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# **CODATA Guidelines on Reporting Data for Chemical Kinetics**

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The CODATA Task Group on Data  
for Chemical Kinetics

August 1974

Final Report

Prepared for

**The CODATA Symposium on Chemical Kinetics Data  
for the Lower and Upper Atmosphere,  
September 1974  
Warrenton, Virginia**



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**U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary**

**NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director**



CODATA Guidelines on Reporting  
Data for Chemical Kinetics

Abstract

This document is a copy of the report, June 1974, of the Task Group on Data for Chemical Kinetics of the Committee on Data for Science and Technology (CODATA). In this report recommendations are made about the reporting of experimental chemical kinetics data.

The Report and its recommendations have been approved by CODATA. They will be published in definitive form as CODATA Bulletin No. 13.

Keywords: chemical kinetics, guidelines, recommended procedures for reporting data, standardization, units

I. Report of the CODATA Task Group  
on Data for Chemical Kinetics

on

The Presentation of Chemical Kinetics  
Data in the Primary Literature

A set of recommendations entitled, "Reporting Experimental Data for Chemical Kinetics," is here submitted to CODATA for consideration, approval and publication.

The purpose of these recommendations is to ensure that accurate rate measurements are preserved and not lost through inadequate reporting. To this end the recommendations tell what types of data and auxiliary information should be reported and also point out the significant items of documentation that should be included. The Task Group believes that adherence by authors to these relatively few elementary recommendations when reporting experimental work can increase the durability of the results and improve the possibility of evaluating and comparing related studies.

These are recommendations for the discipline of chemical kinetics as a whole. They are part of a larger CODATA effort to provide guidelines for various branches of science. A more general document, "Guide for the Presentation in the Primary Literature of Numerical Data Derived from Experiments," has been prepared by the CODATA Task Group on Publication of Data in the Primary Literature and published as CODATA Bulletin No. 9, December 1973. It too should be studied by kineticists interested in improving the quality of the published literature. We have made use of ideas in it and, at times, have included some of its statements verbatim in our recommendations.

General guidelines applicable to an entire discipline, however, are not sufficient; detailed recommendations are needed for various specialized types of rate measurements. The Task Group has made an interim attempt to do this for some sub-disciplines. These recommendations are given in Appendix I of the report. They should be replaced by more comprehensive recommendations prepared by panels of experts in each specialty.

The Task Group undertook this work at the request of CODATA. Our starting point was a good set of guidelines prepared by Academician V. N. Kondratiev. An expanded version was prepared and circulated to about 1400 kineticists. More than 200 replies were received, most of them containing substantive suggestions. The Task Group has reviewed these comments and has incorporated many of them in its present report. We are very grateful to our colleagues throughout the world for their careful and constructive review of our work.

It is our hope that, through continued cooperation, kineticists will be able to raise the accepted standard of reporting to a point where guidelines on the subject become unnecessary.

S. W. Benson, Chairman	K. U. Ingold
D. L. Baulch	J. A. Kerr
E. T. Denisov	T. W. Newton
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J. Durup	R. Tamamushi
D. Garvin	V. I. Vedeneev
H. Hartmann	H. G. Wagner
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## II. Reporting Experimental Data for Chemical Kinetics

Because of the widespread and growing use of the numerical results of chemical kinetics research in other fields of science and technology, it is important that those results can be properly compared, evaluated and compiled for use by nonspecialists. Because of the variety of techniques employed in chemical kinetics and the wide range of systems studied, the quality of this reevaluation depends critically on the standards of reporting in the primary literature. In these recommendations we give criteria for the presentation of experimentally determined numerical rate data.

Our criteria apply most specifically to kinetics papers in which numerical data are reported. Our aim is to ensure that accurate rate measurements are preserved and not lost through inadequate reporting. In general we confine ourselves to measurements of macroscopic rate constants; these guidelines are not concerned with the interpretation of rates in terms of mechanisms.

The recommendations are not necessarily applicable to all papers in chemical kinetics. There are valuable studies of a general or semiquantitative nature to which many of our suggestions may be irrelevant. We do not discourage the publication of these papers. We do want sufficient information included in them so that the work can be assessed. Nor are these recommendations a guide to literary style or the organization of a paper. Our entire concern is with the factual content..

### 1. General

We base our recommendations on the following principles:

(i) The work should be described in sufficient detail to allow the equipment, conditions, procedure and, logically, the results to be reproduced, and to allow the quality of the work to be appraised.

(ii) The results should be presented in a form that will permit them to be reanalyzed and reinterpreted by others.

(iii) There should be an assessment of the accuracy and reproducibility of the numerical results.

In expanding these points in the following paragraphs we cannot anticipate the consequences for all the many possible chemical systems. We confine ourselves to points of general importance.

## 2. Experimental

### 2.1 Materials

The names of reactants, catalysts, ionic-strength adjusting chemicals, third body molecules (gas phase reactions), etc. should be given explicitly. Common names are often ambiguous and should be clarified; abbreviations should be specified, particularly for ligands in coordination compounds. The use of systematic nomenclature, chemical formulae and chemical structure diagrams is encouraged. Wherever possible, precise composition and structure and, where appropriate, stereo-descriptions should be given.

The origins, methods of purification and storage of reagents, solvents and other relevant materials should be stated. Criteria for purity, analytical results and known impurities should be given.

Where solid phases are used, other information may be necessary, such as the chemical composition, the structure (pellet, powder, film), the microstructure (where possible), and a description of the solid's pretreatment and history.

### 2.2 Apparatus

The report should include, either directly or by reference, descriptions of:

(i) Materials of construction, particularly those in contact with the reactants or products.

(ii) The reaction vessel including, where appropriate, dimensions, surface-to-volume ratio, materials of construction and pretreatment. Where the reaction does not occur homogeneously throughout the vessel (e.g., in some high temperature processes or photolyses), the "effective reaction volume", spatial distribution of the reaction or both should be given.

(iii) All relevant ancillary equipment and measuring devices. Performance capabilities should be stated for detection devices (noise, baseline stabilities), thermostatting equipment (stability, temperature profile), temperature measuring instruments, etc.

In the case of novel or complex apparatus it may be necessary to supplement the description with a realistic diagram of important features of the apparatus, giving dimensions and relevant geometry. Construction details should be made available on demand.

Modifications to standard or previously used apparatus should always be described.

### 2.3 Experimental Methods

The account of the experimental method should include, either directly or by reference:

(i) Description of the preparation of the reaction mixture, any methods used for initiating the reaction and those used to follow the course of the reaction.

(ii) An indication of the sequence of operations, in mixing or generating reactants, in analyzing the change and in separating products.

(iii) An explanation of the way in which any method is used, with quantitative details, e.g., reactant concentrations generated, detection conditions (signal-to-noise ratio), or wavelength and extinction coefficient used in spectrophotometric measurements. For photochemistry and radiation chemistry the spectrum (energy distribution of the incident radiation), beam geometry and rate of energy input are of particular importance.

(iv) The applicability of novel procedures should be justified.

(v) It must be made clear what physical properties are measured and how they are related to the concentrations of the chemical species or to their rate of change.

### 3. Presentation of Results

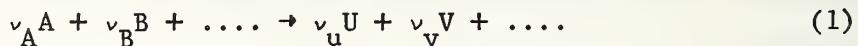
In this section we consider general points common to most kinetics studies. Problems peculiar to various sub-disciplines are considered in Appendix I.

By "results" we do not mean meter readings but those typical outputs of kinetics studies: the measured rate of reaction, the stoichiometric change in the system, the dependence of rate upon concentration, the rate constants and their variation with temperature, bond strengths, and so on.

### 3.1 General

(i) Whenever a rate is reported care should be taken to state clearly to what process it refers. When possible the process should be stated as a chemical equation.

Ambiguities in the meaning of the rate may occur for reactions such as (1)



if stoichiometric numbers,  $v_x$ , other than unity occur. A clear definition of the rate of reaction,  $R_1$ , is required. We recommend use of the convention

$$R_1 = - \frac{1}{v_A} \frac{d[A]}{dt} = - \frac{1}{v_B} \frac{d[B]}{dt} = \frac{1}{v_u} \frac{d[U]}{dt} = \dots$$

= some function of concentrations (2)

(ii) The results should be reported in a form that does not depend on interpretations made in the paper, still showing the experimental scatter and with as little dependence as possible on theoretical assumptions. Some processing of instrument readings is usually necessary before a convenient reporting stage is reached. This is acceptable, but the relationship between the reported results and the initial data should not be lost.

(iii) The procedures and expressions used to derive quantities from direct experimental measurements, or from already processed results, should be explained. At times the procedure may be relatively trivial, but at least it should be outlined; in other instances a very complete explanation or a worked example may be necessary.

(iv) The use of graphs to show trends, to compare data and as a basis for conclusion and generalization is valid and often extremely valuable. Our experience suggests, however, that a graph is not appropriate for recording accurately determined rate data. Inaccuracies occur in transferring results to a graph and, unless the graph is unusually large, the results cannot be recovered with sufficient accuracy for evaluation and reprocessing. For these reasons it is vital that accurate numerical data be presented in tabular form.

When there is a large amount of data an acceptable alternative may be an easily used analytical expression together with a graph showing the deviation of the individual points from the expression (e.g., see Blades, Int. J. Chem. Kin. 3, 187 (1971)). However, in experiments where several conditions change over the range of experiments (e.g., initial concentration or degree of conversion), tabulation is strongly preferred.

As far as possible all tables and graphs should be self-explanatory.

(v) Care should be taken always to include a comprehensive statement, preferably in the tables, of the variables (pressure, temperatures, concentrations, etc.) relevant to a particular rate or rate constant measurement. All relevant variables should be given. For example, in flow experiments, the flow velocity and distance should be quoted in preference to (or as well as) the reaction time. The number of determinations on which a measured rate constant is based should be included.

(vi) The amount of a product and/or reactant being analyzed or the magnitude of the physical change being monitored should be given. Sufficient data should be quoted to allow the degree of conversion to be calculated. Possible perturbation of the reaction by the analytical procedures should be discussed.

(vii) Negative results and unsuccessful experiments are often important. Wherever relevant they should be reported.

### 3.2 Rate Constants and Results Derived from Them

(i) All reported rate constants should be defined by giving an explicit mathematical statement of the pertinent rate equation, i.e., an expression equivalent to equation (2) above.

(ii) The formulation of the actual rate-determining step in a complex reaction is often difficult and subject to conflicting interpretation. Such formulations are not discouraged, but for the purposes of consistent data compilation, it is desirable that the rate laws and rate constants based on principal species be given in addition to other more speculative possibilities and that at some stage a rate constant defined in terms of the net, or observed, reaction be reported.

(iii) Rate constants are often derived by using numerical analysis to fit the observed change in a system to a hypothetical reaction scheme involving a number of variables, usually rate constants, some of which are known, some unknown. In such procedures:

(a) The reaction scheme should be justified, preferably on the basis of independent experiments or theory.

(b) An indication should be given of the sensitivity of the fit to the values assumed for the variables.

(c) The sensitivity of the fit to other possible models should be indicated.

These conditions should be met whether analytical or numerical analysis is being used, but they are particularly important for computer modeling.

Where steady-state expressions are used to analyse results, the validity of the steady-state approximation should be justified and any uncertainty in the procedure estimated.

(iv) Where auxiliary data are used in deriving rate constants and the like, the literature source should be given. If the auxiliary data are measured or calculated, the methods used should be described. In either case the accuracy of the data over the range of conditions in which they are applied should be quoted.

In the case of thermodynamic data it is important to define the standard state used.

(v) A variety of functions are used to express the rate constant,  $k$ , as a function of temperature,  $T$ . We recommend the use of one of the following forms:

$$k = A \exp (-B/T) \quad (3)$$

$$k = A'T^n \exp (-B'/T) \quad (4)$$

$$k = A''T^n \quad (5)$$

where the  $A$ 's,  $B$ 's and  $n$ 's are constants. Commonly,  $n$  in equation (4) is preset on the basis of theory.

Unless there are overriding reasons, equations of these types should be used to determine only two independent constants. When energies, enthalpies and entropies of activation are derived, it must be made clear which of these equations has been used.

### 3.3 Errors: Accuracy and Precision

(i) At some stage in the reporting of experimentally determined numerical data there should be a statement of the precision and accuracy.

The statistical or random uncertainty (precision) should be estimated using an appropriate standard statistical technique. However, it is only one component of the total error analysis and is not a sufficient statement of the reliability of the experiments.

Estimation of the other potential sources of error or limitations of the work is more difficult. There are no clear rules; subjective judgement is involved. However, these estimates of accuracy are more important than estimates of precision because the difference between values reported by two laboratories is often larger than the random errors.

(ii) Wherever possible the various sources of error, such as measurement precision, numerical analysis limitations, assumptions made in processing the data or uncertainties in auxiliary data, should be identified. The methods for estimating these errors should be indicated.

(iii) Precision. The quoted precision should be clearly defined. e.g., is the standard deviation of the value being given or a multiple thereof? It is important to specify the number of data being processed; techniques appropriate to the sample size should be applied.

When least-squares methods are used in processing the data, it is important to specify what quantity is minimized and/or what weighting scheme is used. For example, is the sum of squares of absolute, or relative, errors minimized?

It is important to take account of the fact that in experiments carried out over a range of a particular variable, say temperature, results obtained at the extremes of the range are usually much less accurate than those near the center. In these cases a weighted least-squares procedure should be used.

(iv) When data are presented on graphs, realistic error bars should be shown.

### 3.4 Units

It is extremely important that all physical quantities reported should have their units clearly specified. Table headings and axes of graphs should be labelled in dimensionless form, e.g.,  $\text{k}/\text{m}^3\text{mol}^{-1}\text{s}^{-1}$ , and the units of quantities used in analytical expressions, e.g., Arrhenius equation, should be stated.

Units used in reporting the final results should be compatible with the International System of Units (S.I.).

The unit of time should be the second. For concentration, the S.I. unit is  $\text{mol m}^{-3}$ , but permissible alternatives are  $\text{mol dm}^{-3}$ ,  $\text{mol cm}^{-3}$  and molecule  $\text{cm}^{-3}$ , which are all commonly used. Rate constants may be given in any appropriate combination of these units.

The S.I. unit of energy is the joule.

The use of non-S.I. units, and especially the use of nonmetric units, for reporting rate data is discouraged.

Occasionally there may be overriding reasons for using such units. In these cases the author should give factors for conversion to S.I. units. This may be done in a footnote: "Throughout this paper 1 torr = (101.325/760) kPa, and 1 kcal = 4.184 kJ."

### 3.5 References

Pertinent references must be given for all methods, results and auxiliary quantities quoted. In every case the reference cited should be the actual reference consulted by the author.

Readily accessible references are preferred; authors quoting less accessible references should indicate how they may be obtained.

References to long articles and books should cite specific pages wherever possible.

### 4. Accessibility of Data

Our recommendations request authors to be more explicit and more careful in their reporting. We do not believe that their implementation will require a substantial increase in the length of papers, except possibly for 3.1 (iv), which recommends the use of tabulation of results. In most cases we expect that it will be sufficient to tabulate rate constants and the associated experimental conditions (section 3.1 (v)). Only in exceptional cases will more be required.

The ideal situation is to have all the relevant information in the published article. However, if this is not practical, the supplementary material should be put in an auxiliary publication (submitted together with a shorter manuscript) and either placed in a suitable depository service or published as microform together with the article. In any event, the details must be available to the public from some source other than the author. The means of obtaining such auxiliary information must be clearly stated in the publication.

### 5. Referee's Check List

One of the problems encountered by referees is that of keeping in mind all the criteria outlined here. To assist in this we recommend that referees be supplied with a check list on which our criteria are suitably itemized. A suggested form is given in Appendix II. It is, of course, the prerogative of the referee to decide whether the items on the list are appropriate or relevant to the paper under consideration.

## Appendix I

### Interim Recommendations Applicable to Specific Fields of Chemical Kinetics

In this appendix we supplement the general recommendations with discussions of problems frequently encountered in interpreting reports of research in the areas of homogeneous gas phase, liquid phase, solid phase and heterogeneous reaction kinetics.

These are interim recommendations. They are not comprehensive. We believe that all these areas require further scrutiny by experts before more specific guidelines are prepared.

#### 1. Homogeneous Gas Phase Reactions

(i) It is usual in defining a rate constant to assume constant volume conditions. In systems where the volume is not constant, appropriate corrections should be made. This is particularly important for shock tube and flow systems if the reaction is appreciably exothermic or endothermic.

(ii) Pressure is often an important variable in gas phase systems, particularly when addition and dissociation reactions are involved. Thus dissociation reactions, first order at high pressures, become second order at low pressures, and analogous changes from second to third order occur for addition reactions. Formulations of the type (1) and (2) are often used to denote the reaction (in this example, addition) in these two kinetic regions.



Although this practice is permissible, it is essential that reports on such reactions include the pressure at which the measurements were made and, if known, the order of the reaction under those conditions. Also, the composition of the system, often just denoted by M, should be given explicitly.

In studies at very high pressures where the gas behavior is far from "ideal," it is preferable to express results in terms of concentrations rather than pressures.

(iii) Any effects due to reaction vessel surface should be reported directly or by reference. If no tests were made, this should be stated.

(iv) Modern kinetics techniques often involve reactants and products in states far removed from thermal equilibrium. Beam studies (neutral and ionic), flash photolysis, shock tube experiments and any strongly exothermic or endothermic reaction may produce nonequilibrium conditions. In such cases every effort must be made to specify completely the energy states or energy distribution of the species involved. This may require extensive tabulation of measured cross-sections, conditions of measurement (e.g., strength of electric fields, pressure) and internal and kinetic energy of reactants and products.

## 2. Liquid Phase Reactions

(i) The properties of the reaction medium often play a more important role in reactions in liquids than in the gas phase. It is important that the composition of the medium be specified in detail. This may include a statement of the solvent used, its origin and history (section 2.1), the composition of solvent mixture used (vague statements such as "60% acetone-water" are not acceptable without clarification), ionic strength, reactant concentrations and concentrations of other species present that may affect the reaction, e.g., hydrogen ion. Also, wherever possible, impurity concentrations, including the presence of dissolved air, should be given and their possible role considered.

(ii) It should be clearly stated whether the reported rate constants are based on concentrations or activities.

(iii) When rate constants are defined in terms of minor, but probably kinetically active species, the values used for the necessary ionization or complexing constants should be quoted. If required, information on the temperature coefficients of these constants should also be included. As for all such auxiliary data, literature source or measurement techniques should be given.

(iv) In liquid phase studies results are often reported in terms of the transition state theory parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ . When this is done:

(a) It is extremely important to state clearly the process and the standard state to which these "thermodynamic" quantities refer. Ambiguity may arise when overall rate parameters are interpreted in terms of an assumed mechanism. It should be made quite clear whether the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  refer to the overall process, to an assumed rate determining step, or to some combination of rate constants and possibly equilibrium constants for reactions involved in the mechanism.

(b) It is helpful for compilation and evaluation and for users of the data to have the Arrhenius parameters given as well as the transition state quantities.

### 3. Solid Phase Reactions

(i) Because rate processes in the bulk of a solid may be very sensitive to the solid's structure and to the impurities present, these should be specified (section 2.1). The "reactivity" of the solid may be affected by such physical properties as specific surface area, pore size and pore size distribution, and crystallite size and distribution. Defects, impurities and potentially active centers are similarly important. All these properties should be characterized wherever possible.

(ii) It is necessary to specify the stage of the reaction to which any rate parameters pertain since changes in the solid structure may affect the reaction rate.

(iii) In the early stages of reaction, appearance and growth of reaction centers will occur. It is desirable to give rate parameters for these processes and the distribution of these centers through the solid as well as parameters for the net reaction.

(iv) Kinetics of solid state reactions are affected by heat evolution and absorption and hence by physical properties such as thermal conductivity. In such cases the effects of self-heating or cooling should be considered in deriving kinetic data.

(v) The extent of a solid state reaction is often expressed in terms of the fractional reaction: the meaning of this term should be clearly explained.

(vi) Any equation used to relate the variation of reaction rate to extent of reaction should be stated and the terms defined. The range of conditions over which it is applicable should also be stated.

(vii) The simple Arrhenius relation is often not applicable to reactions occurring in solids. Where Arrhenius parameters are quoted, the method used for calculating them should be explained.

### 4. Reactions at the Surfaces of Solids

(i) The general criteria for the description of the solid (section 2.1) should include the method of preparation. The pretreatment of the solid should be described.

(ii) Some attempt should be made to characterize the surface. The surface area should be determined and, if possible, the concentration of active sites on the surface. With supported metal catalysts, the metallic surface area and thence the dispersion of the metal should also be determined. The methods used in these determinations should be specified.

(iii) Information as to the texture of a catalyst or adsorbent should be given, in particular, the particle size, the pore volume and the pore size distribution. Methods used in determining the last two quantities should be specified.

(iv) The kinetic equations used to calculate the rate constants should be specified. Rates of reaction and rate constants may be given per unit mass, per mole, or per unit area of the catalyst or adsorbent, but the units chosen should be clearly indicated. Where possible, it may be convenient to express the rates of catalytic reactions as turnover numbers, the number of molecules reacting per site per second. The method used for determining the number of sites should be described.

(v) Since concentration gradients in the pores of a catalyst or adsorbent often influence rates, the data needed to evaluate the degree of severity of this effect should always be given. Diffusion limitations should be considered.

(vi) As for solid state reactions, the effects of self-heating or self-cooling should be considered.

(vii) In systems involving gas flow over a surface, both total flow and flow velocity may be important and should be specified.

## Appendix II

### Referee's Check List

This check list attempt to cover only the most important, standard features to be considered in refereeing papers on chemical kinetics. In many instances further unlisted points will require comment.

Referees are requested to indicate whether they consider the particular point listed to be treated satisfactorily or whether a suggestion for improvement is appended.

#### 1. Apparatus and Procedures

Is the author's description of the following items satisfactory?

- (i) Reaction vessel
- (ii) Ancillary equipment and measuring device
- (iii) Procedure
- (iv) Calibration of apparatus

#### 2. Materials

Has the author provided sufficient information on:

- (i) Origins and/or preparation, and purity of reagents used?
- (ii) Chemical formula, structure, history, storage and pretreatment of reagents and/or materials used?

Satisfactory	Comment Appended

		Satisfactory	Comment Appended
3.	<u>Results</u>		
	(i) Are sufficient primary data presented to allow reworking of the results independent of any assumption or interpretations of the author?		
	(ii) Are <u>all</u> the relevant variables recorded for each set of rate measurements presented?		
	(iii) Are the reported rates specified unambiguously in terms of the stoichiometric change in the reaction?		
	(iv) Are all reported rate constants unambiguously defined in terms of rate equations?		
	(v) Are the procedures and expressions used to derive numerical results from the data adequately explained and their use justified?		
	(vi) Are error limits quoted and justified for measured, derived, and auxiliary quantities?		
4.	<u>General</u>		
	Is the referencing adequate?		
	Is the nomenclature clear?		
	Are all symbols defined?		

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