

GUIDE TO THE DATA SHEETS

1. Gas-Phase Reactions

The data sheets are principally of two types: (i) those for individual thermal reactions and (ii) those for the individual photochemical reactions.

1.1. Thermal Reactions

The data sheets begin with a statement of the reactions including all pathways that are considered feasible. This is followed by the corresponding enthalpy changes at 298 K, calculated from the enthalpies of formation summarized in the Thermodynamics Data summary. In the kinetic data summary table, reactions with multiple channels are indicated by 'products', unless individual rate constants for the channels are well defined.

The available kinetic data on the reactions are summarized under two headings: (i) Absolute Rate Coefficients, and (ii) Relative Rate Coefficients. Under these headings, we include new data that have been published since the last complete IUPAC evaluation⁶ as well as the data used in deriving the preferred values. Under both of the headings above, the data are presented as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature-dependent form over a stated temperature range. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form, $k = A \exp(-B/T)$, where $B = E/R$. For a few bimolecular reactions, we have listed temperature dependences in the alternative form, $k = A'T^n$ or $CT^n \exp(-D/T)$, where the original authors have found this to give a better fit to their data. For pressure-dependent combination and dissociation reactions, the non-Arrhenius temperature dependence is used. This is discussed more fully in a subsequent section of this Introduction.

Single temperature data are presented as such and wherever possible the rate coefficient at, or close to, 298 K is quoted directly as measured by the original authors. This means that the listed rate coefficient at 298 K may differ slightly from that calculated from the Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked with an asterisk indicate that the value was calculated by extrapolation of a measured temperature range that did not include 298 K. The tables of data are supplemented by a series of comments summarizing the experimental details. The following list of abbreviations, relating to experimental techniques, is used in the Techniques and Comments sections:

A	-	absorption
AS	-	absorption spectroscopy
CCD	-	charge coupled detector
CIMS	-	chemical ionization mass spectroscopy/spectrometric
CL	-	chemiluminescence
CRDS	-	cavity ring-down spectroscopy
DF	-	discharge flow

EPR	-	electron paramagnetic resonance
F	-	flow system
FP	-	flash photolysis
FTIR	-	Fourier transform infrared
FTS	-	Fourier transform spectroscopy
GC	-	gas chromatography/gas chromatographic
HPLC	-	high-performance liquid chromatography
IR	-	infrared
LIF	-	laser induced fluorescence
LMR	-	laser magnetic resonance
LP	-	laser photolysis
MM	-	molecular modulation
MS	-	mass spectrometry/mass spectrometric
P	-	steady state photolysis
PLP	-	pulsed laser photolysis
PP	-	pulse radiolysis
RA	-	resonance absorption
RF	-	resonance fluorescence
RR	-	relative rate
S	-	static system
TDLS	-	tunable diode laser spectroscopy
UV	-	ultraviolet
UVA	-	ultraviolet absorption
VUVA	-	vacuum ultraviolet absorption

For measurements of relative rate coefficients, wherever possible the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different from that reported by the original author owing to a different choice of rate coefficient of the reference reaction. Whenever possible the reference rate data are those preferred in the present evaluation.

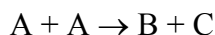
The preferred rate coefficients are presented (i) at a temperature of 298 K and (ii) in temperature-dependent form over a stated temperature range.

This is followed by a statement of the uncertainty limits in $\log k$ at 298 K and the uncertainty limits either in (E/R) or in n , for the mean temperature in the range. Some comments on the assignment of uncertainties are given later in this introduction.

The "Comments on Preferred Values" describe how the selection was made and give any other relevant information. The extent of the comments depends upon the present state of our knowledge of the particular reaction in question. The data sheets are concluded with a list of the relevant references.

1.2. Conventions Concerning Rate Coefficients

All of the reactions in the table are elementary processes. Thus the rate expression is derived from a statement of the reaction, *e.g.*,



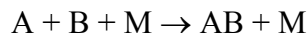
$$-\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]^2.$$

Note that the stoichiometric coefficient for A, *i.e.*, 2, appears in the denominator before the rate of change of [A] (which is equal to $2k[A]^2$) and as a power on the right-hand side.

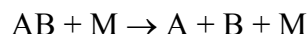
Representations of k as a function of temperature characterize simple "direct" bimolecular reactions. Sometimes it is found that k also depends on the pressure and the nature of the bath gas. This may be an indication of complex-formation during the course of the bimolecular reaction, which is always the case in combination reactions. In the following sections the representations of k which are adopted in these cases are explained.

1.3. Treatment of Combination and Dissociation Reactions

Unlike simple bimolecular reactions such as those considered in section 1.2, combination reactions



and the reverse dissociation reactions



are composed of sequences of different types of physical and chemical elementary processes. Their rate coefficients reflect the more complicated sequential mechanism and depend on the temperature, T , and the nature and concentration of the third body, [M]. In this evaluation, the combination reactions are described by a formal second-order rate law:

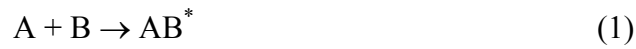
$$\frac{d[AB]}{dt} = k[A][B]$$

while dissociation reactions are described by a formal first-order rate law:

$$\frac{d[AB]}{dt} = k[AB]$$

In both cases, k depends on the temperature and on $[M]$.

In order to rationalize the representations of the rate coefficients used in this evaluation, we first consider the Lindemann-Hinshelwood reaction scheme. The combination reactions follow an elementary mechanism of the form,



while the dissociation reactions are characterized by:



Assuming quasi-stationary concentrations for the highly excited unstable species AB^* (*i.e.*, that $d[AB^*]/dt \sim 0$), it follows that the rate coefficient for the combination reaction is given by:

$$k = k_1 \left(\frac{k_2[M]}{k_{-1} + k_2[M]} \right)$$

while that for the dissociation reaction is given by:

$$k = k_{-2}[M] \left(\frac{k_{-1}}{k_{-1} + k_2[M]} \right)$$

In these equations the expressions before the parentheses represent the rate coefficients of the process initiating the reaction, whereas the expressions within the parentheses denote the fraction of reaction events which, after initiation, complete the reaction to products.

In the low-pressure limit ($[M] \rightarrow 0$) the rate coefficients are proportional to $[M]$; in the high pressure limit ($[M] \rightarrow \infty$) they are independent of $[M]$. It is useful to express k in terms of the limiting low pressure and high pressure rate coefficients,

$$k_0 = \lim_{[M] \rightarrow 0} k([M])$$

and,

$$k_\infty = \lim_{[M] \rightarrow \infty} k([M])$$

respectively. From this convention, the Lindemann-Hinshelwood equation is obtained

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty}$$

It follows that for combination reactions, $k_0 = k_1 k_2 [M] / k_{-1}$ and $k_\infty = k_1$, while for dissociation reactions, $k_0 = k_{-2} [M]$ and $k_\infty = k_{-1} k_{-2} / k_2$. Since detailed balancing applies, the ratio of the rate coefficients for combination and dissociation at a fixed T and $[M]$ is given by the equilibrium constant $K_c = k_1 k_2 / k_{-1} k_{-2}$.

Starting from the high-pressure limit, the rate coefficients fall-off with decreasing third body concentration $[M]$ and the corresponding representation of k as a function of $[M]$ is termed the "falloff curve" of the reaction. In practise, the above Lindemann-Hinshelwood expressions do not suffice to characterize the falloff curves completely. Because of the multistep character of the collisional deactivation ($k_2[M]$) and activation ($k_{-2}[M]$) processes, and energy- and angular momentum-dependencies of the association (k_1) and dissociation (k_{-1}) steps, as well as other phenomena, the falloff expressions have to be modified. This can be done by including a broadening factor F to the Lindemann-Hinshelwood expression,¹⁰⁻¹²

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty} F = k_0 \left(\frac{1}{1 + \frac{k_0}{k_\infty}} \right) F = k_\infty \left(\frac{\frac{k_0}{k_\infty}}{1 + \frac{k_0}{k_\infty}} \right) F$$

The broadening factor F depends on the ratio k_0/k_∞ , which is proportional to $[M]$, and can be used as a measure of "reduced pressure". The first factors on the right-hand side represent the Lindemann-Hinshelwood expression and the additional broadening factor F , at not too high temperatures, is approximately given by:⁸⁻¹²

$$\log F \cong \frac{\log F_c}{1 + [\log(k_0 / k_\infty) / N]^2}$$

where $\log = \log_{10}$ and $N = [0.75 - 1.27 \log F_c]$. In this way the three quantities k_0 , k_∞ , and F_c characterise the falloff curve for the present application. Alternatively the three quantities k_∞ , $[M_c]$ and F_c (or k_0 , $[M_c]$ and F_c) can be used.

The temperature dependence of F_c can be estimated theoretically such as described in references 8-12. For radical-radical recombination reactions without an energy barrier, and for the temperature range 200 – 300 K, it was demonstrated in ref. 12 that F_c can be assumed to be temperature independent. For the majority of combination reactions discussed in this evaluation, therefore, temperature independent values of F_c apply. For combination reaction proceeding over an energy barrier, on the other hand, F_c decreases with increasing temperature.

If a given falloff curve is fitted, changes in F_c require changes in the limiting k_0 and k_∞ values. For the purpose of this evaluation, this is irrelevant, if the preferred k_0 and k_∞ are used consistently together with the preferred F_c values. If the selected F_c value is too large, and the values of k_0 and k_∞ obtained by fitting the falloff expression to the experimental data are underestimated. If F_c is too small, k_0 and k_∞ are overestimated. However uncertainties in F_c do influence the fitted k_0 and k_∞ in different ways.

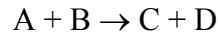
A simpler policy of fitting falloff was chosen by the NASA/JPL panel⁷ in putting $F_c = 0.6$ and $N = 1$. This generally leads to different values of the fitted k_0 and k_∞ and their temperature dependencies than derived here, although experimental data over the range of atmospheric interest can be generally be reproduced equally well. However the derived k_0 and k_∞ differ from the true limiting rate coefficients and thus should not be interpreted by theory. It should be mentioned that that the present form of F_c is also simplified and differs slightly from theoretical falloff calculations¹². However this difference generally leads to errors of the extrapolated k_0 and k_∞ which are smaller than experimental uncertainties. The dependence of k_0 and k_∞ on the temperature T is represented in the form:

$$k \propto T^{-n}$$

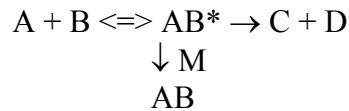
except for cases with an established energy barrier in the potential. We have used this form of temperature dependence because it usually gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. It should be emphasised that the chosen form of the temperature dependence is often only adequate over limited temperature ranges such as 200 – 300 K. Obviously, the relevant values of n are different for k_0 and k_∞ . In this evaluation, values of k_0 are given for selected examples of third bodies M, and if possible for M = N₂, O₂ or air.

1.4. Treatment of Complex-Forming Bimolecular Reactions

Bimolecular reactions may follow the "direct" pathway



and/or involve complex formation,



We designate the rate coefficients of the individual steps as in section 1.3. above:



Assuming quasi-stationary concentrations of AB^* (i.e., $d[AB^*]/dt \sim 0$), a Lindemann-Hinshelwood type of analysis leads to:

$$\frac{d[AB]}{dt} = k_S[A][B]$$

$$\frac{d[C]}{dt} = k_D[A][B]$$

$$\frac{d[A]}{dt} = (k_S + k_D)[A][B]$$

where

$$k_S = k_1 \left(\frac{k_2}{k_{-1} + k_2 + k_3} \right)$$

$$k_D = k_1 \left(\frac{k_3}{k_{-1} + k_2 + k_3} \right)$$

Note that since k_2 is proportional to $[M]$, k_S and k_D are dependent on the nature and concentration of the third body M , in addition to their temperature dependence. In reality, as for the combination and dissociation reactions, the given expressions for k_S and k_D have to be

extended by suitable broadening factors F in order to account for the multistep character of process (2) and the energy dependencies of processes (1), (-1) and (3). These broadening factors, however, differ from those for combination and dissociation reactions. For simplicity, they are ignored in this evaluation such that k_D at high pressure approaches

$$k_D \Rightarrow k_1 k_3 / k_2$$

which is inversely proportional to $[M]$. k_D may also be expressed by

$$k_D \approx k_{D0} k_S / k_{S0}$$

where k_{D0} and k_{S0} are the respective limiting low-pressure rate coefficients for the formation of C + D or A + B at the considered $[M]$. When it is established that complex-formation is involved, this equation is used to characterize the increasing suppression of C + D formation with increasing $[M]$.

1.5. Photochemical Reactions

The data sheets begin with a list of feasible primary photochemical transitions for wavelengths usually down to 170 nm, along with the corresponding enthalpy changes at 0 K where possible or alternatively at 298 K, calculated from the data in the Thermodynamic Data summary. Calculated threshold wavelengths corresponding to these enthalpy changes are also listed, bearing in mind that the values calculated from the enthalpy changes at 298 K are not true "threshold values".

This is followed by tables summarizing the available experimental data for (i) absorption cross-sections and (ii) quantum yields. These data are supplemented by a series of comments.

The next table lists the preferred absorption cross-section data and the preferred quantum yields at appropriate wavelength intervals. For absorption cross-sections the intervals are usually 1 nm, 5 nm or 10 nm. Any temperature dependence of the absorption cross-sections is also given where possible. The aim in presenting these preferred data is to provide a basis for calculating atmospheric photolysis rates. For absorption continua the temperature dependence is often represented by Sulzer-Wieland type expressions.¹³ Alternately a simple empirical expression of the form: $\log_{10}(\sigma_{T1}/\sigma_{T2}) = B(T_1 - T_2)$ is used.

The comments again describe how the preferred data were selected and include other relevant points. The photochemical data sheets are also concluded with a list of references.

1.6. Conventions Concerning Absorption Cross-Sections

These are presented in the data sheets as "absorption cross-sections per molecule, base e." They are defined according to the equations

$$I/I_0 = \exp(-\sigma[N]l),$$

$$\sigma = \{1/([N]l)\} \ln(I_0/I),$$

where I_0 and I are the incident and transmitted light intensities, σ is the absorption cross-section per molecule (expressed in this paper in units of cm^2), $[N]$ is the number concentration of absorber (expressed in molecule cm^{-3}), and l is the path length (expressed in cm). Other definitions and units are frequently quoted. The closely related quantities "absorption coefficient" and "extinction coefficient" are often used, but care must be taken to avoid confusion in their definition. It is always necessary to know the units of concentration and of path length and the type of logarithm (base e or base 10) corresponding to the definition. To convert an absorption cross-section to the equivalent Napierian (base e) absorption coefficient (expressed in cm^{-1}) of a gas at a pressure of one standard atmosphere and temperature of 273 K, multiply the value of σ in cm^2 by 2.69×10^{19} .

1.7. Assignment of Uncertainties

Under the heading "reliability," estimates have been made of the absolute accuracies of the preferred values of k at 298 K and of the preferred values of E/R over the quoted temperature range. The accuracy of the preferred rate coefficient at 298 K is quoted as the term $\Delta \log k$, where $\Delta \log k = D$ and D is defined by the equation, $\log_{10} k = C \pm D$. This is equivalent to the statement that k is uncertain to a factor of F , where $D = \log_{10} F$. The accuracy of the preferred value of E/R is quoted as the term $\Delta(E/R)$, where $\Delta(E/R) = G$ and G is defined by the equation $E/R = H \pm G$. D and G are expanded uncertainties corresponding approximately to a 95% confidence limit.

For second-order rate coefficients listed in this evaluation, an estimate of the uncertainty at any given temperature within the recommended temperature range may be obtained from the equation:

$$\Delta \log k(T) = \Delta \log k(298 \text{ K}) + 0.4343 \{ \Delta E/R (1/T - 1/298) \}$$

The assignment of these absolute uncertainties in k and E/R is a subjective assessment of the evaluators. They are not determined by a rigorous, statistical analysis of the database, which is generally too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experimental measurements, the potential for systematic errors, and the number of studies conducted and their agreement or lack thereof. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, *i.e.*, the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 90% confidence limits, of $\pm 10\%$ or less are frequently reported in the literature. Unfortunately, when evaluators come to compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients often differ by a factor of 2 or even more. This can only mean that one or more of the studies has involved large systematic uncertainties which are difficult to detect. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

The arbitrary assignment of uncertainties made here is based mainly on our state of knowledge of a particular reaction which is dependent upon factors such as the number of independent investigations carried out and the number of different techniques used. On the whole, our assessment of uncertainty limits tends towards the cautious side. Thus, in the case

where a rate coefficient has been measured by a single investigation using one particular technique and is unconfirmed by independent work, we suggest that minimum uncertainty limits of a factor of 2 are appropriate.

In contrast to the usual situation for the rate coefficients of thermal reactions, where intercomparison of results of a number of independent studies permits a realistic assessment of reliability, for many photochemical processes there is a scarcity of apparently reliable data. Thus, we do not feel justified at present in assigning uncertainty limits to the parameters reported for the photochemical reactions.

2. Acknowledgements

The Chairman and members of the Committee wish to express their appreciation to I.U.P.A.C. for the financial help which facilitated the preparation of this evaluation. We also acknowledge financial support from the following organisations: Agricultural Experiment Station, University of California, the UK Natural Environmental Research Council, the Upper Atmosphere Research Program of the National Aeronautics and Space Administration, the Standard Reference Data Program (N.I.S.T), the Fonds National Suisse de la Recherche Scientifique (FNSRS) and the Office Fédéral de l'Education et de la Science, the Deutsche Forschungsgemeinschaft (SFB 357). We thank Dr. G Carver and Dr R.G Hynes for assistance in preparing the website.

3. References to Introduction

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