amounts of up to about 1 percent SO(_2) added to fuel rich CH(_2)H(_2)/air atm pressure flames. [H] measured by the Na/Li method. Wheeler 1968.</td>
<td>Questionable analysis. Assumes a 1st order dependence on H which is not experimentally found.</td>
</tr>
<tr>
<td>$&lt;1.4 \times 10^{-33}$</td>
<td>Ar</td>
<td>298</td>
<td>H atoms produced by RF discharge of 1–5 percent H(_2)/Ar mixtures in flow tube and measured by the intensity of the HNO emission from a trace of added NO. SO(_2) added at entry ports after the discharge. Blue S(_2) chemiluminescence observed. Fair and Thrust 1969.</td>
<td>No clear evidence for this reaction. The observed H atom decay attributed to the previously observed sulfur catalysed heterogeneous decay.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2110</td>
<td>Seven isothermal fuel rich C(_6)H(_6)/O(_2)/N(_2) atm pressure flames with addition of 0.1–1 percent SO(_2). [H] measured by Li absorption method. Included flames of higher [OH] than previously, [OH]/[H] ~ 0.4–3.8. Duric, Johnson, and Smith 1971.</td>
<td>Recombination kinetics 2nd order in [H]. Confirms findings of Halstead and Jenkins (1969). OH+SO(_2)+M reaction appears unimportant in flames.</td>
</tr>
</tbody>
</table>
confirmed by Durie, et al. (1971), which is explained by including the reverse of the first reaction. At their temperatures (1940–1990 K and 2110 K, respectively) it appears that the first reaction can become essentially balanced so that the rate is then controlled by the subsequent reactions. This second order dependence previously had also been reported by McAndrew and Wheeler (1962) for propane-air flames at a similar temperature. Halstead and Jenkins (1969) suggest that it may not be unreasonable for the order of the reaction to change over to 1st at lower temperatures in agreement with the interpretation of Fenimore and Jones (1965) and possibly also with Kallend’s findings (1967). The recalculation by Wheeler (1968) of their previous data [McAndrew and Wheeler, 1962] but assuming a 1st order dependence on [H] appears unjustified and consequently the value is highly questionable.

Kallend (1967) used flames for which M=H₂+H₂O+ N₂. The rate constant did not significantly vary for changes in [N₂] by a factor of 3, [H₂] by a factor of 2 or [H₂O] by 20 percent inferring that none of these is particularly more efficient than another.

A major difficulty is to reconcile the high temperature data with the negative results of Fair and Thrush (1969) who attempted to observe this reaction at room temperature. It would be necessary for the reaction to have a positive activation energy of about 3 kcal mol⁻¹ which seems unlikely. Consequently, the rate is still very uncertain and further work is necessary using more easily interpreted systems to better specify the observed reactions.

References


4.17. O+CS₂→CS+SO

Thermodynamic data

<table>
<thead>
<tr>
<th>TK</th>
<th>ΔH₀ kcal mol⁻¹</th>
<th>ΔS₀ cal deg⁻¹ mol⁻¹</th>
<th>log₁₀K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-30.912</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>-30.750</td>
<td>8.554</td>
<td>69.070</td>
</tr>
<tr>
<td>298</td>
<td>-30.899</td>
<td>8.020</td>
<td>24.401</td>
</tr>
<tr>
<td>300</td>
<td>-30.902</td>
<td>8.009</td>
<td>24.261</td>
</tr>
<tr>
<td>500</td>
<td>-31.297</td>
<td>7.000</td>
<td>15.210</td>
</tr>
<tr>
<td>1000</td>
<td>-32.278</td>
<td>5.640</td>
<td>8.287</td>
</tr>
<tr>
<td>1500</td>
<td>-33.224</td>
<td>4.872</td>
<td>5.905</td>
</tr>
</tbody>
</table>

*Recent data of Hildenbrand [Chem. Phys. Letters 15, 379 (1972)] indicate that the values for ΔH₀ and K given in this table should be modified.

Equilibrium Constant

\[ K = 3.75 \times 10^4 \ T^{-1.472} \exp \left( 30,330/RT \right) \]

(300–2500 K range).

This expression reproduces the 100 K interval data derived from the JANAF Thermochemical tables with deviations up to 0.6 percent in the temperature range.

Recommended Rate Constant

\[ k = 2.0 \times 10^{-11} \exp (-1030/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]

Temperature range: 200–1000 K.

Suggested temperature range: 700–2000 K.

\[ \log_{10} A = 11.29 \pm 0.06 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \]

\[ E = 1030 \pm 80 \text{ cal s}. \]

Reported rate constants

<table>
<thead>
<tr>
<th>Rate constant ( k ) (cm(^3) molecule(^{-1}) s(^{-1}))</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.17 \times 10^{-12}</td>
<td>305</td>
<td>Flash photolysis of CS(_2)/NO(_2)/Ar mixtures with wavelengths &gt;3000(\AA). [CS(_2)] \sim 0.1 \text{ torr} and CS(_2)/NO(_2) \sim 10:1. Total pressure \sim 80 \text{ torr}. [CS] monitored in absorption. SO also detected. ( k ) refers to the rate of production of ground state CS. Smith 1968.</td>
<td></td>
</tr>
<tr>
<td>5.35 \times 10^{-12}</td>
<td>410</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.19 \times 10^{-11}</td>
<td>917</td>
<td>Heated flow tube at 3–6 \text{ torr} total pressure. O(_2)/Ar subjected to microwave discharge or O from N/NO titration. 0.08 percent CS(_2)/Ar added downstream such that O atoms about 6 times in excess. Sampled with TOP mass spectrometer. Homann, Krome, and Wagner 1968.</td>
<td></td>
</tr>
<tr>
<td>2.97 \times 10^{-11}</td>
<td>930</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.37 \times 10^{-11}</td>
<td>866</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.94 \times 10^{-11}</td>
<td>704</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.58 \times 10^{-12}</td>
<td>302</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.35 \times 10^{-12}</td>
<td>305</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.07 \times 10^{-12}</td>
<td>227</td>
<td>Flow system, O atoms from discharged 0.03 percent O(_2)/He mixture. CS(_2) added downstream in amounts 5 to 10 times [O]. [O] measured by ESE, SO formation also observed. Stable products mass analyzed. Pressure \sim 2 \text{ torr}. Westenberg and De Haas 1969.</td>
<td>Only the NO(_2) photodissociated. Rather complex analysis but CS(_2)/NO(_2) ratio chosen to minimize complications. O reacts almost exclusively with CS(_2). Experimental time appears to have been too short for complications from the O+CS reaction. ( k ) derived from decrease in [CS(_2)] and increase in [SO]. [O] taken as its mean value.</td>
</tr>
<tr>
<td>2.99 \times 10^{-12}</td>
<td>297</td>
<td></td>
<td>Established a value of 2 for the O/CS(_2) stoichiometry. Initial reaction followed by the fast O+CS(_2) \rightarrow CO+8 reaction.</td>
</tr>
<tr>
<td>7.80 \times 10^{-12}</td>
<td>538</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Discussion

Three independent investigations have produced values for this rate constant. Those of Smith (1968), Westenberg and De Haas (1969), and the two low temperature datum points of Homann, Krome, and Wagner (1968) are in good agreement, considering the different techniques and analyses involved. These form the basis for the recommended value which appears quite reliable. The high temperature values of Homann, et al. (1968) are suspect and appear to be about a factor of two high. Smith (1968) and Westenberg and De Haas (1969) had concentrations of CS\(_2\) in excess of the O atom concentration. Homann, et al. (1968) maintained an excess of O atoms. They appear to have measured \( k \) by following both the decrease in [CS\(_2\)] and the rate of increase in [SO] and so an explanation for the twofold discrepancy is not easy. A better understanding of the system at high temperatures is required.

Sheen (1970) has studied the oxidation of CS\(_2\) in a shock tube, monitoring CS and SO in emission and absorption and the SO\(_2\) afterglow. However, the analysis of the data is complex and reactions such as

\[
O + (CS) \rightarrow CO + S, \\
S + O_2 \rightarrow SO + O, \\
\]

were not included. No reliable values can be derived from his analysis.

References


These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.4 percent (300–1000 K) and 0.3 percent (1000–3000 K).

**Recommended Rate Constant**

$$k = 6.8 \times 10^{-11} \exp (-5080/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$  
Temperature range: 270–1500 K.  
Suggested error limits: ±35 percent.

$$\log_{10} A = 11.83 \pm 0.08 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$  
$$E = 5080 \pm 140 \text{ cal s.}$$

**Discussion**

It is most gratifying when the values of five independent studies agree so well as is the situation for this reaction. Although investigated in each case by a flow tube technique, the experimental conditions differ considerably from an excess of OCS at one extreme to an excess of O atoms at the other.

The reaction appears very well established and there is no evidence for the alternate displacement reaction [Westenberg and DeHaas, 1969; Rolles, Reeves, and Hartack, 1965],

$$E = 4.20 \times 10^4 T^{-0.97} \exp (50410/RT) \text{ (1000–3000 K range).}$$

which would be about 54 kcal mol$^{-1}$ exothermic.
Reported rate constants—Continued

<table>
<thead>
<tr>
<th>Rate constant ( k ) (cm(^3) molecule(^{-1}) s(^{-1}))</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(8.96 \times 10^{-13})</td>
<td>273</td>
<td>Flow system at 0.5–2.5 torr. O from discharge in (&lt;0.1) percent O(_2)/He or Ar mix or from N(_2)/NO titration with N(_2) carrier gas. OCS concentration in large excess added downstream. O, SO detected by ESR. Stable products mass analyzed. (k) derived from decay of [O]. Westenberg and De Haas (1969).</td>
<td>1 oxygen atom consumed per OCS molecule.</td>
</tr>
<tr>
<td>(1.41 \times 10^{-14})</td>
<td>297</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7.14 \times 10^{-14})</td>
<td>374</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3.49 \times 10^{-13})</td>
<td>508</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9.46 \times 10^{-13})</td>
<td>688</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2.06 \times 10^{-12})</td>
<td>808</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3.15 \times 10^{-11}) exp (-4530/RT)</td>
<td>273–808</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1.19 \times 10^{-14})</td>
<td>297</td>
<td>O atoms produced in a flow system by microwave discharge of O(_2)/He mixture. OCS added downstream. Pressures around 0.5 torr. [O], [SO] monitored by ESR. Breckenridge and Miller (1972).</td>
<td>Procedure similar to that used by Westenberg and De Haas (1969).</td>
</tr>
</tbody>
</table>

\(A_0+O_2/A_0+OCS=0.671\)

\(E_{O+OCS}-E_{O+O}=170\) cals

\(A_0+\text{TMP}^*/A_0+OCS=0.928\)

\(E_{O+OCS}-E_{O+\text{TMP}}=2280\) cals

\(A_0+\text{OCS}^*/A_0+\text{OCS}=0.80\)

\(E_{O+\text{OCS}^*}-E_{O+OCS}=300\) cals

*TMP is 2-Trifluoromethylpropene

Because of the excellent agreement between studies, a best fit to all the available data is the basis for the recommended value. A recent photolysis study by Krezeneski, Simonaitis, and Heicklen (1971) measured the rate of this reaction relative to those of O+O\(_2\) and O+TMP (2-trifluoromethylpropene). This has not been included owing to the uncertainties in the rates of these reactions. Using the most reliable data for their rate constants, values for \(k_{O+OCS}\) are 1.32 times higher than that here recommended at 197 K and 1.17 times too low at 299 K (O+O\(_2\) data). Similarly the calculated values are 1.59 (298 K) and 2.43 (523 K) times too low based on the O+TMP data. The latter probably infers a too low literature value for \(k_{O+\text{TMP}}\).

References


4.19. O+H₂S→OH+HS

Equilibrium Constant

\[ K = 1.72 \times 10^{-16} \exp \left( \frac{10,650}{RT} \right) \text{ (300–1000 K range)}, \]

\[ = 3.44 \times 10^{-8} \exp \left( \frac{9480}{RT} \right) \text{ (1000–2500 K range)}. \]

These expressions reproduce the 100 K interval data derived from the JANAF Thermochernical tables with deviations of up to 1.4 percent (300–1000 K) and 0.3 percent (1000–2500 K).

Recommended Rate Constant

\[ k = 6.3 \times 10^{-13} \exp \left( -1830/RT \right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]

Temperature range: 200–350 K.

Suggested error limits: better than a factor of two in this range.

\[ \log_{10} A = 13.80 \pm 0.20 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \]

\[ E = 1830 \pm 250 \text{ cal}. \]

Discussion

This reaction has been studied successfully only in discharge flow systems with either mass spectrometric or ESR detection. However, the experimental conditions are different for each of the investigations. Liuti, Dondes, and Hartack (1966) operated at a total pressure of about 0.5 torr and had similar concentrations of O and H₂S. Their results could be explained in terms of the three reactions

\[ \text{O+H}_2\text{S} \rightarrow \text{OH}+\text{HS}, \]

\[ \text{O+HS} \rightarrow \text{H}+\text{SO}, \]

\[ \text{H}+\text{HS} \rightarrow \text{H}_2+\text{HS}. \]

Reported rate constants

<table>
<thead>
<tr>
<th>Rate constant ( k ) (cm³ molecule⁻¹ s⁻¹)</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0 \times 10^{-14}</td>
<td>295</td>
<td>Flow system at pressures ( \sim 0.5 ) torr, sampled by TOF mass spectrometer. DC discharge in O₂ or 10 percent O₂/Ar mixtures. O also produced from N/NO titration. H₂S/Ar mixture added downstream. [O] measured from initial decrease in O₂ at mass 32 when the discharge initiated and also from the NO₃ titration. O and H₂S concentrations small and of a similar magnitude. Liuti, Dondes, and Hartack 1966.</td>
<td>Estimates made concerning the average reaction chain length required in the analysis.</td>
</tr>
<tr>
<td>4.5 \times 10^{-14}</td>
<td>300</td>
<td>Discharge flow system at about 10 torr, sampled by a TOF mass spectrometer. Low concentrations of O and H₂S, low conversions. [O]&gt;[H₂S]. Niki and Weinstock 1967.</td>
<td></td>
</tr>
<tr>
<td>8.11 \times 10^{-14}</td>
<td>205</td>
<td>Flow system at pressures of about 2 torr. Electrodeless discharge in 0.3–1.4 percent O₂/He mixtures. Small additions of H₂S downstream. [H₂S]&gt;[O]. Assume [H₂S] constant, decay of O-atoms monitored by ESR. Hollinden, Kurylo, and Timmons 1970. Assume a 3.5 O atoms:1 H₂S stoichiometry.</td>
<td>Computer fit of the experimental data to that calculated assuming a 7 stage mechanism. Agreement for cases of O&gt;[H₂S]. Error found recently in the original analysis leads to a slightly higher value than initially published.</td>
</tr>
<tr>
<td>1.09 \times 10^{-14}</td>
<td>244</td>
<td>Flow system at pressures of about 10 torr. Electrodeless discharge in 0.3–1.4 percent O₂/He mixtures. Small additions of H₂S downstream. [H₂S]&gt;[O]. Assume [H₂S] constant, decay of O-atoms monitored by ESR. Hollinden, Kurylo, and Timmons 1970.</td>
<td></td>
</tr>
<tr>
<td>1.58 \times 10^{-14}</td>
<td>273</td>
<td>Flow system at pressures of about 2 torr. Electrodeless discharge in 0.3–1.4 percent O₂/He mixtures. Small additions of H₂S downstream. [H₂S]&gt;[O]. Assume [H₂S] constant, decay of O-atoms monitored by ESR. Hollinden, Kurylo, and Timmons 1970.</td>
<td></td>
</tr>
<tr>
<td>2.81 \times 10^{-14}</td>
<td>300</td>
<td>Flow system at pressures of about 10 torr. Electrodeless discharge in 0.3–1.4 percent O₂/He mixtures. Small additions of H₂S downstream. [H₂S]&gt;[O]. Assume [H₂S] constant, decay of O-atoms monitored by ESR. Hollinden, Kurylo, and Timmons 1970.</td>
<td></td>
</tr>
<tr>
<td>2.9 \times 10^{-14} \exp (-1500/RT)</td>
<td>205–300</td>
<td>Flow system at pressures of about 10 torr. Electrodeless discharge in 0.3–1.4 percent O₂/He mixtures. Small additions of H₂S downstream. [H₂S]&gt;[O]. Assume [H₂S] constant, decay of O-atoms monitored by ESR. Hollinden, Kurylo, and Timmons 1970.</td>
<td></td>
</tr>
<tr>
<td>1.51 \times 10^{-14}</td>
<td>295</td>
<td>Flow system at pressures of about 10 torr. Electrodeless discharge in 0.3–1.4 percent O₂/He mixtures. Small additions of H₂S downstream. [H₂S]&gt;[O]. Assume [H₂S] constant, decay of O-atoms monitored by ESR. Hollinden, Kurylo, and Timmons 1970.</td>
<td></td>
</tr>
</tbody>
</table>

The latter two form a chain mechanism. OH appeared to play no major role in their system and only 1.1–1.25 O atoms were consumed per H$_2$S. For each H$_2$S consumed about 0.8 molecule of H$_2$ was formed. Therefore it was estimated that the reaction rate of H$_2$S was about 5±1.5. The overall rate of consumption of H$_2$S and O occurred with a reaction rate of 2×10$^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 295 K. This was corrected by the chain factor to give a value in this rather restricted temperature range that should be accurate to better than a factor of 2.

Lithium, Dondes, and Harteck (1967) used a similar technique but with differing experimental conditions. Levy and Merryman (1965) investigated H$_2$S/O$_2$ mixtures and atmospheric and reduced pressures. The gases were analysed by microprobe sampling and wet chemical or mass spectrometric methods. However, the system is very complicated and because of insufficient experimental data it is not possible to estimate with any certainty the rate constants of the dominant reactions.

The rate constant recommended for this reaction is based on the 5 datum points obtained by Liuti, Dondes, and Harteck (1966) and Hollinden, Kurylo, and Timmons (1970). These have been weighted equally and give a value in this rather restricted temperature range that should be accurate to better than a factor of two. The reaction has a low pre-exponential factor.

Cupitt and Glass (1970) who find that the [O]/[H] ratio is not large in H$_2$S rich mixtures yet $k_{H+H_2S}/k_{O+H_2S}$ is about a factor of 30. Therefore it would seem that their data must have been influenced somewhat by this reaction. Its inclusion though would set up the same chain mechanism considered by Liuti, et al. (1966) and result in a lower value for $k$.

Cupitt and Glass (1970) by systematically varying the rate constants in the seven step mechanism

\[
\begin{align*}
O+H_2S & \rightarrow OH+HS, \\
O+OH & \rightarrow H+O_2, \\
H+H_2S & \rightarrow H_2+HS, \\
HS+O & \rightarrow H+SO, \\
H+HS & \rightarrow H_2+S, \\
SO+OH & \rightarrow SO_2+H, \\
S+O_3 & \rightarrow SO+O, \\
\end{align*}
\]

managed to reproduce the experimental data for cases where [O] > [H$_2$S]. However, the values used in their analysis differ somewhat from those currently recommended. The value for $k_4$ (4.3×10$^{-11}$) possibly is too high by a factor of 2, Baulch, et al. (1969) recommend 2.2×10$^{-11}$. This also is the case for $k_5$. The calculations were insensitive to $k_4$ and $k_5$, but these rates likewise were taken at about 2.5 and 4 torr, operated with 2.5 and 4 times too fast, respectively. $k_7$ was taken as 1.2×10$^{-12}$ rather than 2.2×10$^{-12}$ (see S+O$_2$ evaluation). Moreover, it appears that the value derived for $k_4$ is too high by about a factor of 1.8 (see H+H$_2$S evaluation). This is the same factor by which $k_{O+H_2S}$ falls below the value recommended here. This allows for an arithmetic error found in their original analysis. The SO concentrations originally reported were too high. Their value is the lowest reported at room temperature.

Levy and Merryman (1965) and Merryman and Levy (1967) investigated H$_2$S/O$_2$/N$_2$ or Ar flames at atmospheric and reduced pressures. The gases were analysed by microprobe sampling and wet chemical or mass spectrometric methods. However, the system is very complicated and because of insufficient experimental data it is not possible to estimate with any certainty the rate constants of the dominant reactions.

References


4.20. H\(_2\) + H\(_2\)S \rightarrow H\(_2\) + HS

Thermodynamic data

<table>
<thead>
<tr>
<th>TK</th>
<th>(\Delta H^o) kcal mol(^{-1})</th>
<th>(\Delta S^o) cal deg(^{-1}) molecule(^{-1})</th>
<th>(\log_{10} K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-12.998</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>100</td>
<td>-12.840</td>
<td>0.441</td>
<td>28.542</td>
</tr>
<tr>
<td>200</td>
<td>-12.620</td>
<td>1.394</td>
<td>9.553</td>
</tr>
<tr>
<td>300</td>
<td>-12.493</td>
<td>1.493</td>
<td>9.496</td>
</tr>
<tr>
<td>500</td>
<td>-12.492</td>
<td>1.971</td>
<td>5.851</td>
</tr>
<tr>
<td>1000</td>
<td>-12.517</td>
<td>1.870</td>
<td>3.144</td>
</tr>
</tbody>
</table>

Equilibrium Constant

\(K = 0.672 \exp(-12,630/RT)(300-1000 \text{ K range})\).

This expression reproduces the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.1 percent.

Recommended Rate Constant

\(k = 1.5 \times 10^{-11} \exp(-1700/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

Temperature range: 190-500 K.

Suggested error limits: \pm 30 percent in this range.

\(\log_{10} A = 11.18 \pm 0.07 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\),

\(E = 1700 \pm 90 \text{ cal/s}\).

Discussion

Perner and Franken (1969) determined a value for this rate constant from the maximum in the growth and decay profile of the HS concentration after an energizing pulse. HS is formed by this reaction and had a second order decay in their system which was attributed to the reaction of two HS radicals. The HS absolute concentration had to be estimated indirectly from the yield of H\(_2\) in pure H\(_2\)S assuming 85 percent of the HS was formed by this rather than alternate reactions.

Kurylo, et al. (1971) obtained most of their data using flash wavelengths >2000 \(\AA\). However, they did investigate the system with wavelengths <2000 \(\AA\) but found agreement only at low flash intensities where it appeared that competing reactions were unimportant.

Cupitt and Glass' (1970) analysis to derive values for both \(k_{O+H_2S}\) and \(k_{H_2+HS}\) has been commented upon.

Reported rate constants

<table>
<thead>
<tr>
<th>Rate constant (k) (cm(^3) molecule(^{-1}) s(^{-1}))</th>
<th>(k_{O+H_2S})</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3 \times 10^{-12}</td>
<td>298</td>
<td></td>
<td>Pulsed radiolysis study of H(_2)S mixtures at total pressures (\sim 0.5-1) atm. A large excess of xenon added to thermalize H atoms. [HS] monitored in absorption. Extent of dissociation &lt;10(^{-1}) percent. Perner and Franken 1969.</td>
<td></td>
</tr>
<tr>
<td>1.7 \times 10^{-11} \exp(-1650/RT)</td>
<td>0.0 \times 10^{-11}</td>
<td>243-368</td>
<td>Flow system, 1-20 torr pressure. H formed by microwave discharge in H(_2)/Ar, He, or Xe mixtures. H(_2)S added downstream in concentrations similar to [II]. [III], [IV], and [V] monitored by ESR. Mass spectral analysis of stable products. Mihelcic and Schindler 1970.</td>
<td>Values derived from H decay and HS growth in agreement.</td>
</tr>
<tr>
<td>1.53 \times 10^{-12}</td>
<td>295</td>
<td></td>
<td>Low pressure flow system, O atoms produced by microwave discharge in 5 percent O(_2)/He mixtures. Small addition of H(_2)S downstream. ESR detection of O, H, and SO. Concentration profiles followed with reaction time. Cupitt and Glass 1970.</td>
<td>Experimental and computed profiles matched by adjusting the reaction rates for a 7 stage mechanism. Best agreement for [O]+[H(_2)S] case. An error found in the original analysis leads to a lower value than initially published.</td>
</tr>
</tbody>
</table>
## KINETIC RATE CONSTANTS

Reported rate constants—Continued

<table>
<thead>
<tr>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$k_{298}$</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.3 \times 10^{-11}$ exp ($-1709/RT$)</td>
<td>$7.2 \times 10^{-12}$</td>
<td>190–464</td>
<td>Flash photolysis with wavelengths $&gt;2000$ Å of 40–125 millitorr H$_2$S in $\sim 50$ torr He. [H] followed by Lyman $\alpha$ resonance fluorescence at 1216 Å. Kurylo, Peterson, and Braun 1971.</td>
<td></td>
</tr>
<tr>
<td>$k_{H+H_2S}$</td>
<td>166</td>
<td>323</td>
<td>Photolysis of 9.5 torr H$_2$S/889 torr CO$_2$/0.2 torr I$_2$ and 0.9 torr H$_2$S/600 torr CO$_2$/1.0 torr Br$_2$ mixtures with $&gt;2000$ Å (mainly 2537 Å). Quantum yields of H$_2$ used as a measure of the reaction in presence and absence of halogen. Darwent, Wadlinger, and Allard 1967.</td>
<td>Gives values for $k_{H+H_2S} \sim (1.8-5.2) \times 10^{-12}$.</td>
</tr>
<tr>
<td>$k_{H+Br_2}$</td>
<td>11.7</td>
<td>323</td>
<td>2490 Å photolysis of about 12 torr H$_2$S/1-60 torr C$_2$H$_4$ diluted to about 1 atm with CO$_2$ to thermalize H atoms. Decomposition $\leq$ 1 percent. Rate of production of H$_2$ measured. Woolley and Cvetanovic 1969.</td>
<td>Gives a value $k_{H+Br_2} \sim 1 \times 10^{-11}$.</td>
</tr>
<tr>
<td>$k_{H+C_2H_4}$</td>
<td>0.828</td>
<td>296.5</td>
<td>Mercury arc photolysis of H$_2$S/O$_2$/CO$_2$ mixtures. Quantum yield of H$_2$ formation measured. H assumed to disappear via H + H$_2$S and H + O$_2$ + M reactions. Conversion kept to $\leq$ 1 percent. Wadlinger and Darwent 1967.</td>
<td>Taking $E_{H+O_2+M} = -1000$ Baulch, et al. (1969) gives $E_{H+H_2S} = 1700$ cal mol$^{-1}$.</td>
</tr>
</tbody>
</table>

$E_{H+H_2S} - E_{H+O_2+M} = 2700$ cal

![Figure 18. Experimental values of $k_{H+H_2S \rightarrow H_2+HS}$.](image)

**Figure 18.** Experimental values of $k_{H+H_2S \rightarrow H_2+HS}$.

already in the evaluation of the $k_{O+H_2S}$ data. The remarks made there apply equally well to their value quoted here. Their values for $k_{H+H_2S}$ and $k_{O+H_2S}$ appear too high and too low, respectively. Allowance has been made for an arithmetic error found in the original analysis which resulted in too high SO concentrations.

Earlier photochemical studies of D$_2$S by Darwent and Roberts (1953) were complicated by "hot" D atom effects and do not provide reliable data. Later work utilized mixtures diluted with excess CO$_2$ to thermalize the H atoms.

Woolley and Cvetanovic (1969) measured the ratio $k_{H+H_2S}/k_{H+CH_4} = 0.828$ at 296.5 K. The value for $k_{H+CH_4}$ has not been evaluated yet but is known to be a function of pressure. At this temperature the mean of five references [Braun and Lenzi, 1967; Dodonov, et al., 1969; Barker and Michael, 1969; Eyre, et al., 1970; Kurylo, et al., 1970] which report a value for its high pressure limit is $1.2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. This gives $k_{H+H_2S} \sim 1 \times 10^{-12}$ in agreement with the recommended value, figure 18. Similarly Darwent, et al. (1967) obtained values relative to $k_{H+I_2}$ and $k_{H+Br_2}$ at 323 K. Taking the latter two as $3 \times 10^{-10}$
Values for $k_H + H_2 S$ of 1.8 and $5.2 \times 10^{-12}$, respectively, a little on the high side. Both the latter studies assume that no hydrogen results from reactions other than that of $H+H_2 S$.

Wadlinger and Darwent (1967) derived an estimate for the activation energy which is in remarkably good agreement with that recommended here.

At present, the data of Mihelcic and Schindler (1970) and Kurylo, Peterson, and Braun (1971) seem least questionable. A mean value based on their measurements is recommended.

References


Equilibrium Constant

$$K_s=0.182 \ T^{-1.00} \ \exp (90,700/RT) \ \text{atm}^{-1}$$

(300–1000 K range),

$$=9.88 \times 10^{-4} \ T^{-0.40} \ \exp (93,150/RT)$$

(1000–3000 K range).

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.5 percent (300–1000 K) and 0.8 percent (1000–3000 K).

Recommended Rate Constant

Reliable rate constants for this, and the reverse dissociation reaction, appear to be unreported in the literature.

Discussion

Reliable rate constants for this reaction and its reverse appear unreported in the literature. Gas phase studies of $H_2 S$, until recently, mainly have been photochemical in nature. Owing to the difficulties of interpreting such data because of complicating ‘hot’ $H$-atom effects [Darwent, et al., 1967; Gann and Dubrin, 1967; Sturman and White, 1969; Compton, et al., 1969, 1970] information, particularly on the reactions of $H_2 S$ and HS has been slow in emerging and still requires more extensive investigations.

Darwent and Roberts (1953) studied the thermal dissociation of $H_2 S$ and measured the rate of hydrogen production at 760–975 K with initial $H_2 S$ pressures of 30–300 torr. They established that above 870 K the decomposition became homogeneous and was second order with respect to the $H_2 S$ concentration. The hydrogen production had an apparent activa-
tion energy of about 50 kcal mol\(^{-1}\). A scheme involving such reactions as

\[
\begin{align*}
H_2S + M & \rightarrow H + HS + M \quad \Delta H^\text{in} = +91.58 \text{ kcal mol}^{-1} \\
H + H_2S & \rightarrow H_2 + HS \\
HS + HS & \rightarrow H_2 + S_2 \\
S + HS & \rightarrow S_2 + H \\
\end{align*}
\]

probably is involved but cannot explain the low activation energy observed.

Levy and Merryman (1965) included the bimolecular dissociation reaction of \(H_2S\) in their kinetic scheme describing \(H_2S\)/O\(_2\) atm pressure flames. However, such flames propagate via fast atom and radical attack of \(H_2S\) such that it is impossible to study the thermal dissociation of \(H_2S\) in their system.

**References**


---

**KINETIC RATE CONSTANTS**

**4.22. \(HS + HS \rightarrow H_2S + S\)**

<table>
<thead>
<tr>
<th>(TK)</th>
<th>(\Delta H^o) kcal mol(^{-1})</th>
<th>(\Delta S^o) cal deg(^{-1}) mol(^{-1})</th>
<th>(\log_{10} K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-6.940</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>-7.027</td>
<td>-2.270</td>
<td>14.870</td>
</tr>
<tr>
<td>298</td>
<td>-7.400</td>
<td>-4.221</td>
<td>4.504</td>
</tr>
<tr>
<td>500</td>
<td>-7.404</td>
<td>-4.231</td>
<td>4.472</td>
</tr>
<tr>
<td>1000</td>
<td>-7.632</td>
<td>-4.871</td>
<td>2.679</td>
</tr>
</tbody>
</table>

**Equilibrium Constant**

\[K=0.478 T^{-4.239} \exp (7360/RT) \quad (300-1000 \text{ K range})\]

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.0 percent (300–1000 K) and 0.4 percent (1000–2500 K).

**Recommended Rate Constant**

There is a large uncertainty in the magnitude of the rate constant for this reaction. At room temperature a value is suggested of about \(1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) which is probably reliable to within a factor of 4.

A small or zero activation energy is probable. The rate and rate constant are defined by

\[
\text{d}[H_2S]/\text{dt} = -k[HS]^2 = -0.5 \text{ d}[HS]/\text{dt}.
\]

**Reported rate constants**

<table>
<thead>
<tr>
<th>Rate constant (k) (cm(^3) molecule(^{-1}) s(^{-1}))</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 \times 10^{-11}</td>
<td>298</td>
<td>Flash photolysis of 30 torr (H_2S) and 30 torr (H_2S/100-400) torr (CO_2) mixtures. [(\text{SH}), [(S]) followed in absorption. Strauss, Donovan, and De Sorgo 1968.</td>
<td>Stated to be reliable to within a factor of 3. (k) has been divided by 2 to correct for the rate constant definition.</td>
</tr>
<tr>
<td>2.7 \times 10^{-11}</td>
<td>298</td>
<td>Pulsed radiolysis study of (H_2S) in excess (Xe). [(\text{HS}) followed in absorption and products analysed for (H_4) formation. (\text{HS}) absolute concentrations had to be estimated approximately from the (H_3) yields. Perner and Franken 1969.</td>
<td>2nd order decay observed. (k) determined from the maximum (\text{HS}) concentration. (k) has determined by 2 to correct for the rate constant definition.</td>
</tr>
<tr>
<td>1.1 \times 10^{-11}</td>
<td>295</td>
<td>Flow system, (H) formed by microwave discharge of (H/Ar), (He), or (Xe) mixtures. (H_2S) added downstream in amounts comparable to ([\text{H}]); (H), (HS), and (S) concentrations monitored by ESR. Mass spectral analysis also of stable products. Mihelic and Schindler 1970.</td>
<td>2nd order decay observed. (k) determined from the (\text{HS}) peak concentration.</td>
</tr>
</tbody>
</table>
Discussion

The three measured rate constants vary by an order of magnitude at room temperature. Mihelcic and Schindler (1969) defined their rate according to

\[ -\frac{d[\text{HS}]}{dt} = 2k[\text{HS}]^2. \]

Strausz, et al. (1968), and Perner and Franken (1969) did not define their rate constants but it appears that their values are for 2k. Consequently, they have been halved in this tabulation.

The reaction is fast at room temperature and the activation energy is either very small or zero [Dzantiev and Shishkov, 1967; Darwent and Roberts, 1953].

Disagreement possibly stems from the difficulties of measuring HS concentrations absolutely. Strausz, et al. (1968) quote an extinction coefficient for the (1,0) band of HS used in their analysis. Perner and Franken (1969) calibrated the HS concentrations in a very approximate way by measuring the hydrogen formation in the case of pure H₂S. From this, by assuming 85 percent of the H₂ was formed from the H⁺H₂S→H₂+HS reaction, values were estimated for the diluted systems. Mihelcic and Schindler (1970) used an analysis similar to that of Westenberg (1965) for OH to calibrate the HS ESR signals. The latter may be the most reliable and is heavily weighted in the assessment of the recommended value.

The recombination of two HS radicals can occur via two exothermic reaction paths

(1) \[ \text{HS} + \text{HS} \rightarrow \text{H}_2 \text{S}_2 \]

(2) \[ \text{H} + \text{H}_2 \text{S}_2 \rightarrow \text{H}_2 + \text{S}_2 \]

The former of these is the predominant mechanism, probably owing to the four center nature of the other. All the studies above measured the sum \( k_1 + k_2 \). These have been taken as \( k \) values owing to the difference in magnitude between the two. Reaction (2) is discussed more fully next in this paper.

References


### KINETIC RATE CONSTANTS

#### Reported rate constants

<table>
<thead>
<tr>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;5 \times 10^{-14}$</td>
<td>295</td>
<td>Flow system, D atoms formed by microwave discharge of D$_2$/Ar, He, or Xe mixtures at about 2 torr. H$_2$S added downstream in amounts comparable to [D]. [D] monitored by ESR and stable products analysed by mass spectrometer. Mihelcic and Schindler 1970.</td>
<td>Small amounts of H$_2$ detected in the products appear to result from this reaction.</td>
</tr>
<tr>
<td></td>
<td>410–500</td>
<td>HS radicals formed from the reaction of CH$_4$ with H$_2$S.</td>
<td>No H$_2$ could be detected.</td>
</tr>
</tbody>
</table>

#### References


#### 4.24 H+HS$\rightarrow$H$_2$+S

Thermodynamic data

<table>
<thead>
<tr>
<th>TK</th>
<th>$\Delta H^\circ$ kcal mol$^{-1}$</th>
<th>$\Delta S^\circ$ cal deg$^{-1}$ mol$^{-1}$</th>
<th>$\log_{10} K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-19.938</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>-19.867</td>
<td>-1.829</td>
<td>43.022</td>
</tr>
<tr>
<td>298</td>
<td>-20.020</td>
<td>-2.827</td>
<td>14.057</td>
</tr>
<tr>
<td>300</td>
<td>-20.021</td>
<td>-2.828</td>
<td>13.968</td>
</tr>
<tr>
<td>500</td>
<td>-20.029</td>
<td>-2.855</td>
<td>8.130</td>
</tr>
<tr>
<td>1000</td>
<td>-20.149</td>
<td>-3.001</td>
<td>3.747</td>
</tr>
</tbody>
</table>

Equilibrium Constant

$$K = 0.318 \times 10^{-0.042} \exp \left( \frac{20,000}{RT} \right) \quad (300-1000 \text{ K range})$$

$$K = 1.67 \times 10^{-0.557} \exp \left( \frac{19,660}{RT} \right) \quad (1000-2500 \text{ K range})$$

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.4 percent (300–2500 K).

### Recommended Rate Constant

No recommendation is possible at present but the reaction does appear to be fast at room temperature. It is much faster than theoretically predicted.

### Discussion

Recently, Cupitt and Glass (1971) have studied the H/H$_2$/O$_2$ system in a flow tube. Under the conditions of excess O$_2$ and [H] > [H$_2$S] it was found that the measurements could be described by the four reactions

$$\begin{align*}
\text{H} + \text{H}_2\text{S} & \rightarrow \text{H}_2 + \text{HS}, \\
\text{H} + \text{HS} & \rightarrow \text{H}_2 + \text{S}, \\
\text{S} + \text{O}_2 & \rightarrow \text{SO} + \text{O}, \\
\text{HS} + \text{O} & \rightarrow \text{H} + \text{SO}.
\end{align*}$$

By applying the steady state approximation for HS this gives the expression

$$k_1[H] [H_2S] = [HS](k_{4}+k_{3}[O]).$$

It was possible to determine $k_4/k_3$ from this by using their measured value of $k_4/k_3=6.5$. [H$_2$S] was not monitored directly but based on [H]S, = [SO] measurements since at these high O$_2$ concentrations H$_2$S appeared to be quantitatively converted into SO. Their assumptions are reasonably well substantiated and the values they also report for $k_{4+3H}$ and $k_{4+3O}$ are within a factor of two of those currently recommended.

A very preliminary value for $k_{4+3H}$ is derived from flash photolysis studies of H$_2$S [Oldershaw, 1972] confirms Cupitt and Glass’ measurements.

It appears that the theoretical calculation of Mayer and Schieder (1968) which at room temperature predicts a value of $3 \times 10^{-13}$ is in error.

### References


### 4.24 Reported rate constants

<table>
<thead>
<tr>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$7.7 \times 10^{-11} T^{0.26} \exp (-2800/RT)$</td>
<td>298–2500</td>
<td>Theoretical computation based on a modified Johnston-Parr method. Mayer and Schieler 1968.</td>
<td>$k_{298} = 3.2 \times 10^{-13}$</td>
</tr>
<tr>
<td>$3.1 \times 10^{-11}$</td>
<td>295</td>
<td>5 percent H$_2$/Ar mixture discharged, O$_2$ added after the discharge followed by H$_2$S addition further downstream at a total pressure ≤ 1.7 torr. [H]$&gt;[H_2S]$ with O$_2$ in excess. [H], [HS], [S], [O], and [SO] monitored by ESR. Cupitt and Glass 1971.</td>
<td></td>
</tr>
</tbody>
</table>

### 4.25. S + HS $\rightarrow$ S$_2$ + H

**Thermodynamic data**

<table>
<thead>
<tr>
<th>TK</th>
<th>$\Delta H^\circ$ kcal mol$^{-1}$</th>
<th>$\Delta S^\circ$ cal deg$^{-1}$ mol$^{-1}$</th>
<th>log$_{10}K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-18.155</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>-18.152</td>
<td>-3.917</td>
<td>38.818</td>
</tr>
<tr>
<td>298</td>
<td>-18.340</td>
<td>-4.913</td>
<td>12.371</td>
</tr>
<tr>
<td>300</td>
<td>-18.341</td>
<td>-4.917</td>
<td>12.287</td>
</tr>
<tr>
<td>500</td>
<td>-18.352</td>
<td>-4.970</td>
<td>6.936</td>
</tr>
<tr>
<td>1000</td>
<td>-17.957</td>
<td>-4.438</td>
<td>2.955</td>
</tr>
</tbody>
</table>

**Equilibrium Constant**

$$K = 1.50 \times 10^{-2} T^{0.36} \exp (18,550/RT)$$  
(300–1000 K range),  
$$= 2.04 \times 10^{-2} T^{0.35} \exp (18,300/RT)$$  
(1000–2500 K range).

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.9 percent (300–1000 K) and 0.4 percent (1000–2500 K).

### Recommended Rate Constant

The reaction most probably is fast at room temperature but has been insufficiently studied and no recommendation is yet possible.

### Discussion

The reaction is sufficiently energetic and spin allowed to leave the S$_2$ in the ($^1\Delta_g$) electronic state (about 14.6 kcal mol$^{-1}$ above the ground state) but little is known yet of its dynamics. The value of Mihelcic and Schindler (1970) is dependent on $k_{HS+HS}$ which is still quite uncertain. The two estimates differ by a factor of about seven at room temperature.

### References


### Reported rate constants

<table>
<thead>
<tr>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Exp. temp. (K)</th>
<th>Method &amp; reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4.5 \times 10^{-11}$</td>
<td>295</td>
<td>Flow system, H formed by a microwave discharge in H$_2$/Ar, He, or Xe mixtures at about 2 torr. H$_2$S added downstream in amounts comparable to H. [H], [HS], [S] monitored by ESR. Mass spectral analysis of stable products. Mihelcic and Schindler 1970.</td>
<td>Value obtained from the peak S concentration. Equate rates of the reactions H$_2$ + HS = H$_2$S + S, S + HS = S$<em>2$ + H, and use $k</em>{HS+HS} = 1.1 \times 10^{-11}$ (295 K).</td>
</tr>
<tr>
<td>$6.85 \times 10^{-11} T^{0.26} \exp (-900/RT)$</td>
<td>298–2500</td>
<td>Theoretical computation based on a modified Johnston-Parr method. Mayer and Schieler 1968.</td>
<td>$k_{298} = 6.7 \times 10^{-11}$.</td>
</tr>
</tbody>
</table>
These are reactions for which only limited information, if any, is yet available.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^\circ_{298}$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>O + H$_2$ + M $\rightarrow$ H$_2$O + M</td>
<td>-117.3</td>
<td>This reaction is spin forbidden and not observed experimentally. The third body is not capable of spin-flipping the activated complex. The reaction appears unlikely since it involves the formation of 2 O–H bonds with an H–H bond breakage.</td>
</tr>
<tr>
<td>O(D) + H$_2$ + M $\rightarrow$ H$_2$O + M</td>
<td>-162.7</td>
<td>Is an allowed reaction [De More, 1967] but necessarily competes with O(D) + H$_2$ $\rightarrow$ OH + H which is known to proceed at near collision frequency [Schofield, 1972].</td>
</tr>
<tr>
<td>N + NO + M $\rightarrow$ N$_2$O + M</td>
<td>-114.9</td>
<td>$k_{H_2} &lt; 10^{-22}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ [Harteck and Donnes, 1957]. Harteck [1957; Harteck and Donnes, 1957] studied the NO decomposition at 543 K resulting from the energy released on fission of $^{235}$UO$_2$ in a quartz vessel initially filled with 500 torr of gas at 294 K. During the initial stages of radiation when this reaction could be observed, if it were occurring, no N$_2$O was detectable. The quoted $k$ was derived from this negative result. Both N(S) and N(D) will be produced in the experiment. Verbeke and Winkler (1960) found no N$_2$O on interacting NO at temperatures up to 673 K with ‘active’ nitrogen produced by an electric discharge. These reactions will always be overshadowed by the extremely rapid corresponding bimolecular interactions between N and NO.</td>
</tr>
<tr>
<td>N(D) + NO + M $\rightarrow$ N$_2$O + M</td>
<td>-169.9</td>
<td>SO$_2$ is a symmetrical, planar molecule. Consequently, this reaction would involve formation of two S–O linkages with a breaking of the O–O bond. The reaction seems unlikely and is equivalent to the reactions</td>
</tr>
<tr>
<td>SO + O$_2$ + M $\rightarrow$ SO$_2$ + M</td>
<td>-96.23</td>
<td>$k = (2.5 \pm 0.3) \times 10^{-12}$ cm$^3$ molecule$^{-2}$ s$^{-1}$ and $k = (200 \pm 400)$ cm$^3$ molecule$^{-2}$ s$^{-1}$ [Harteck and Donnes, 1957]. SO$_2$ and SO were studied in detail, and the rate constant is reliable in this low temperature range to within a factor of 2 to 3. 1–3 percent SO$_2$/Ar mixtures were subjected to RF discharge. O$_3$ added in excess of the SO in the region where O atoms had decayed. Total pressures 0.3–3 torr in the flow system. [SO] measured by titration with NO$_2$ and the reaction was followed by monitoring the SO$_2$ chemiluminescence which is proportional to [SO]. Rates of production of electronically excited states of SO$_2$ were also derived.</td>
</tr>
<tr>
<td>SO + O$_2$ $\rightarrow$ SO$_2$ + O$_2$</td>
<td>-106.7</td>
<td>Halstead and Thrush (1965, 1966) have studied this reaction in detail, and the rate constant is reliable in this low temperature range to within a factor of 2 to 3. 1–5 percent SO$_2$/Ar mixtures were subjected to RF discharge. O$_3$ added in excess of the SO in the region where O atoms had decayed. Total pressures 0.3–3 torr in the flow system. [SO] measured by titration with NO$_2$ and the reaction was followed by monitoring the SO$_2$ chemiluminescence which is proportional to [SO]. Rates of production of electronically excited states of SO$_2$ were also derived.</td>
</tr>
</tbody>
</table>
| O + SO$_2$ $\rightarrow$ SO$_2$ + O$_2$ | -35.92 | Kaufman (1968), studying the effect at room temperature of added SO$_2$ on the air afterglow, reported that the activation energy must be equal to or greater than 7 kcal mol$^{-1}$. More recently Merryman and Levy (1971) have measured [SO$_2$] and [O] concentration profiles in OCS/O$_2$/N$_2$ premixed flames at pressures of 75 and 245 torr. The flames were sampled with a quartz microprobe. [SO$_2$] was determined by wet chemical analysis and [O] by the addition of excess NO$_2$ to the sample followed by mass spectral analysis. Based on the assumption that the predominant formation/loss mechanisms in these flames are the O + SO$_2$ + M and O + SO$_2$ reactions and taking a value of $k_{O + SO_2 + M} = 6.6 \times 10^{-12}$ cm$^3$ molecule$^{-2}$ s$^{-1}$ (200 fold larger at 1500 K than the value currently recommended in this report for M = O$_2$, N$_2$) they measure:

$k_{O + SO_2} = 4.6 \times 10^{-13}$ cm$^3$ molecule$^{-2}$ s$^{-1}$ (1480–1550 K).

Owing to the complexity of the system studied, the narrow temperature range and the uncertainty of $k_{O + SO_2 + M}$ this can only be very tentatively accepted until confirmed. |
These are reactions for which only limited information, if any, is yet available—Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H^{\circ}_{298 \text{ K}} )</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO + OH = SO₂ + H</td>
<td>-29.92</td>
<td>This reaction has been studied in a flow system at room temperature [Fair and Thrush, 1969]. H₂Ar mixtures were discharged and O₂ and H₂S added. H atoms were in excess. NO₂ added further downstream to form OH. Measured from the decays of O and SO which were monitored by the air and SO₃ afterglows. Obtained ( k_{\text{SO} + \text{OH}}/k_{\text{SO} + \text{OH}} = 0.4 ) (298K). Using ( k_{\text{SO} + \text{OH}} = 2.1 \times 10^{-11} ) [Baulch, et al., 1969] this gives ( k_{\text{SO} + \text{OH}} = 5.4 \times 10^{-11} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1} ) with an uncertainty of at least a factor of 2.</td>
</tr>
<tr>
<td>S + OH = SO₂ + H</td>
<td>-22.37</td>
<td>No information yet available.</td>
</tr>
<tr>
<td>S₂ + O = SO₂ + S</td>
<td>-22.08</td>
<td>An approximate value has been obtained by Homann, et al. (1968) using a heated flow tube at a total pressure of a few torr. S₂/Ar vapor was reacted with atomic O (from N/NO titration) the SO being monitored by a TOF mass spectrometer. ( k \sim 7 \times 10^{-12} ) at 1050 K.</td>
</tr>
<tr>
<td>O + CS₂ = OCS + S</td>
<td>-53.94</td>
<td>Homann, et al. (1968) used a heated flow tube at 3-6 torr pressure to study the O + CS₂ reactions. These were monitored with a TOF mass spectrometer. In addition to the main O + CS₂ → CS + SO reaction (q.v.) they report finding a contribution from this reaction at higher temperatures and give ( k_{\text{CS}_2 + \text{O}} \sim 2 \times 10^{-11} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1} ). Hancock and Smith (1971) found in the room temperature flash photolysis of CS₂/NO₂, ( \lambda &gt; 3000 \text{ Å} ), that the reaction of O + CS₂ → CS + SO was dominant. No SO absorption could be detected and it was concluded that the alternate reaction path being discussed here must be at least two orders of magnitude slower, i.e. ( &lt; 4 \times 10^{-14} ) at room temperature.</td>
</tr>
<tr>
<td>CS + O₂ = CO + SO</td>
<td>-94.78*</td>
<td>This reaction is a four center interaction and consequently is not expected to be fast. Previous studies tend to confirm this. Kondratiev and Magaziner (1940), monitoring CS spectroscopically, reported that at 20-100°C practically no reaction between CS and O₂ occurred. Flash photolysis studies of CS₂/O₂ mixtures by Wright (1960), Callear (1963), and DeSorgo, et al. (1965) further support this. Wright found that at about 1 ms after the flash the rate of removal of CS was constant within a factor of 2 over a 25 fold range of O₂ pressure. Callear (1963) noted that in the presence of 50 torr O₂ that CS survived for 1 s with no significant change. DeSorgo, et al. (1965) found no effect even with 90 torr O₂/22 torr CS₂/280 torr N₂ mixtures. McGarvey and McGrath (1964) flash photolyzed CS₂/inert gas mixtures. In the presence of O₂, CS absorption was weak and disappeared rapidly. However, in their case the CS₂ concentration was low and the [CS] decay probably occurred via the reactions ( \text{CS} + h_v \rightarrow \text{CS} + \text{S}, \text{S} + \text{O}_2 \rightarrow \text{CS} + \text{O} + \text{O}<em>2 \rightarrow \text{CO} + \text{S} ). Flash photolysis of higher concentrations of CS₂ in O₂ incompletely dissociates the CS₂ which then removes the flash generated O atoms. Thereafter the CS concentration remains essentially steady for long periods. Callear and Dickson (1972) estimate ( k \sim 3 \times 10^{-14} ) and it could be considerably less. Recent interpretation by Heicklen, et al. (1969) and Wood and Heicklen (1971) of their photolysis data includes this reaction. 2-70 torr CS₂/1-745 torr O₂ were photolyzed at 3130A in a 200 cm³ quartz vessel at room temperature and the products analyzed gas chromatographically. Quantum yields were low and exposure times 10-500 min. Relative quantum yields of OCS and CO were considered formed from this and the alternative reaction path. They give ( k</em>{\text{CS} + \text{O}<em>2 \rightarrow \text{OCS} + \text{O}} : k</em>{\text{CS} + \text{O}<em>2 \rightarrow \text{CO} + \text{S}} = 1.2 ), at room temperature. An additional study of the explosive limits of 0.0025-0.5 CS₂/O₂ mixtures at pressures of about 10-400 torr [Wood and Heicklen, 1971b] showed that the data could be reproduced by computer fit to an eight reaction kinetic scheme in which rate constant ratios were adjusted to give a best fit to the experimental data. Values for ( k</em>{\text{CS} + \text{O}<em>2 \rightarrow \text{OCS} + \text{O}} : k</em>{\text{CS} + \text{O}_2 \rightarrow \text{CO} + \text{S}} ) were taken as 1.05 (341 K) and 1.04 (415 K). However, there were several supporting studies which contradict this interpretation these values all must be regarded with a certain skepticism until additional information is obtained.</td>
</tr>
</tbody>
</table>

See footnote at end of table.
### KINETIC RATE CONSTANTS

These are reactions for which only limited information, if any, is yet available—Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH_{298}^\circ</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS + O → OCS + O</td>
<td>-43.52</td>
<td>This reaction corresponds closely to CO + O → CO₂ + O which is known to have a large activation energy of about 50 kcal mol⁻¹. Available information, discussed above under the alternate reaction path, CS + O → CO + SO, tends to confirm this although it is still somewhat controversial in the light of the recent interpretation by Heicklen, et al. (1969) and Wood and Heicklen (1971).</td>
</tr>
<tr>
<td>O + CS → CO + S</td>
<td>-89.30</td>
<td>At 3-6 torr pressure in a heated flow tube [Hommert, et al., 1968], O₂/Ar subjected to a microwave discharge (or O atoms from N₂/NO titration). Mixed with 0.03 percent CS₂/Ar so that O atoms in excess. Sampled with TOF mass spectrometer. At 900 K, k is at least 5 times greater than kₕ₀+CS (q.v.) giving $k_{ₕ₀+CS} \geq 5 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Similarly, Westenberg, and De Haas (1969) established a value of 2 for the O₂CS₂ stoichiometry at 227-338 K. 0.03 percent O₂/He mixtures were discharged at about 2 torr and CS₂ added downstream in amounts 5-10 times [O]. The latter was monitored by ESR and the stable products mass analyzed. The value of two suggests a mechanism based on the reaction O + CS₂ → CS + SO being followed by the faster O + CS → CO + S. More recently Hancock and Smith (1971) have monitored in a flow system the intensity of IR chemiluminescence identified with this reaction and measured the decrease in intensity caused by the presence of NO₂. The reactants are extensively diluted with argon. Typical experimental conditions were [O₂], [CS₂]~0.2 millimolar, [NO₂] 0.1-0.9 millimolar, total pressure 2.9 torr. An approximate value of $k_{ₕ₀+CS}/k_{ₕ₀+NO₂} = 2.3$ was estimated and leads to $k_{ₕ₀+CS} \approx 1.4 \times 10^{-11}$ (298 K). Callear and Dickson also have obtained a value ~10⁻¹¹ by monitoring the decay of CS in flash photolysis experiments with CS₂/O₂ mixtures. These estimates all support a high value for $k_{ₕ₀+CS}$ in the 200-900 K range. For this reason it seems unlikely that its activation energy will exceed 1 kcal mol⁻¹. A large fraction of the available chemical exothermicity appears as vibrational energy in the CO. Hancock, Morley, and Smith (1971) and Hancock, Ridley, and Smith (1972) recently have measured the relative rates at which the vibrationally excited CO is formed in specific vibrational levels. The maximum rate is that populating the $v=13$ state which is close to the highest energetically accessible.</td>
</tr>
<tr>
<td>S + OCS → CO + S₂</td>
<td>-29.18</td>
<td>Gunning and Strauss (1966) state that at room temperature $k_{S + OCS} &lt; 0.04 k_{S + CH₄}$. Since the latter has a value in the range (0.5-1.5) x 10⁻¹² (300 K) [Donovan, et al., 1970; Connor, et al., 1971; Davis, et al., 1972] this gives a value $k_{S + OCS} \leq (2-6) \times 10^{-14}$ (300 K). At 2570 K, from a shock tube-mass spectrometric study of the thermal decomposition of OCS in Ar, Hay and Belford (1967) assess its value at approximately $1 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. Based on these two estimates a very approximate expression for the upper limit value is tentatively $k_{S + OCS} = 1.5 \times 10^{-13}$ exp (−2500/RT).</td>
</tr>
<tr>
<td>OH + H₂S → H₂O + HS</td>
<td>-27.75</td>
<td>The rate for this is not known [Fair and Thrush, 1969; Lunt, et al., 1966].</td>
</tr>
<tr>
<td>HS + O₂ → OH + SO</td>
<td>-23.53</td>
<td>Four center interaction, not expected to be fast. Cupitt and Glass (1971) have observed HS co-existing with large O₂ concentrations in a flow system at room temperature.</td>
</tr>
<tr>
<td>HS + OH → SO + H₂</td>
<td>-42.39</td>
<td>Four center interaction, not expected to be fast.</td>
</tr>
<tr>
<td>HS + OH → H₂O + S</td>
<td>-35.15</td>
<td>No information yet available [Fair and Thrush, 1969].</td>
</tr>
</tbody>
</table>

See footnote at end of table.

---

*See footnote at end of table.*
These are reactions for which only limited information, if any, is yet available—Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^\circ_{298}$ K</th>
<th>Comments</th>
</tr>
</thead>
</table>
| HS + O → H + SO            | -40.42                   | Appears to be more important than the alternative reaction which gives OH + S as products [Fair and Thrush, 1969; Liuti et al., 1966]. Cupitt and Glass (1971) have obtained $k_{HS+O}/k_{HS} = 6.5 \pm 0.7$ at 295 K from a flow system at $< 1 \text{torr}$ total pressure. 5 percent H$_2$/Ar was discharged and O$_2$ added after the discharge with H$_2$S addition further downstream. [O], [H], [SO], [HS], and [S] were monitored by ESR. For $[H]/[H_2S]$ and an excess of O$_2$ the system could be described by the reactions  
\begin{align*}
H + HS & \rightarrow H_2 + HS, \\
H + HS & \rightarrow H_2 + S, \\
S + O_2 & \rightarrow SO + O, \\
HS + O & \rightarrow H + SO,
\end{align*}
which give $k_1/k_2 = [H]/[O]$ for steady state concentrations of O and S. $k_3/k_1$ was also measured as 37.8 ± 7. Based on a value of $k_{HS+O} = 8.3 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (295 K). From a theoretical computation based on a modified Johnston-Parr method, Mayer and Schieler (1968) give $k = 3.8 \times 10^{-12} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ exp $(-1900/RT)$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The value at 295 K is $6.7 \times 10^{-12}$. |
| HS + O → OH + S            | -18.05                   | *These values are based on $\Delta H^\circ_{298}$ (CS) = 70.0 kcal mol$^{-1}$ [Hildenbrand, Chem Phys. Letters 15, 379(1972)] rather than the JANAF value of 55.0 which is now recognized as being too low. |

References

Callear, A. B., and D. R. Dickson, to be published (1972).
Hancock, G., B. A. Ridley, and I. W. M. Smith, to be published (1972).

5. Rate Constants—A Summary

Detailed rate constant evaluations

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( h ) (cm^3 molecule s units)</th>
<th>( T ) K</th>
<th>Comments</th>
<th>Suggested error limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O + H + Ar \rightarrow OH + Ar )</td>
<td>(~2 \times 10^{-16})</td>
<td>1000-3000</td>
<td>Limited data</td>
<td>Factor of 10?</td>
</tr>
<tr>
<td>( CO + Ar \rightarrow C + O + Ar )</td>
<td>( \leq 5 \times 10^{-16})</td>
<td>800</td>
<td>One measurement</td>
<td>( \pm 50% )</td>
</tr>
<tr>
<td>( CO + Ar \rightarrow C + O + Ar )</td>
<td>(~1.46 \times 10^{-23} \text{ exp} (-285,760/RT))</td>
<td>7000-15,000</td>
<td>Overall rate</td>
<td>( \pm 75% ) (&lt;10,000 K), ( \pm 50% ) (&gt;10,000 K), ( \pm 25% )</td>
</tr>
<tr>
<td>( N_2O + Ar \rightarrow N_2 + O + Ar )</td>
<td>(~7.8 \times 10^{-11} \text{ exp} (-58,000/RT))</td>
<td>1500-2500</td>
<td>Very approximate</td>
<td>Factor of 2.</td>
</tr>
<tr>
<td>( N_2O + Ne \rightarrow N_2 + O + Ne )</td>
<td>(~4.2 \times 10^{-11} \text{ exp} (-43,600/RT))</td>
<td>1500-2600</td>
<td>1st order</td>
<td>Factor of 2-3.</td>
</tr>
<tr>
<td>( N_2O + Kr \rightarrow N_2 + O + Kr )</td>
<td>(~1.2 \times 10^{-11} \text{ exp} (-40,700/RT))</td>
<td>1750-2800</td>
<td>Limited data</td>
<td>( \pm 50% )</td>
</tr>
<tr>
<td>( N_2O + O_2 \rightarrow N_2 + O_2 )</td>
<td>(~4.7 \times 10^{-14} \text{ exp} (-59,400/RT))</td>
<td>850-1050</td>
<td>One measurement</td>
<td>Factor of 2.</td>
</tr>
<tr>
<td>( N_2O + N_2O \rightarrow N_2 + O_2 + N_2 )</td>
<td>(~k = 1.4 \times 10^{10} \text{ exp} (-59,500/RT))</td>
<td>800-2100</td>
<td>One set of data</td>
<td>Factor of 2.</td>
</tr>
<tr>
<td>( O + N_2 + N_2O \rightarrow N_2O + N_2 )</td>
<td>(~\leq 5 \times 10^{-14})</td>
<td>300-588</td>
<td>Very approximate</td>
<td>Factor of 2.</td>
</tr>
<tr>
<td>( O_2 + N_2 \rightarrow O_2 + N_2 )</td>
<td>(~\leq 5 \times 10^{-14})</td>
<td>300-588</td>
<td>Limited data</td>
<td>Factor of 2.</td>
</tr>
<tr>
<td>( N_2O + N_2 \rightarrow NO + NO + N_2 )</td>
<td>(~3.3 \times 10^{-15} \text{ exp} (-11,000/RT))</td>
<td>250-350</td>
<td>Very approximate</td>
<td>Factor of 2.</td>
</tr>
<tr>
<td>( N_2O + Ar \rightarrow N_2 + O + Ar )</td>
<td>(~7.2 \times 10^{-15} \text{ exp} (-79,500/RT))</td>
<td>1800-3200</td>
<td>Factor of 10?</td>
<td>Factor of 2.</td>
</tr>
<tr>
<td>( N_2O + H + NH_2 \rightarrow NH_3 + NH_3 )</td>
<td>(~3 \times 10^{-9})</td>
<td>298</td>
<td>Very approximate</td>
<td>Factor of 2.</td>
</tr>
<tr>
<td>( SO + O + Ar \rightarrow SO_2 + Ar )</td>
<td>(8.5 \times 10^{-21})</td>
<td>300</td>
<td>Factor of 2. Childs</td>
<td>Factor of 2.</td>
</tr>
<tr>
<td>( SO_2 + Ar \rightarrow SO + O + Ar )</td>
<td>(~4.2 \times 10^{-15} \text{ exp} (-110,000/RT))</td>
<td>4500-7500</td>
<td>One measurement</td>
<td>Factor of 2.</td>
</tr>
<tr>
<td>( SO + O_2 \rightarrow SO + O )</td>
<td>(~3.0 \times 10^{-15} \text{ exp} (-5600/RT))</td>
<td>4000-2500</td>
<td>One set of data</td>
<td>Factor of 2.</td>
</tr>
<tr>
<td>( SO_2 + O + Ar \rightarrow SO_2 + Ar )</td>
<td>(~1 \times 10^{-18} \text{ exp} (+1000/RT))</td>
<td>220-1000</td>
<td>Factor of 2.</td>
<td>Factor of 2 (300 K), larger at other temperatures.</td>
</tr>
<tr>
<td>( SO_2 + M \rightarrow SO_2 + O + M )</td>
<td>()</td>
<td>()</td>
<td>Data too speculative</td>
<td>Not known.</td>
</tr>
<tr>
<td>( SO + O_2 \rightarrow SO_2 + S )</td>
<td>(~\leq 3 \times 10^{-15})</td>
<td>300</td>
<td>Upper limit estimates only</td>
<td>(\pm 30%).</td>
</tr>
<tr>
<td>( S + O_2 \rightarrow SO + O )</td>
<td>(~\leq 2 \times 10^{-13})</td>
<td>1000</td>
<td>()</td>
<td>()</td>
</tr>
<tr>
<td>( \Pi + SO_2 + M \rightarrow \Pi SO_2 + M )</td>
<td>(~2.2 \times 10^{-12} \text{ exp} (-0/RT))</td>
<td>250-450</td>
<td>()</td>
<td>()</td>
</tr>
<tr>
<td>( O + CS_2 \rightarrow CS + SO )</td>
<td>(~2.0 \times 10^{-11} \text{ exp} (-1030/RT))</td>
<td>200-1000</td>
<td>()</td>
<td>()</td>
</tr>
<tr>
<td>( O + OCS \rightarrow CO + SO )</td>
<td>(~6.8 \times 10^{-11} \text{ exp} (-5080/RT))</td>
<td>270-1500</td>
<td>()</td>
<td>()</td>
</tr>
<tr>
<td>( O + H_2S \rightarrow OH + HS )</td>
<td>(~6.3 \times 10^{-12} \text{ exp} (-1830/RT))</td>
<td>200-350</td>
<td>()</td>
<td>()</td>
</tr>
<tr>
<td>( H + H_2S \rightarrow H + HS )</td>
<td>(~1.6 \times 10^{-11} \text{ exp} (-1750/RT))</td>
<td>190-500</td>
<td>()</td>
<td>()</td>
</tr>
<tr>
<td>( H + HS \rightarrow H_2 + HS )</td>
<td>(~1.5 \times 10^{-11})</td>
<td>298</td>
<td>()</td>
<td>()</td>
</tr>
<tr>
<td>( HS + HS \rightarrow H_2 + S )</td>
<td>(~&lt;5 \times 10^{-14})</td>
<td>295</td>
<td>()</td>
<td>()</td>
</tr>
<tr>
<td>( HS + HS \rightarrow H_2 + S )</td>
<td>(~3 \times 10^{-11})</td>
<td>295</td>
<td>()</td>
<td>()</td>
</tr>
<tr>
<td>( S + HS \rightarrow S_2 + H )</td>
<td>(~4 \times 10^{-12})</td>
<td>295</td>
<td>()</td>
<td>()</td>
</tr>
</tbody>
</table>
Miscellaneous reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$ (cm$^3$ molecule$^{-1}$ s units)</th>
<th>$T$ K</th>
<th>Comments</th>
<th>Suggested error limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O + H_2 + M \rightarrow H_2O + M$</td>
<td>No data</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O(D) + H_2 + M \rightarrow H_2O + M$</td>
<td>Negative results</td>
<td>673</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N + NO + M \rightarrow N_2O + M$</td>
<td>No evidence of it</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N(2D) + NO + M \rightarrow N_2O + M$</td>
<td>No evidence of it</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$SO + O_2 \rightarrow SO_2 + M$</td>
<td>$2.5 \times 10^{-12}$ exp $(-2100/RT)$</td>
<td>223-303</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O + SO_2 \rightarrow SO_3 + M$</td>
<td>$5 \times 10^{-18}$ exp $(-12,000/RT)$</td>
<td>1480-1550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$SO + OH \rightarrow SO_2 + H$</td>
<td>$5 \times 10^{-11}$</td>
<td>298</td>
<td>One set of good data</td>
<td>Factor of 2-3.</td>
</tr>
<tr>
<td>$S + OH \rightarrow SO + H$</td>
<td>No data</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$CS + O_2 \rightarrow CO + SO$</td>
<td>$&lt;3 \times 10^{-11}$</td>
<td>298</td>
<td>Estimated value</td>
<td>Factor of 2?</td>
</tr>
<tr>
<td>$CS + O \rightarrow CS + O$</td>
<td>$&lt;3 \times 10^{-11}$</td>
<td>298</td>
<td>Estimated value</td>
<td>Factor of 2?</td>
</tr>
<tr>
<td>$S + O_3 \rightarrow SO_2 + S$</td>
<td>$7 \times 10^{-11}$</td>
<td>900</td>
<td>One value</td>
<td>Factor of 2?</td>
</tr>
<tr>
<td>$O + CS \rightarrow CO + S$</td>
<td>$1.5 \times 10^{-11}$ exp $(-2500/RT)$</td>
<td>300-2570</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$OH + H_2S \rightarrow H_2O + HS$</td>
<td>No data</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$HS + OH \rightarrow OH + S$</td>
<td>$2 \times 10^{-11}$</td>
<td>295</td>
<td>One value</td>
<td>Factor of 2?</td>
</tr>
<tr>
<td>$HS + O_3 \rightarrow OCS + S$</td>
<td>$3.5 \times 10^{-12}$ exp $(-1900/RT)$</td>
<td>298-2500</td>
<td>Theoretical estimate</td>
<td>Uncertain.</td>
</tr>
</tbody>
</table>

6. Acknowledgments

The author wishes to thank the members of the NSRDS program and in particular The Chemical Kinetics Information Center for their invaluable assistance in supplying extensive bibliographies. This project has been supported by the Office of Standard Reference Data, National Bureau of Standards, U.S. Department of Commerce under contract NBS-218-70.

Appendix

Current Sources of Evaluated Rate Constants, Useful Compilations, and Reviews

For it to be of any general use, a compilation of data has to be readily available, presented in simple, easily usable form, and be at least partially evaluated or annotated. Fortunately, in recent years, efforts have been made by various individuals and groups to start condensing the mass of available gas phase kinetic rate data and a variety of publications have appeared, reviewing the available rate constants particularly for the light gas molecule reactions. The last decade has been such a tremendously productive era in the field of gas phase kinetics and has seen emerge such a variety of evaluations and reviews that it may be opportune to present as comprehensive a list as possible for the general user, with annotations on their usefulness and general character. Five groups will be discussed in more detail, those concerning evaluated data, tabulations of non-evaluated data, specialized reviews emphasizing either particular types of reactions or techniques, and certain miscellaneous reviews. The references are alphabetized by author at the end of this section for convenience.

Evaluated Data

Article by Schofield (1967) for which a reference addendum is available on request. (110 reactions of $H_2$, $O_2$, $N_2$, $N$, $O$, $OH$, $HO_2$, $O_3$, oxides of nitrogen, and hydrocarbons.)

Leeds University Reports Nos. 1-5 by Baulch, et al. (1968-70), now being published by Butterworth. (47 reactions of hydrogen/oxygen, carbon and nitrogen oxides.)

NSRDS-NBS 20 by Johnston (1968). (6 reactions of $O_2$, $O_3$, and $O_4$.)

NBS Technical Note 484 by Bortner (1969). (7 reactions of high temperature air, $O_3$, $N_2$, $N$, $O$, $NO$, $O_3$.)

Article by Herron (1969). (The reactions $O + CH_4$ and $C_2H_4$.)

NSRDS-NBS 21 by Benson and O'Neal (1970). (About 516 unimolecular reactions, the majority concerning organic or organometallic molecules or radicals.)

KINETIC RATE CONSTANTS

Review by Drysdale and Lloyd (1970). (About 60 reactions of OH.)
Review by Lloyd (1971). (F₂ and Cl₂ dissociation and recombination reactions.)
Review by Cohen (1971). (Reactions in the H₂/F₂ laser system.)
Review by Waage and Rabinovitch (1971). (Critical examination of the C₆H₆–CH₄ radical system.)
Article by Schofield (1972). (14 reactions of H, O, N, S, I, H₂, O₂, H₂O, CH₄, NO, N₂O, OCS, Cl₂, Br₂, CH₄; comparing rates of ground state and electronically excited reactants.)
Review by Wilson (1972). (Abstraction reactions of OH.)
Review by Lloyd (1972). (20 reactions of the HO₂ radical.)
NBS evaluation project, Hampson et al. (1972). (Data sheets for 27 reactions of potential interest for stratospheric chemistry, reactions of O(³P,1D), H, OH, O₂ (Δg, Σg), O₃, HO₂, H₂O₂, NO, NO₂, N₂O, N₃O, HNO, HNO₂, HNO₃.)
Book by Kerr and Parsons (1972). (Reactions of atoms and radicals with alkenes, alkynes, and aromatic compounds.)
Current efforts in the compiling and evaluating of chemical kinetic data have been outlined by Gevantman and Garvin (1972).

Tabulations of Non-Evaluated Data

General review articles tend to date rapidly. They are most useful for their bibliographic content, for illustrating the development of the field, and for discussions of the limitations and difficulties of particular experimental techniques. Those containing more extensive lists of information on reactions have greater longevity. Several publications have appeared recently, of value for their extensive coverage of the available data but, generally, no evaluation has been made. The master reference source by Hochstim, et al. (1969) for 1900–1966 publications is a monumental work. However, it is of main value only for the evaluator and is not a ready reference of data for the general user.

Tabulations and reviews that are most useful for establishing quickly the availability of information on certain reactions are:


Jensen and Kurzius (1967). 72 neutral reactions important in nozzle and rocket exhaust calculations.

Jensen and Jones (1971). 73 neutral reactions important in nozzle and rocket exhaust calculations.


Carnicom (1966). Of limited use since mainly superseded by more recent evaluated data reports.

Carnicom (1968). 89 neutral reactions of air with carbon and sodium impurities.

Tunder, et al. (1967). Several hundred reactions are listed of importance for reentry and propellant performance programs.

Cherry, et al. (1967, 1968). 82 reactions important in propellant performance programs. Reaction rates are discussed and references listed in the original report.


Benson and DeMore (1965). Review containing useful tables of referenced data.

Franklin (1967). Review containing useful tables of referenced data.


Kerr (1967). Review containing useful tables of referenced data.


Specialized Reviews

The following reviews restrict themselves to specifically defined areas and discuss in some detail particular groups of reactions. Many of these articles, particularly the more recent ones, still are quite useful as an initial inroad to the available information.


Avramenko and Kolesnikova (1964). Reactions of OH and O.


Brocklehurst and Jennings (1967). Reactions of N atoms.

Wright and Winkler (1968). Tables with references of data for reactions of N atoms.

Schiff (1969). 17 reactions involving O, N, NO.


Gunning and Strausz (1966); Strausz (1967). Reactions of Cl atoms.


Thomas (1965). Oxidation reactions of NO₂.
Hecklen and Cohen (1968). Reactions of NO.
Tedder and Walton (1967). Halogenomethyl radical reactions.
The following reviews emphasize particular research techniques used for rate constant measurements. They tend to be of interest mainly in illustrating the problems, limitations, and state of activity in the field of discussion.
Campbell and Thrush (1965). Discharge-flow system studies.

Miscellaneous Reviews

These reviews are of some bibliographic assistance and illustrate the development of gas kinetics over recent years. However, they are rather limited in their value as rate data reference sources. The latter ones, being more current, do discuss certain relevant problem areas.


Kondratiev (1965). Several reactions reviewed.


Spicer and Rabinovitch (1970). Discussion of various problem areas in elementary gas phase kinetics.


References


Hampson, R. F., private communication (1972).


