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PHYSICAL CHEMISTRY DIVISION

SUBCOMMITTEE ON CHEMICAL KINETICS*

SYMBOLISM AND TERMINOLOGY IN CHEMICAL KINETICS

(Appendix No. V to Manual of Symbols and Terminology for Physicochemical Quantities and Units)

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Comments on these recommendations are welcome and should be sent within 8 months from March 1981 to the Chairman of the Subcommittee:

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Comments from the viewpoint of languages other than English are especially encouraged. These may have special significance regarding the publication in various countries of translations of the nomenclature eventually approved by IUPAC.

*Membership of the Subcommittee for 1979-81 is as follows:
Chairman: K. J. LAIDLER (Canada); Members: E. T. DENISOV (USSR); K. H. HOMANN (FRG); T. M. SUGDEN (UK).
This report is concerned with making precise definitions of terms used in chemical kinetics and with recommending symbols. This first IUPAC report on kinetics deals only with general and fundamental aspects of kinetics, and it is hoped that later reports will deal with more specialized topics.

A number of other groups have been concerned with related problems in other areas of physical chemistry, and their reports are listed in the Bibliography.

Any group concerned with making recommendations for symbols and terminology must make compromises between established usage and strict logic. When symbols and terms have become firmly entrenched we have maintained them except for very good reasons even though, if we were starting afresh, we might prefer to recommend differently.

1. BASIC KINETIC PRINCIPLES
1.1 Reaction stoichiometry
A chemical reaction of known stoichiometry can be written in general as

\[ aA + bB + \ldots = \ldots + yY + zZ \]

Early letters of the alphabet are recommended for reactants, late letters for products; the letter X is conveniently reserved for a reaction intermediate.

The symbol \( \nu_x \) is used to refer to the stoichiometric coefficient of a chemical species (Note a) and is negative for reactants, positive for products. The numbers \( y \) and \( z \) are the stoichiometric coefficients for the products, while \(-a\) and \(-b\) are the stoichiometric coefficients for the reactants.

Sometimes the stoichiometric equation applies throughout the course of the reaction, in which case the reaction may be said to have time-independent stoichiometry. If intermediates are formed in significant amounts during the course of a reaction, the overall stoichiometric equation does not apply throughout, and the reaction can then be said to have time-dependent stoichiometry.

Various symbols can be used to relate reactants and products in a stoichiometric equation. An equal sign can be used, as in

\[ H_2 + Br_2 \rightarrow 2 HBr, \]

if one is concerned simply with the balancing of the equation. Two half arrows, as in

\[ H_2 + Br_2 \rightleftharpoons 2 HBr \]

are conveniently used when the emphasis is on the equilibrium state of the reaction.
A single full arrow (Note b) as in

\[ H_2 + Br_2 \rightarrow 2 HBr \]

and in

\[ H_2 + Br_2 \rightarrow 2 HBr \]

can be used to refer to the reaction occurring in a single direction. Two full arrows, as in

\[ H_2 + Br_2 \leftrightarrow 2 HBr \]

can be used when there is interest in the kinetics of the reaction in both the forward and reverse directions. A single filled-in arrow, as in

\[ H + Br_2 \rightarrow HBr + Br \]

can be used to emphasize that the reaction is believed to be elementary (see Section 2).

The progress of a reaction can be measured with respect to a number of quantities, including mass, number of molecular entities, amount of substance, and concentration; it can also be measured with respect to physical properties of the system. In what follows we consider the procedures that seem to be of widest applicability, but other procedures may be more convenient in particular circumstances. Since heterogeneous systems have already been dealt with by a IUPAC commission (Ref. 2), the emphasis in the present report is on homogeneous systems.

1.2 Rates of consumption and formation

Kinetic studies can be carried out in static systems or in flow systems; in the former case the extent of reaction is studied as a function of time, while in flow systems time is replaced by distance travelled along the reactor. We have not treated both cases, but have confined our attention to static systems. The formalism for flow systems can easily be developed from the equations given in this report.

We recommend that for a specified reactant the rate of consumption or rate of disappearance (Note c) be defined as

\[ \nu_r = -\frac{1}{V} \frac{dn_r}{dt} \]

where \( t \) is the time, \( n_r \) the amount of a reactant, and \( V \) is the volume. We recommend that the term rate of formation be used for

\[ \nu_p = \frac{1}{V} \frac{dn_p}{dt} \]

where \( n_p \) is the amount of a specified product. The symbol \( \nu \) with a subscript denoting the reactant or product is used for these rates.

If the volume is constant throughout the reaction \( \frac{dn}{V} \) may be replaced by \( \frac{dc}{\tau} \), where \( \tau \) is the concentration of the species. For the reaction written above, at constant volume

\[ \frac{dc}{\tau} = \frac{dn}{V} = \frac{dc}{\tau} = -\frac{dc}{\tau} \]

These rates are not necessarily the same, and should not be called the rate of reaction. The symbols \([A],[B], \ldots\) can also be used for concentrations.

If the volume changes during reaction we have, for the rate of consumption of \( A \),

Note b. The single full arrow is also useful for an unbalanced reaction.

Note c. Since the word 'disappearance' is not appropriately translatable into certain languages, the word 'consumption' is to be preferred. In texts in English the word 'disappearance' might be reserved for cases in which a reactant is almost completely removed.
\[ v_A = \frac{1}{V} \frac{d\xi_A}{dt} = -\frac{1}{V} \frac{d(\sigma A)}{dt} = -\frac{d\xi_A}{dt} = -\frac{\frac{\partial A}{\partial v}}{dt} \tag{5} \]

Similarly, for the rate of formation of Z,

\[ v_Z = \frac{1}{V} \frac{d\xi_Z}{dt} = \frac{1}{V} \frac{d(\sigma Z)}{dt} = \frac{d\xi_Z}{dt} + \frac{\sigma Z}{V} \frac{dv}{dt} \tag{6} \]

In each of these expressions the final term is a correction for the change of concentration brought about by the change of volume.

If the solvent is a reactant or product it may be difficult to measure directly the changes in its concentration; these must be inferred from other concentration changes and the stoichiometry.

1.3 Rate of reaction

When a reaction has time-independent stoichiometry (i.e., the stoichiometric equation is obeyed throughout the course of the reaction) it is possible to define extent of reaction \( \xi \) by

\[ \xi = \frac{n_\xi - n_{\xi,0}}{V} \tag{7} \]

where \( n_{\xi,0} \) is the initial amount of substance \( \xi \) and \( n_\xi \) is the amount at any time. If \( \xi_{eq} \) is the extent of reaction after equilibrium is reached and \( \xi \) is the extent of reaction at time \( t \), the ratio \( \xi_{eq}/\xi \) can be called the fraction of reaction. The extent of reaction is independent of the species; thus for the general reaction written above, and with time-independent stoichiometry, the following relationships are obeyed throughout the course of the reaction:

\[ \frac{d\xi_{eq}/y}{dt} = \frac{d\xi_{eq}/a}{dt} = -\frac{d\xi_{eq}/b}{dt} \tag{8} \]

The time derivative of the extent of reaction may be called the rate of conversion; in our example, the rate of conversion is

\[ \frac{d\xi}{dt} = \frac{d\xi_A}{dt} = \frac{d\xi_B}{dt} = \frac{d\xi_Y}{dt} = \frac{d\xi_Z}{dt} \tag{9} \]

In general for any species B

\[ \frac{d\xi}{dt} = \nu_B \frac{dn_B}{dt} \tag{10} \]

In the Manual (Ref. 1) this quantity is defined as the 'rate of reaction', but this is contrary to almost universal usage in kinetics. Instead, we recommend that rate of reaction be defined as

\[ v = \frac{1}{V} \frac{dn_\xi}{dt} = \frac{\xi}{V} \tag{11} \]

If the volume changes during reaction this definition leads to

\[ v = \frac{1}{V} \frac{d\xi}{dt} + \frac{\sigma \xi}{V} \frac{dv}{dt} \tag{12} \]

(compare equations 5 and 6); if \( V \) is constant the final term in this equation is zero. For the reaction \( aA + bB \rightarrow yY + sZ \), when \( V \) is constant,

\[ v = \frac{1}{a} \frac{d\xi_A}{dt} = \frac{1}{b} \frac{d\xi_B}{dt} = \frac{1}{y} \frac{d\xi_Y}{dt} = \frac{1}{s} \frac{d\xi_Z}{dt} = \frac{v_A}{a} = \frac{v_B}{b} = \frac{v_Y}{y} = \frac{v_Z}{s} \tag{13} \]

A careful distinction should be made between \( v \) without lettered subscript, meaning rate of reaction, and \( v \) with lettered subscript (e.g. \( v_A \)), meaning rate of consumption or formation. Since the stoichiometric coefficients depend on the way in which the reaction is written (e.g. \( H_2 + \frac{1}{2} Br_2 \rightarrow 2 HBr \) or \( \frac{1}{2} H_2 + \frac{1}{2} Br_2 \rightarrow HBr \)), whenever rates of reaction are given the stoichiometric equation must be specified.
For the reaction of a substance adsorbed on a surface $V$ can be replaced by the surface area $A$:

$$
\nu = \frac{1}{v \Gamma} \frac{d\Gamma}{dt} = \frac{1}{v \Gamma} \frac{d\Gamma}{dt}
$$

(14)

where $\Gamma$ is now the surface concentration, equal to $n / A$. The rate now has different units (for example, mol m$^{-2}$ s$^{-1}$).

It is sometimes convenient to express rates in terms of particle number densities (number of molecular particles divided by volume). Such a rate is rate of reaction multiplied by the Avogadro constant. If $C_i$ is the number density of particles of species $i$, and the volume is constant,

$$
\nu_L = \frac{1}{v_i} \frac{dC_i}{dt}
$$

(15)

No special symbol is recommended for this rate, the usual unit for which is m$^{-3}$s$^{-1}$.

The concept of extent of reaction, and hence equations (9)-(14), cannot be used unless both of the following conditions are satisfied: (1) the reaction is of known stoichiometry, and (2) the stoichiometric equation remains valid throughout the course of the reaction. In other words, the reaction must have time-independent stoichiometry. The concepts of rate of consumption and rate of formation are, of course, meaningful even if the stoichiometry has not been established, or if (because of the formation of intermediates) the stoichiometry is time-dependent.

We recognize that in certain areas of kinetics, such as heterogeneous catalysis, it has been customary to define rate of reaction by eq. (10). Our preference is for 'rate of conversion' to be used for this quantity, and we suggest that those who call it rate of reaction should make it clear that they are doing so; in any case the context, and the units used, should avoid ambiguity.

1.4 Empirical rate equations: Order of reaction

In some cases the rate of consumption or formation can be expressed empirically by an equation of the form

$$
V_A = k_A [A]^\alpha [B]^\beta
$$

(16)

where $\alpha$ and $\beta$ are independent of concentration and of time. When this is so the rate of reaction is also expressible as

$$
\nu = k [A]^\alpha [B]^\beta
$$

(17)

but $k_A$ and $k$ are not necessarily the same.

The exponent $\alpha$ is referred to as the order of reaction with respect to the reactant $A$, and can be referred to as a partial order. Similarly the partial order $\beta$ is the order with respect to $B$. These orders are experimental quantities and are not necessarily integral. The sum of all of the partial orders $\alpha, \beta, \ldots$ is referred to as the overall order, and may be given the symbol $n$:

$$
n = \alpha + \beta + \ldots
$$

(18)

A distinction should be made between order with respect to concentration, and order with respect to time. The former is obtained from experiments in which initial rates are measured at a series of initial reactant concentrations; it is therefore unaffected by the products formed during the reaction. The order with respect to time is determined on the basis of individual runs, and is obtained from the dependence of rate on the amounts of reactants that remain in the reaction system after various periods of time; this order is affected by the products formed during the reaction. The order with respect to time is only meaningful if it is independent of time. Comparison of the two orders is often useful in determining whether the reaction is accelerated or retarded as the products accumulate.

The definition of order of reaction for an elementary step in a composite mechanism is considered later (Section 3.2).

Rate equations are frequently more complicated than eq. (16). For example, an empirical rate equation might be of the form

$$
\nu = \frac{k[A]^\alpha [B]^\beta}{1 + \alpha [A]^\gamma [B]^\delta}
$$

(19)
The coefficients \( k \) and \( k' \) in such an equation may be called **coefficients in the rate equation** to distinguish them from rate coefficients in equations such as (16) and (17). Sometimes **apparent orders of reaction** are obtained from plots of \( \ln v \) against \( \ln (\text{concentration}) \), and are defined by equations such as

\[
\alpha_{\text{app}} = \frac{d \ln v}{d \ln [A]}
\]

(20)

If these are dependent on concentration the fact must be clearly stated.

In developing empirical equations such as (16)-(19) one is often concerned with reactants that exist in two forms that are in rapid equilibrium with each other; for example, there may be two states of ionization,

\[
A + H^+ \rightleftharpoons AH^+
\]

In such cases it may be convenient to write the empirical rate equation with respect to the sum of the concentrations of the two forms; in the above example this sum is

\[
[A]_t = [A] + [AH^+]
\]

(21)

and the subscript \( t \) (for total) may be used in such cases.

1.5 Rate coefficients and rate constants
The coefficients in eq. (16) and (17) are known in general as **rate constants** or **rate coefficients**. It is convenient to use the former term when the reaction is believed to be elementary (Section 2) and the latter term when the reaction is believed to be composite (Section 3).

Sometimes a reaction is studied with certain concentrations held constant. If, for example, the rate equation is

\[
v = k[A]^a[B]^b
\]

(22)

and \([B]\) is maintained constant, the rate can be expressed as

\[
v = k_{\text{obs}}[A]^a
\]

(23)

The term 'coefficient' is then preferable to 'constant', and the coefficient \( k_{\text{obs}}(= [B]^b) \) can be called the **observed rate coefficient**. For the case of \( a = 1 \) it is sometimes called the **pseudo-first-order rate coefficient**.

If the rate constant or coefficient relates to the rate of consumption of \( A \),

\[
v_A = -\dot{\Delta}_A = k_A[A]^a[B]^b
\]

(24)

it is called the **rate constant (or coefficient) with respect to \( A \)** and given the symbol \( k_A \); if it relates to the rate of formation of \( Y \) it is called the **rate constant (or coefficient) with respect to \( Y \)** and given the symbol \( k_Y \). If it relates to the rate of reaction the term rate constant or rate coefficient is sufficient; no subscript is then used except that specifying the reaction (e.g. \( k_1 \) for reaction 1). It is recommended that rate constants or coefficients which relate to the rate of reaction be used as far as possible, but this can only be done for reactions having time-independent stoichiometry.

1.6 Half life
For a given reaction the **half life** \( t_1/2 \) of a reactant is the time required for its concentration to reach a value that is the arithmetic mean of its initial and final (equilibrium) values. For reactions obeying equations of the form of (17) the half life of a reactant \( A \) is proportional to \([A]^\alpha\) where \( \alpha \) is the partial order with respect to \( A \); the half life is therefore independent of a concentration only when the partial order is unity.

It is permissible to speak of the half life of a reaction only in special cases: (1) for any first-order reaction, (2) for reactions of higher orders in which the concentrations of the reactants are in their stoichiometric ratios.

For first-order (or pseudo-first-order) reactions the half life is related to the rate coefficient \( k \) by

\[
t_1/2 = \frac{\ln 2}{k}
\]

(25)

For any reaction obeying an equation of the form of (17) the half life is inversely proportional to the rate coefficient. If the kinetic equation is more complicated than (17) there is no simple relationship between the half-life of a reactant and the rate coefficients.
1.7 Relaxation time

If a system is disturbed from its state of equilibrium it relaxes to that state; the branch of kinetics concerned with this effect is known as relaxation kinetics. Techniques include temperature jump (T-jump), and pressure jump, in which temperature and pressure respectively are changed very rapidly and the relaxation studied. The relaxation time, \( \tau \), is defined as the time it takes for the extent of reaction to change by \( 1-(1/e) \) of the total change during the relaxation process (\( e \) is the base of the natural logarithms).

If the reactions in both directions are elementary (Section 2), the relaxation time is related to the rate constants in forward and reverse directions and, in general, to concentrations. If the reactions are composite (Section 3) there is no simple relationship between overall relaxation time and rate coefficients; in that case the relaxation to equilibrium can in principle be interpreted in terms of more than one relaxation time, each one of which can be related to rate constants for elementary steps.

2. ELEMENTARY REACTIONS

An elementary reaction is one in which no reaction intermediates have been detected, or need to be postulated in order to describe the chemical reaction on a molecular scale. Until evidence to the contrary is discovered, an elementary reaction is assumed to occur in a single step and to pass through a single transition state.

Whereas reaction order is a purely empirical quantity, the molecularity of an elementary reaction is the number of reactant particles (atoms, molecules, free radicals or ions) that are involved in the microscopic chemical event. It is also the number of reactant particles present in the transition state. The term molecularity should not be applied to a composite reaction, even if there is a clearly-identified rate-determining step.

The rate of an elementary reaction in one direction only (i.e. the 'chemiflux'; see Section 3.2) is always expressible in the form of eq. (17), in which \( k \) is the rate constant for the elementary reaction. The partial orders, \( \alpha, \beta, \) etc. correspond to the numbers of molecules A, B, etc. taking part in the microscopic chemical event, and the overall order is equal to the molecularity.

A reaction having a molecularity of one is said to be unimolecular, of two, bimolecular, and of three, trimolecular. With reactions in solution, solvent molecules are counted in the molecularity if they enter into the overall reaction, but not if they exert merely an environmental or solvent effect. A third body, by definition, does not enter into the overall reaction and is therefore not counted in the molecularity.

3. COMPOSITE REACTIONS

A composite, complex or stepwise reaction (Note d) is one that involves more than one elementary reaction. Elementary reactions that occur in composite mechanisms are conveniently referred to as elementary steps. Composite reactions sometimes (but not always) involve rate equations more complicated than eq. (17), in which case one cannot speak of reaction orders.

The elementary reactions occurring in a composite mechanism should be numbered in such a way that reverse reactions are easily identified, and the reaction numbers should be used as subscripts to \( v \) or \( k \). The preferred schemes are:

1. \( k_1, k_{-1}, k_2, k_{-2}, k_3, k_{-3}, \) etc. \( v_1, v_{-1}, \) etc.
2. \( k_{+1}, k_{-1}, k_{+2}, k_{-2}, \) etc.; \( v_{+1}, v_{-1}, \) etc.
3. \( k_{12}, k_{21}, k_{23}, k_{32}, k_{34}, k_{43}, \) etc.; \( v_{12}, v_{21}, \) etc.

In schemes (1) and (2), reaction \(-1\) is the reverse of reaction 1, and in scheme (3) reaction 21 is the reverse of reaction 12.

Note d. Our preference is for 'composite'. The word 'complex' is overworked in chemistry, and in any case it would seem unsatisfactory to describe a two-step reaction as 'complex'.
3.1 Types of composite reactions

Composite reaction mechanisms can have a number of features. Reactions occurring in parallel, such as

\[
\begin{align*}
A & \rightarrow^1 Y \\
A & \rightarrow^2 Z
\end{align*}
\]

can be called simultaneous or parallel reactions. When there are simultaneous reactions there is sometimes competition, as in the scheme

\[
\begin{align*}
A + B & \rightarrow^1 Y \\
A + C & \rightarrow^2 Z
\end{align*}
\]

where B and C compete with one another for A.

Reactions occurring in forward and reverse directions can be called opposing, for example:

\[
A + B \begin{array}{c}
\rightleftharpoons \\
\end{array} Z
\]

Reactions occurring in sequence, such as

\[
A \rightarrow^1 X \rightarrow^2 Y \rightarrow^3 Z
\]

are known as consecutive reactions, and the overall process is said to occur by consecutive steps. Reactions are said to exhibit feedback if a substance formed in one step affects the rate of a previous step. For example, in the scheme

\[
A \rightarrow^1 X \rightarrow^2 Y \rightarrow^3 Z
\]

the intermediate Y may catalyze reaction 1 (positive feedback) or inhibit reaction 1 (negative feedback). A final product as well as an intermediate may bring about feedback.

3.2 Chemical flux, or chemiflux

Except in special cases, the concept of "extent of reaction" has no meaning for an overall composite reaction, or for an elementary reaction occurring in a composite mechanism. One cannot, therefore, in general speak of 'rate of reaction', as defined by eq. (11), for an overall reaction or for one of its component elementary steps. One can, however, specify rates of consumption of reactants and rates of formation of products, and rates of change of concentrations of intermediates. The special cases in which it is possible to define extent of reaction and rate of reaction for an overall composite reaction are when there is time-independent stoichiometry; this arises (1) when the intermediates are formed in negligibly small amounts, and (2) when the overall rate is almost entirely controlled by a single step.

The definition of rate of reaction given in Section 1.3 (equation 11) is satisfactory as it stands for elementary reactions occurring in isolation in one direction. A special treatment has been suggested (Ref. 5) for elementary steps that are components of a composite reaction, and for systems at equilibrium or close to equilibrium. For a system at equilibrium, for example, the rate of reaction defined according to eq. (11) is zero. For such cases it is convenient to define a quantity which has been called the chemical flux, or the chemiflux, with the symbol \( \phi \). This quantity is the rate of a single reaction occurring in one direction only, if that reaction occurred in isolation (Note e).

Consider, for example, the reaction scheme

\[
A \begin{array}{c}
\rightleftharpoons \\
-1
\end{array} 2Z
\]

Note e. The terms 'chemical flux' and 'chemiflux' are provisional at this stage; objections have been raised to them, but we can suggest no better term. If the expression 'chemical flux' is employed it is important to include the adjective 'chemical' to avoid confusion with other kinds of flux.
in which the reactions in both directions are elementary. If Z is removed as fast as it is formed, the rate of transformation of A is

$$\phi_1 = \phi_{-A,2Z} = k_1[A]$$

(26)

and this rate, which applies to reaction 1 in one direction only, can be called the chemical flux or chemiflux for reaction 1. It can be given the symbol $\phi_1$ or $\phi_{A,2Z}$, the latter subscript indicating the process of conversion of A into 2Z. The chemiflux $\phi_{-1}$ or $\phi_{-2Z,A}$ is the rate of reaction -1 if it occurred in isolation:

$$\phi_{-1} = \phi_{-2Z,A} = k_{-1}[Z]^2$$

(27)

In general, with A and Z both present, the net rate of reaction from left to right is the difference between these chemifluxes:

$$v_1 = \frac{d[A]}{dt} = \frac{d[Z]}{dt} = \phi_1 - \phi_{-1} = k_1[A] - k_{-1}[Z]^2$$

(28)

At equilibrium this rate is zero and

$$\left(\frac{[Z]^2}{[A]}\right)_{eq} = \frac{k_1}{k_{-1}} = k_c$$

(29)

For the composite mechanism

$$A + B \xleftrightarrow[k_{-1}]{k_1} X \xleftrightarrow[k_2]{k_{-2}} Z$$

there are four elementary steps and the corresponding chemifluxes are:

$$\phi_1 = k_1[A][B]$$

(30)

$$\phi_{-1} = k_{-1}[X]$$

(31)

$$\phi_2 = k_2[X]$$

(32)

$$\phi_{-2} = k_{-2}[Z]$$

(33)

The four orders of reaction are defined with respect to these chemifluxes, not with respect to any rates of reaction that could be defined by eq. (11).

For a species X, the total chemiflux into X, $\Sigma \phi_X$, is the sum of the chemifluxes of all reactions which produce X. The total chemiflux out of X, $\Sigma \phi_{-X}$, is the sum of the chemifluxes of all reactions that remove X. For example, for the mechanism

$$A \xleftrightarrow[k_{-1}]{k_1} X \xleftrightarrow[k_2]{k_{-2}} Z$$

the total chemiflux into X is

$$\Sigma \phi_X = \phi_1 + \phi_{-2} = k_1[A] + k_2[Z]$$

(34)

and the total chemiflux out of X is

$$\Sigma \phi_{-X} = \phi_{-1} + \phi_2 = (k_{-1} + k_2)[X]$$

(35)

The Subcommittee is not, at this stage, making a specific recommendation that the concept of chemiflux should always be employed; it is merely suggesting a procedure that has been found useful.
3.3 The steady state
If an intermediate X is such that it is always present in amounts much less than those of the reactants, the rate of change of its concentration is much smaller than that of the reactants; the total chemiflux into X, \( \Sigma \Phi_X \), is nearly the same as the total chemiflux out of X, \( \Sigma \Phi_{-X} \). To a good approximation

\[
\frac{d[X]}{dt} = \Sigma \Phi_X - \Sigma \Phi_{-X} = 0
\]  

and X is said to be in a steady state. The use of this approximation to obtain an overall rate expression is known as the steady-state treatment or the steady-state approximation.

3.4 Chain reactions
A composite reaction mechanism sometimes includes a closed sequence (cycle) of reactions such that certain active intermediates are consumed in one step and are regenerated in another. The active intermediates may be atoms, free radicals or ions.

If the closed sequence (cycle) of reactions is repeated more than once then the reaction is called a chain reaction, and the reactions occurring in the sequence are known as propagation steps. A chain reaction also involves an initiation step, which produces active intermediates, and sometimes has a termination, or chain-ending, step, which removes them.

The chain length of a chain reaction is defined as the average number of times the closed cycle of reactions is repeated in the steady state, and is equal to the rate of the overall reaction divided by the rate of the initiation step.

A branching chain reaction is one which includes a propagation step or steps in which there is an increase in the number of active intermediates; for example, \( H + \text{O}_2 \rightarrow \text{OH} + O \) is a branching reaction since one active intermediate (\( H \)) gives rise to two (\( \text{OH} \) and \( O \)).

3.5 Photochemical and radiation-chemical reactions and chemiluminescence
It has been found useful to distinguish between photochemical and radiation-chemical (Note f) reactions, although the distinction is not a sharp one. Both photochemistry and radiation chemistry are concerned with the absorption of radiation resulting in chemical change. A distinction is sometimes made on the basis of whether or not ions can be detected in the system. If they can, as is the case with electromagnetic radiation from the mid-ultraviolet and beyond, and with high-energy particle radiation, the reaction may be called a radiation-chemical reaction; otherwise, as with electromagnetic radiation of longer wavelengths, the resulting reaction may be called a photochemical reaction. Another, and probably more significant, criterion is based on the specificity of the chemical effects; the reaction is said to be photochemical if the effects are specific, and radiation-chemical if a variety of reaction products are obtained. The behavior may be specific even if ions are detected, so that this second criterion puts the boundary between photochemical and radiation-chemical reactions at higher energies.

Whereas photochemistry is concerned with chemical change resulting from radiation, photophysics is concerned with events in which there may be excitation but no chemical change. An overall photochemical reaction is almost invariably accompanied by photophysical processes.

Various special kinds of photochemical reactions may be identified by the prefix 'photo-'. A photolysis is a photochemical reaction in which there is molecular dissociation. A photoisomerization is a photochemical isomerization. Other terms used are photoaddition, photodissociation, photosubstitution, photocycloaddition, etc. The term photoconversion refers to a process in which radiation brings about excitation of an atom or molecule, known as a photosensitizer, which then brings about chemical change in other molecules, itself remaining chemically unchanged. The term radiolysis refers to a radiation-chemical reaction in which there is molecular dissociation. Chemiluminescence refers to radiation emitted from excited molecular particles (atoms, molecules, free radicals, or ions) that are formed by chemical processes and are not in thermal equilibrium with their surroundings. Such a process is known as a chemiluminescent reaction.

3.6 Catalysis
A catalyst is a substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis, and a reaction in which a catalyst is involved is known as a catalyzed reaction. This definition is equivalent to the statement that the catalyst does not enter into the overall reaction; it is both a reactant and product of the reaction.

Note f. These should not be called 'radiochemical' reactions; radiochemistry is concerned with the use of radioactive materials in the elucidation of chemical problems.
Substances that exert merely an environmental or ionic strength effect are not included under the definition of 'catalyst'.

Sometimes the rate of a reaction is increased by a substance that acts in some ways like a catalyst but which is consumed during the process. Examples are the hydrolysis of amides by acids, with the formation of the ammonium ion, and certain chain reactions in which a substance aids the initiation process. Such substances should not be called catalysts, but may be called pseudo-catalysts (Note g).

If a reaction is catalyzed by one of its products, that product is known as an autocatalyst and the process is known as autocatalysis. Catalysis brought about by a group on a reactant molecular particle is called intramolecular catalysis.

A substrate is a reactant (other than the catalyst itself) in a catalysed reaction. In heterogeneous catalysis the word 'substrate' has sometimes been used to indicate the solid catalyst. We do not recommend this usage, which is also discouraged in Ref. 2.

Catalysis can be subdivided into homogeneous catalysis, in which only one phase is involved, and heterogeneous catalysis or surface catalysis, in which the reaction takes place at an interface between phases. Heterogeneous catalysis and enzyme catalysis are not dealt with explicitly in this report, since they have been covered in other reports [Refs. 2, 8].

If the apparent rate coefficient of a reaction (the rate divided by substrate concentrations raised to appropriate powers) can be expressed in the form

$$k_{\text{app}} = k_0 + 1kC$$

(37)

the coefficient $k_0$ is known as the catalytic constant for the catalyst $C$.

3.7 Inhibition

An inhibitor (Note h) is a substance that diminishes the rate of a chemical reaction, and the process is called inhibition. If a reaction in the absence of an inhibitor occurs with rate $v_0$, and in the presence of a given amount of inhibitor with rate $v$, the degree of inhibition, $\varepsilon_\text{i}$, which is the efficiency of inhibition, may be defined as

$$\varepsilon_\text{i} = \frac{v_0 - v}{v_0}$$

(38)

In contrast to a catalyst, an inhibitor may be consumed during the course of reaction.

A substance that reduces the rate of reaction by removing free-radical or other intermediates in a reaction can be called a scavenger.

4. TEMPERATURE EFFECTS

The rate constants of elementary reactions usually closely obey the equation

$$k = A e^{-E/RT}$$

(39)

which is known as the Arrhenius equation. The quantity $E$ is called the activation energy or energy of activation, and $A$ is best called the pre-exponential factor (Note i).

Convenient styles for expressing a rate constant and its temperature dependence are:

(a) $k = 3.6 \times 10^{10} \exp\left(-\frac{43.2 \text{ kJ mol}^{-1}}{RT}\right) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

(b) $k = 3.6 \times 10^{10} \exp\left(-\frac{5200 \text{ K}}{T}\right) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Note g. The term 'promoter' has also been used, and is recommended in Ref. 7; however, this term is used in surface catalysis in an entirely different sense, and we do not recommend it.

Note h. Inhibitors are sometimes called 'negative catalysts', but since the action of an inhibitor is fundamentally different from that of a catalyst this terminology is discouraged.

Note i. It is often called the frequency factor, but this terminology is not to be recommended since $A$ does not in general have the dimensions of frequency.
The first is the more traditional way; the second has the advantage that the value of \( R \) is not needed to calculate rates at different temperatures. The temperature-dependence of a pre-exponential factor may be expressed in a style such as

\[
k = 4.6 \times 10^6 (T/K)^5 \exp \left(-\frac{40.7 \text{kJ mol}^{-1}}{RT}\right) \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}
\]

The Arrhenius equation, with \( A \) and \( E \) practically constant, applies to many composite reactions as well as to elementary reactions, and the activation energy can then be called the overall activation energy. In general the activation energy is an experimental quantity obtained from a plot of \( \ln k \) against \( 1/T \) at constant pressure \( p \) and is defined by

\[
E = R \left( \frac{\partial \ln k}{\partial (1/2T)} \right) \frac{1}{p}
\]

The rate coefficient \( k \), in this equation must be expressed in units which involve concentration (e.g. \( \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \)) and not, for example, pressure. For some composite mechanisms Arrhenius plots show significant curvature, and if pre-exponential factors and activation energies are quoted in such cases the conditions (concentrations and temperature) should be clearly stated.

5. THEORIES OF REACTION RATES

The rate constants of elementary reactions are treated theoretically in terms of several types of theory, including collision theory, transition-state theory, molecular-dynamical theories, and stochastic theories.

5.1 Collision theory

In simple collision theory the frequencies of bimolecular collisions depend upon the collision diameter, \( da \) or \( db \), which in the simplest form of the theory is the sum of the radii \( (rA, rB) \) of the colliding molecular particles. The collision cross section (Note j), \( \sigma \), is defined as \( \pi d^2 \) or \( \pi d^2 \). These expressions are also applied to the equivalent quantities derived from experimental results.

The collision frequency, \( \delta \), is the number of collisions per unit time experienced by a single molecular particle on collision with molecules of type A. The collision number, \( Z_{AA} \) or \( Z_{AB} \), is the total number of collisions per unit time per unit volume, in a system containing only A gas or solute molecules, or containing two types of molecules A and B. The collision frequency factor \( z_{AA} \) or \( z_{AB} \) is the collision number divided by the Avogadro constant \( N \) and divided by the square of the concentration (for A-A collisions) or the product of the concentrations (for A-B collisions). In simple collision theory the rate constant of a bimolecular reaction between A and B is expressed as

\[
k = P_{AB} z_{AB} \exp(-E/RT)
\]

where \( P_{AB} \), the steric factor, allows for the fact that, even when the energy requirements are satisfied, all collisions are not effective.

5.2 Potential-energy surfaces

A potential-energy hypersurface is a hypersurface resulting from a plot of potential energy against a number of quantities (interatomic distances and angles). A three-dimensional diagram is obtained if potential energy is plotted against two such quantities, all others being held constant, and the resulting surface is known as a potential-energy surface. For a typical bimolecular reaction such a surface consists of two valleys meeting at a col or saddle point. A reaction path, or trajectory, is a path taken by a reaction over the potential-energy surface. The minimal reaction path is the easiest path, and corresponds to the path of steepest descent from the col into the two valleys.

An activated complex, often represented as \( X^+ \), can be defined as those assemblies of atoms which correspond to an arbitrary small region near the col of a potential-energy surface. It can also be defined as being related to a small region close to the position of maximum standard Gibbs energy along the reaction path. The state of an activated complex can be called the transition state, but this term should not be applied to the species itself.

A potential-energy profile is a two-dimensional section through a potential-energy surface along a reaction path or along the minimal reaction path. It represents the potential energy as a function of the reaction coordinate, which can be defined in various ways and is some measure of the progress of an individual reaction. Authors using this expression should

Note j. In the past the symbols \( d \) and \( \sigma \) have both been used for the collision diameter; this has been recommended in the Manual (Ref. 1). Our proposal is that \( d \) should be used for collision diameter and \( \sigma \) for collision cross section.
state clearly what they mean by it.

Potential-energy profiles are sometimes used in a schematic fashion to represent the course of a reaction occurring by consecutive steps. They essentially show only the relative energy levels of reactants, intermediates, activated complexes and products, and care must be taken with their interpretation (Note k).

5.3 Transition-state theory

Transition-state theory (Note 1) treats the rates of elementary reactions as if there were a special type of equilibrium, having an equilibrium constant $K^*$, existing between reactants and activated complexes. According to this theory the rate constant is given by

$$k(T) = \frac{kT}{h} \exp\left(\frac{-\Delta G^*}{RT}\right)$$  \hspace{1cm} (42)

where $k$ is the Boltzmann constant and $h$ is the Planck constant. The rate constant can also be expressed as (Note m)

$$k(T) = \frac{kT}{h} \exp\left(\frac{-\Delta S^*}{R} - \frac{\Delta H^*}{RT}\right)$$  \hspace{1cm} (43)

where $\Delta S^*$, the entropy of activation, is the standard molar change of entropy when the activated complex is formed from reactants and $\Delta H^*$, the enthalpy of activation, is the corresponding standard molar change of enthalpy. The quantities $\Delta E$ and $\Delta H^*$ are not quite the same, the relationship between them depending on the type of reaction. Also

$$k(T) = \frac{kT}{h} \exp\left(-\Delta G^*/RT\right)$$  \hspace{1cm} (44)

where $\Delta G^*$, known as the Gibbs energy of activation, is the standard molar Gibbs energy change for the conversion of reactants into activated complexes. A plot of standard molar Gibbs energy against a reaction coordinate is known as a Gibbs-energy profile; such plots, unlike potential-energy profiles, are temperature-dependent.

In principle equations (42)-(45) must be multiplied by a transmission coefficient, $\kappa$, which is the probability that an activated complex forms a particular set of products rather than reverting to reactants or forming alternative products.

It is to be emphasized that $K^*$, $\Delta G^*$, $\Delta S^*$ and $\Delta H^*$ occurring in eqs. (42)-(44) are not ordinary thermodynamic quantities, since one degree of freedom in the activated complex is ignored.

5.4 Reactions in solution

Most of the preceding applies to reactions in solution as well as to gas reactions. The present section deals with some special topics relating to solution reactions.

For a rapid reaction in solution the observed rate may depend on the rate of mixing of solutions of two reactants. This effect is known as mixing control, or as macroscopic diffusion control.

Microscopic diffusion control, or encounter control, relates to the microscopic rates with which reactant molecules come together. In dealing with reactions in solution it is important to distinguish between collisions and encounters. In the gas phase, when two molecules collide without reacting they at once separate, but in solution they may not


Note 1. It is also often known as activated-complex theory, but the expression 'transition-state theory' is now more commonly used.

Note m. Equations such as (42)-(44) are sometimes criticized as being dimensionally incorrect, and a similar situation exists with the corresponding thermodynamic relations, such as $K = \exp(-\Delta G^*/RT)$. No problem arises if the correct procedure is applied with respect to standard states. The IUPAC Commission on Thermodynamics (Ref. 4) has recently defined a "standard equilibrium constant", $K^*$; this is the practical equilibrium constant divided by the unit quantity so as to make it dimensionless. The parallel procedure in kinetics is to define a "standard rate constant", $k^*$, having the dimensions s$^{-1}$; thus, a practical second-order rate constant $k(T)$, in the units dm$^3$ mol$^{-1}$ s$^{-1}$, would be multiplied by 1 mol dm$^3$ to give $k^*(T)$ in s$^{-1}$. Our recommendation is that this device can be used by those who feel it helpful; the dimensional difficulty is, in our view, rather trivial.
separate immediately because of the cage of surrounding molecules. As a result there may be a group of collisions, such a group being called an encounter. The caging-in of solute molecules is known as the cage effect or the Franck-Rabinowitch effect (Note n).

If hypothetically a bimolecular reaction in solution occurred instantaneously when two reactant molecular entities made an encounter, the rate of the reaction would be equal to the rate of encounter and would be solely determined by the rates of diffusion; in some cases rotational diffusion may be rate limiting. Such a hypothetical reaction is said to be fully diffusion controlled or fully encounter controlled; the rate constant $k_D$ for such a reaction in water at $25^\circ$C would be of the order of $10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ in the absence of electrostatic effects. The hypothetical 'fully diffusion-controlled rate' corresponds to total microscopic diffusion control, and represents the asymptotic limit of the rate as the rate constant for the chemical conversion of the encounter pair into product becomes infinitely large.

Partial microscopic diffusion (or encounter) control refers to a situation where the rates of chemical conversion and of encounter are comparable. If the rate constant corresponding to total diffusion control is $k_D$, and that for the chemical conversion is $k_{\text{chem}}$, the experimental rate constant $k_{\text{exp}}$ is given by

$$\frac{1}{k_{\text{exp}}} = \frac{1}{k_D} + \frac{1}{k_{\text{chem}}} \quad (45)$$

If $k_{\text{chem}} = k_D$ the reaction is 50% diffusion controlled; if $k_{\text{chem}} > k_D$ there is more than 50% diffusion control, and if $k_{\text{chem}} < k_D$ there is less than 50% diffusion control. The degree of microscopic diffusion control cannot usually be determined with any precision.

The dependence on hydrostatic pressure $p$ of the rate coefficient for a reaction in solution is given by

$$\left( \frac{\partial \ln k}{\partial p} \right)_T = -\frac{\Delta V_p}{R T} \quad (46)$$

For the application of this equation the rate coefficients must be in pressure-independent concentration units (e.g. dm$^3$ mol$^{-1}$ s$^{-1}$) at a fixed temperature and pressure. The volume change $\Delta V_p$ is an experimental quantity known as the volume of activation. In transition-state theory $\Delta V_p$ is identified with $\Delta V^*$, the difference between the partial molar volume of the activated complex and the sum of the partial molar volumes of the reactants.

5.5 Molecular Dynamics

The quantitative study of the movement of systems over potential-energy surfaces is known as molecular dynamics; the term 'kinematics', sometimes used in this connection, is not recommended, since kinematics refers only to properties of motion that are independent of the nature of the forces.

A trajectory is a diagram or mathematical description that describes the motion of a system over the potential-energy surface. The Monte-Carlo procedure involves calculating a number of trajectories on the basis of a weighted random selection of initial parameters, obtained from a probability distribution function.

For an interaction between two molecules A and B, the impact parameter, $b$, is the distance of closest approach of the centers of gravity of A and B if there were no forces between A and B and they continued in the directions in which they moved at the beginning of the trajectory.

The threshold energy, $E_0$, is the minimum impact energy that will give rise to chemical reaction.

If a number of trajectories have been calculated, on the basis of a weighted random selection of initial parameters, the fraction of these trajectories that lead to reaction is known as the reaction probability, $P_r$. On the basis of simple hard-sphere collision theory the collision number $Z_A$ or $Z_B$ is proportional to $n d^2$, where $d$ is the collision diameter, and $n d^2$ may be called the hard-sphere collision cross section. Theoretical treatments and rate measurements lead to a corresponding quantity, the reaction cross section, $q_r$, and the reaction probability is given by

$$P_r = \frac{q_r}{n d^2} \quad (47)$$

When the potential-energy surface is such that the system performs a number of vibrations and rotations in the region of the col, the intermediate is known as a long-lived collision complex, and the reaction is said to be indirect. A reaction for which there is a short-lived activated complex is said to be direct. A direct reaction in which the forces are released very rapidly is said to be impulsive.

An attractive potential-energy surface for a system A + B → C is one in which the initial descent of the system into the product valley is associated with a substantial decrease in the A-B distance, and with little separation between the products A-B and C; this means that considerable heat of reaction passes into the A-B bond. Surfaces of this type are also known as early-downhill surfaces, and one speaks of an early transition state. The term electron jump can be applied to a reaction in which there is an electron transfer with the formation of an ionic intermediate.

A repulsive potential-energy surface, or a late-downhill surface, is one in which the initial descent of the system into the product valley is accompanied by little change in the A-B distance but by the separation of the products AB + C. The transition state is generally still in the coordinate of approach, but is located later along that coordinate than for an attractive surface.

An energy barrier in the entry valley has been called a Type-I barrier, while an energy barrier in the exit valley has been called a Type-II barrier.

If a reaction A + B → C is studied in a molecular-beam experiment and the product AB travels in much the same direction as the reactant A, the reaction is known as a stripping reaction. A stripping reaction of an extreme type is known as a spectator-stripping reaction, C being essentially a spectator to the interaction between A and B.

If on the other hand, the product AB travels backward from the center of mass of the system the reaction is known as a rebound reaction.

The term adiabatic should be used with great care with reference to a chemical reaction involving excited electronic states. The term non-adiabatic reaction is often used synonymously with 'reaction in which there is a change of multiplicity', but this is not always satisfactory. If the terms adiabatic and non-adiabatic are used they should be clearly defined with reference to the approximation used in constructing the potential-energy surface.

5.6 Stochastic theories

Theories that treat reaction rates in terms of the probabilities of transitions between the various energy levels in the reactant molecules are known as stochastic theories.

ACKNOWLEDGEMENTS

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GLOSSARY
SYMBOLS FOR CHEMICAL KINETICS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Quantity</th>
<th>SI Unit</th>
<th>Customary Multiple</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, b, y, z, etc.</td>
<td>coefficients in stoichiometric equation</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[A][B], a_A, a_B, etc.</td>
<td>concentration of substance A,B, etc.</td>
<td>mol m(^{-3})</td>
<td>mol dm(^{-3})</td>
</tr>
<tr>
<td>(A)</td>
<td>pre-exponential factor</td>
<td>Same as for rate constant (k)</td>
<td></td>
</tr>
<tr>
<td>(A_B)</td>
<td>surface area</td>
<td>m(^2)</td>
<td>m(^2), cm(^2)</td>
</tr>
<tr>
<td>(b)</td>
<td>impact parameter</td>
<td>m</td>
<td>nm, pm</td>
</tr>
<tr>
<td>(C_P)</td>
<td>molar heat capacity</td>
<td>J K(^{-1}) mol(^{-1})</td>
<td>J K(^{-1}) mol(^{-1})</td>
</tr>
<tr>
<td>(c)</td>
<td>concentration</td>
<td>mol m(^{-3})</td>
<td>mol dm(^{-3})</td>
</tr>
<tr>
<td>(C)</td>
<td>particle number density</td>
<td>m(^{-3})</td>
<td>m(^{-3}), dm(^{-3})</td>
</tr>
<tr>
<td>(D)</td>
<td>diffusion coefficient</td>
<td>m(^2) s(^{-1})</td>
<td>m(^2) s(^{-1}), cm(^2) s(^{-1})</td>
</tr>
<tr>
<td>(D)</td>
<td>molar bond dissociation energy</td>
<td>J mol(^{-1})</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>(d_{AA}, d_{AB})</td>
<td>collision diameter</td>
<td>m</td>
<td>nm, pm</td>
</tr>
<tr>
<td>(e)</td>
<td>base of natural logarithms</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(E)</td>
<td>energy</td>
<td>J</td>
<td>J, kJ</td>
</tr>
<tr>
<td>(E)</td>
<td>energy of activation</td>
<td>J mol(^{-1})</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>(E_0)</td>
<td>threshold energy</td>
<td>J mol(^{-1})</td>
<td>J mol(^{-1}), kJ mol(^{-1})</td>
</tr>
<tr>
<td>(E_D, D)</td>
<td>molar bond dissociation energy</td>
<td>J mol(^{-1})</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>(\Delta H^\ddagger)</td>
<td>standard molar enthalpy of activation</td>
<td>J mol(^{-1})</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>(\Delta G^\ddagger)</td>
<td>standard molar Gibbs energy of activation</td>
<td>J mol(^{-1})</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>(h)</td>
<td>Planck constant</td>
<td>J s</td>
<td>J s</td>
</tr>
<tr>
<td>(I)</td>
<td>intensity of light</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(k, k(T))</td>
<td>rate coefficient or constant (Note o)</td>
<td>((m^3) mol(^{-1}) s(^{-1})(^n)-1 s(^{-1}))</td>
<td>((dm^3) mol(^{-1}) s(^{-1})(^n)-1 s(^{-1}))</td>
</tr>
</tbody>
</table>

Note o. When the rate constant and the Boltzmann constant appear in the same equation they should be clearly distinguished, either by using bold face for the Boltzmann constant or using \(k(T)\) for the rate constant.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Quantity</th>
<th>SI Unit</th>
<th>Customary Multiple</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k^o )</td>
<td>standard rate constant</td>
<td>s(^{-1})</td>
<td>s(^{-1})</td>
</tr>
<tr>
<td>( k_A, k_Y, \text{etc.} )</td>
<td>rate coefficient or constant for the consumption of A or formation of Y</td>
<td></td>
<td>Same as for ( k )</td>
</tr>
<tr>
<td>( k )</td>
<td>Boltzmann constant</td>
<td>J K(^{-1})</td>
<td>J K(^{-1})</td>
</tr>
<tr>
<td>( K^o )</td>
<td>standard equilibrium constant</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( K_c )</td>
<td>equilibrium constant with respect to concentration</td>
<td>(mol m(^{-3}))(\Delta V)</td>
<td>(mol dm(^{-3}))(\Delta V)</td>
</tr>
<tr>
<td>( K_p )</td>
<td>equilibrium constant with respect to pressure</td>
<td>(Pa)(\Delta V)</td>
<td>(Pa)(\Delta V)(kPa)(\Delta V)</td>
</tr>
<tr>
<td>( K_m )</td>
<td>Michaelis constant</td>
<td>mol m(^{-3})</td>
<td>mol dm(^{-3}), mmol</td>
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<td>( L, N_A )</td>
<td>Avogadro constant</td>
<td>mol(^{-1})</td>
<td>mol(^{-1})</td>
</tr>
<tr>
<td>( M )</td>
<td>chemically-inert collision partner (third body)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( N )</td>
<td>number of particles</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( n )</td>
<td>overall order ((\alpha + \beta + \ldots)); amount of substance</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \Delta S^\ddagger )</td>
<td>standard molar entropy of activation</td>
<td>J K(^{-1}) mol(^{-1})</td>
<td>J K(^{-1}) mol(^{-1})</td>
</tr>
<tr>
<td>( p )</td>
<td>pressure</td>
<td>Pa</td>
<td>Pa, kPa</td>
</tr>
<tr>
<td>( P_r )</td>
<td>reaction probability</td>
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<td>-</td>
</tr>
<tr>
<td>( R )</td>
<td>gas constant</td>
<td>J K(^{-1}) mol(^{-1})</td>
<td>J K(^{-1}) mol(^{-1})</td>
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<tr>
<td>( r )</td>
<td>molecular radius</td>
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<td>nm</td>
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<tr>
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<td>thermodynamic or absolute temperature</td>
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<td>K</td>
</tr>
<tr>
<td>( t )</td>
<td>time</td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>( t_\mathbf{1/2} )</td>
<td>half life</td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>( v )</td>
<td>rate of reaction</td>
<td>mol m(^{-3}) s(^{-1})</td>
<td>mol dm(^{-3}) s(^{-1})</td>
</tr>
<tr>
<td>( v_A, v_Z )</td>
<td>rate of consumption or formation</td>
<td>mol m(^{-3}) s(^{-1})</td>
<td>mol dm(^{-3}) s(^{-1})</td>
</tr>
<tr>
<td>( V )</td>
<td>volume</td>
<td>m(^3)</td>
<td>dm(^3), cm(^3)</td>
</tr>
<tr>
<td>( Z_A )</td>
<td>collision frequency (number of collisions per second experienced by a single molecule on collision with molecules of type A)</td>
<td>s(^{-1})</td>
<td>s(^{-1})</td>
</tr>
<tr>
<td>( Z_{AA}, Z_{AB} )</td>
<td>collision number (number of A-A or A-B collisions per unit volume and per unit time)</td>
<td>m(^{-3}) s(^{-1})</td>
<td>dm(^{-3}) s(^{-1}), cm(^{-3}) s(^{-1})</td>
</tr>
<tr>
<td>( z_{AA}, z_{AB} )</td>
<td>collision frequency factor ((Z_{AA} \text{ or } Z_{AB} \text{ divided by the Avogadro constant } L\text{ and divided by the product of the concentrations})</td>
<td>m(^3)mol(^{-1})s(^{-1})</td>
<td>dm(^3)mol(^{-1})s(^{-1})</td>
</tr>
<tr>
<td>Symbol</td>
<td>Quantity</td>
<td>SI Unit</td>
<td>Customary Multiple</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------</td>
<td>---------</td>
<td>--------------------</td>
</tr>
<tr>
<td>( \alpha, \beta ) (( \alpha, \beta ))</td>
<td>order with respect to ( A, B )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \gamma ) (( \gamma ))</td>
<td>surface recombination efficiency</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \Gamma_\sigma ) (( \gamma ))</td>
<td>surface concentration</td>
<td>( \text{mol m}^{-2} )</td>
<td>( \text{mol m}^{-2} )</td>
</tr>
<tr>
<td>( \delta ) (( \delta ))</td>
<td>length of a portion of a reaction path which defines the activated state</td>
<td>( m )</td>
<td>( \text{nm}, \text{pm} )</td>
</tr>
<tr>
<td>( \xi ) (( \xi ))</td>
<td>extent of reaction</td>
<td>( \text{mol} )</td>
<td>( \text{mol} )</td>
</tr>
<tr>
<td>( \xi )</td>
<td>rate of conversion</td>
<td>( \text{mol s}^{-1} )</td>
<td>( \text{mol s}^{-1} )</td>
</tr>
<tr>
<td>( \varepsilon ) (( \varepsilon ))</td>
<td>molecular energy</td>
<td>( \text{J} )</td>
<td>( \text{J, aJ} )</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>relative dielectric constant</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \varepsilon_i )</td>
<td>degree (efficiency) of inhibition</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \eta ) (( \eta ))</td>
<td>viscosity</td>
<td>( \text{kg m}^{-1}\text{s}^{-1} ) (( \equiv \text{N s m}^{-2} ))</td>
<td>( \text{kg m}^{-1}\text{s}^{-1} )</td>
</tr>
<tr>
<td>( \nu ) (( \nu ))</td>
<td>stoichiometric coefficient</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \phi ) (( \phi ))</td>
<td>chemical flux, or chemiflux</td>
<td>( \text{mol m}^{-3}\text{s}^{-1} )</td>
<td>( \text{mol dm}^{-3}\text{s}^{-1} )</td>
</tr>
<tr>
<td>( \phi )</td>
<td>photochemical yield</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \rho ) (( \rho ))</td>
<td>density</td>
<td>( \text{kg m}^{-3} )</td>
<td>( \text{g dm}^{-3} )</td>
</tr>
<tr>
<td>( \rho ) (( \rho ))</td>
<td>density of states</td>
<td>( \text{J}^{-1} )</td>
<td>( \text{J}^{-1} )</td>
</tr>
<tr>
<td>( \sigma ) (( \sigma ))</td>
<td>reaction cross section</td>
<td>( \text{m}^2 )</td>
<td>( \text{nm}^2, \text{pm}^2 )</td>
</tr>
<tr>
<td>( \tau ) (( \tau ))</td>
<td>relaxation time</td>
<td>( s )</td>
<td>( s )</td>
</tr>
</tbody>
</table>

**EXPONENTS**

- \( \alpha, \beta \) | order with respect to \( A, B \) (e.g., \( v = k[A]^\alpha B^\beta \))

**SUPERSCRIPTS**

- \( \dagger \) | activated complex
- \( * \) | excited state

**SUBSCRIPTS**

- \( o \) | to indicate initial (\( t = 0 \)) conditions; e.g. \( [A]_0, \sigma_{0,A} \)
- \( o \) | to indicate the low-pressure limit of a second-order rate coefficient for a unimolecular gas reaction
- \( o \) | to indicate a property at the absolute zero (e.g. \( E_0 \))
- \( o \) | to indicate a threshold property
- \( \infty \) | to indicate the high-pressure limit of a first-order rate coefficient for a unimolecular gas reaction
to indicate a limiting value (e.g. a concentration) at $t = \infty$.

$i, A, X, \text{etc.}$ the species $i, A, X \text{etc.};$ a negative sign indicates the consumption of that species.

$s$ surface, as in $As$

$1, -1, +1, -1, 12, 21, \text{etc.}$ with $k$, to refer to numbered reactions