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A GLOSSARY OF TERMS USED IN CHEMICAL KINETICS, INCLUDING REACTION DYNAMICS

(IUPAC Recommendations 1996)

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A glossary of terms used in chemical kinetics, including reaction dynamics (IUPAC Recommendations 1996)

Synopsis

This Glossary is a compilation of terminology recommendations in the field of chemical kinetics. Every effort has been made to include what appear to be the most commonly accepted definitions. Is is hoped that the Glossary will be a helpful guide to those who are writing books and articles in the field. The reader is warned, however, that alternative definitions of some of the terms, such as Adiabatic and Rate-Controlling Step, are frequently to be found in the scientific literature.

Expressions shown in *italics* are to be found as separate items in this glossary.

Acid-Base Catalysis. General

Catalysis by acids or bases in solution is said to be general when it is possible to detect *catalysis* brought about by species other than the ions formed from the solvent itself (e.g., when water is the solvent, by species other than H^+ and OH^- ions).

See *Catalysis*.

Acid-Base Catalysis, Specific

Catalysis by acids or bases in solution is said to be specific when the only observable catalytic effects are those due to the ions formed from the solvent itself (e.g., if when water is the solvent the only observable *catalysis* is that due to the H^+ and OH^- ions).

See *Catalysis*.

Activated Complex

An activated complex is defined as a species corresponding to an arbitrary infinitesimally small region at or near the col (saddle-point) of a *potential-energy surface*. The term 'transition state' is synonymous with activated complex. The superscript ‡ is used to denote an activated complex.

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The activated complex is also sometimes defined as being related to a small region close to the position of maximum standard Gibbs energy along the reaction path.

Some workers regard an activated complex as a species having enough energy to react, with no specification of structure. This definition, however, is no longer recommended; such a species is better called an *energized species.*

PAC 1983, **55**, 1285; see also PAC 1981, **53**, (764).

Activation

This word is used in different senses:

(1) Input of external energy into a chemical system is said to bring about activation of the system.

(2) An added substance that increases the rate of a catalyzed reaction is known as an activator, and the effect is called activation.

If v_0 is the rate of the catalyzed reaction in the absence of the activator, and v is the rate in its presence, the degree of activation ϵ_a is defined by

$$\epsilon_a = (v - v_0) / v_0 = (v / v_0) - 1$$

(3) When some of the energy required for a reaction to occur is provided by a previous exothermic chemical reaction there is said to be chemical activation.

See *Chemical Activation*, *Catalysis.*
Contrast *Inhibition.*

Activation Energy, E_a

The activation energy, also known as the energy of activation, is an operationally defined quantity expressing the dependence of a *rate constant* or *rate coefficient* k on the temperature, according to the relationship

$$E_a = -R\,\partial \ln k / \partial(1/T)$$

This equation is derived from the Arrhenius equation, $k = A \exp(-E_a/RT)$, in which A is termed the pre-exponential factor.

The Arrhenius equation, with A and E_a 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.

The *rate constants* used to obtain the activation energy may be experimental or calculated ones. For an *elementary reaction* the activation energy can be shown to be the average energy of molecules actually undergoing reaction minus the average energy of reactant molecules.

See also *Intrinsic Activation Energy, Enthalpy of Activation.*

PAC 1983, **55**, 1313; 1981, **53**, 764; Green Book, 55.

Adiabatic

This word is used with various different meanings, and when it is used it should be defined.

In thermodynamics 'adiabatic' is used in a macroscopic sense to refer to a process occurring in a thermally insulated system, so that there is no flow of heat to or from the surroundings.

In reaction dynamics, the word has been used in a microscopic sense, with a range of meanings which have only a tenuous relationship to the thermodynamic meaning or the etymology. Whereas the thermodynamic meaning relates to conditions imposed on a process by an observer, the microscopic meaning relates to conditions under which the process occurs naturally.

The microscopic meanings, as used in reaction dynamics, all have in common the feature that quantum states remain unchanged during the course of reaction. Different quantum states may be referred to:

(1) A reaction in which there is no change of electronic state or multiplicity has been called adiabatic, or more specifically electronically adiabatic.

(2) A reaction in which there is no change of vibrational state during the course of reaction has been said to be vibrationally adiabatic. More loosely, the expression has been applied to a process in which excess vibrational energy in the *reactants* appears as vibrational energy in the *products*, or in which ground-state vibration in the reactants leads to ground state vibration in the products.

(3) A reaction in which excess rotational energy in the reactants appears as rotational energy in the products, or in which ground-state rotation in the reactants leads to ground-state rotation in the products, has been referred to as rotationally adiabatic.

(4) In the *Rice-Ramsperger-Kassel-Marcus (RRKM)* theory of unimolecular reactions, a degree of freedom whose quantum number is more or less preserved during energization and subsequent reaction has been called 'adiabatic'; the word 'inactive' has also been applied to it.

A reaction that is not adiabatic is referred to as nonadiabatic or diabatic, and some workers make a distinction between the two words.

For a dissussion of how the meaning in dynamics evolved from the thermodynamic meaning see Laidler (1994).

See also *Diabatic Coupling*

Adiabatic Transition-State Theory

This is a form of *transition-state theory* in which the system is assumed to preserve its internal quantum states as it moves over the *potential-energy surface*. A detailed state-to-state scattering theory version of adiabatic transition-state theory has been referred to as the adiabatic channel model. For further details see Quack and Troe (1975).

Adiabatic Treatments of Reaction Rates

These are treatments of reaction rates in which the system is assumed to remain on a single *potential-energy surface* during the entire course of reaction, or to remain in a conserved internal state.

Angular Distribution

With reference to the center of mass, the *products* of a bimolecular reaction are scattered with respect to the initial velocity vector, and the distribution of scattering angles is known as the angular distribution.

Arrhenius *A* Factor See *Pre-Exponential Factor.*

Arrhenius Equation

This is an equation that represents the dependence of the *rate constant* k of a reaction on the absolute temperature T:

$$k = A \exp(-E_a/RT)$$

In its original form the *pre-exponential factor* A and the *activation energy* E_a are considered to be temperature-independent.

See also *Modified Arrhenius Equation.*

PAC 1981, **53**, (763); 1983, **55**, 1291; Gold Book, 39; Green Book, 55.

Atom-Molecule Complex Mechanism

This is a mechanism that sometimes applies to the combination of atoms, but rarely of free radicals. In this mechanism the atom A first combines with a third body or *chaperon,*

$$A + M \rightarrow AM,$$

and the complex AM then forms A_2 + M by collision with another atom A

Contrast the *Energy-Transfer Mechanism.*

Attractive-Mixed-Repulsive (AMR) Classification

This is a classification of *potential-energy surfaces* in which a highly attractive surface is at one extreme and a highly repulsive surface is at the other. The energy release in intermediate cases is referred to as mixed.

Attractive Potential-Energy Surface

This is a *potential-energy surface* for a process A + B-C 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. In terms of a *potential-energy profile*, the energy barrier occurs in the early stage of the reaction path.

Attractive surfaces are also called early-downhill surfaces, and the barrier in such a surface is called a Type-I barrier.

Beam-Gas Experiments See *Molecular Beams.*

Bond-Energy-Bond-Order Method

This is an empirical procedure for estimating *activation energies*, involving empirical relationships between bond length, bond dissociation energy, and bond order.

Branching Ratio

The ratio of alternative *products* formed in a reaction (e.g. the HF/DF ratio in the reaction between F and HD), is known as the branching ratio.

Brønsted Relationship or Brønsted Relation

This expression applies to either of the equations

$$k_a/p = G_a(K_a q/p)^{\alpha} \quad \text{(for acid catalysis)}$$

or

$$k_b/q = G_b(K_b p/q)^{\beta} \quad \text{(for base catalysis)}$$

where α, β, G_a and G_b are constant for a given reaction series, α and β are called Brønsted exponents, k_a and k_b are *catalytic coefficients* (or rate coefficients of reactions whose rates depend on the concentrations of an acid or a base, respectively), K_a is the acid dissociation constant of the acid catalyst, p is the number of equivalent acidic protons in the acid, and q is the number of equivalent basic sites in its conjugate base. The second equation is the corresponding equation for a base catalyst.

The Brønsted relation is often termed the Brønsted *catalysis* law (or the Catalysis Law). Although justifiable on historical grounds, this name is not recommended, since Brønsted relations are now known to apply to many uncatalyzed reactions (such as simple *proton-transfer reactions*).

See also *Linear Gibbs Energy Relation.*

PAC 1983, **55**, 1295; Gold Book, 49.

Cage

This word applies to an aggregate of molecules, generally in the condensed phase, that surround the fragments formed by thermal or photochemical dissociation of a species. Because the cage hinders the separation of the fragments by diffusion, they may preferentially react with one another (*cage effect*) but not necessarily to re-form the precursor species. For example,

$$\text{R-N=N-R} \rightarrow [\text{R}\bullet + \text{N}\equiv\text{N} + \text{R}\bullet]_{\text{cage}} \rightarrow \text{R-R} + \text{N}_2$$

See also *Geminate Recombination.*

PAC 1983, **55** 1295; Gold Book, 51.

Cage Effect

When in a condensed phase, or in a dense gas, *reactant* molecules come together, or species are formed in proximity to one another, and are caged in by surrounding molecules, they may undergo a set of collisions known as an *encounter*; the term "cage effect" is then applied.

The cage effect is also known as the Franck-Rabinowitch effect.

See also *Cage, Encounter.*

PAC 1981, **53**, (766); Gold Book 51.

Canonical Rate Constant

The *rate constant* for a system in which the *reactants* are in thermal equilibrium at a given temperature is known as the canonical rate constant.

In statistical mechanics the expression "canonical ensemble" is used to refer to a closed system in thermal equilibrium, the species being present in a statistical distribution. By contrast, a microcanonical ensemble is composed of systems all having the same energy: a canonical ensemble therefore consists of a statistical distribution of microcanonical ensembles. The canonical or thermal rate constant can be obtained from the microcanonical rate constant by summing over the energy, taking into account the statistical distribution.

Canonical Variational Transition-State Theory (CVTST)

This is a development of *transition-state theory* in which the position of the *dividing surface* is varied so as to minimize the *rate constant* at a given temperature.

Compare *Microcanonical Variational Transition-State Theory.*

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. The catalyst is both a *reactant* and *product* of the reaction. The words catalyst and catalysis should not be used when the added substance reduces the rate of reaction (see *Inhibitor*).

Catalysis can be classified as homogeneous catalysis, in which only one phase is involved, and heterogeneous catalysis, in which the reaction occurs at or near an interface between phases. Catalysis brought about by one of the products of a reaction is called autocatalysis. Catalysis brought about by a group on a reactant molecule itself is called intramolecular catalysis.

The term catalysis is also often used when the substance is consumed in the reaction (for example: base-catalysed hydrolysis of esters). Striclty such a substance should be called an activator.

PAC 1981, **53**, 762.

Catalytic Coefficient

If the *rate of reaction*, v, is expressible in the form

$$v = (k_o + \textstyle\sum_i k_i [C_i]^{n_i}) [A]^{\alpha}[B]^{\beta}.....$$

where A, B,... are *reactants* and C_i represents one of a set of catalysts, then the proportionality factor k_i is the catalytic coefficient of the particular catalyst C_i. Normally the partial *order of reaction* n_i with respect to a catalyst is unity, so that k_i is an $(\alpha + \beta + ... + 1)$th order rate coefficient. The proportionality factor k_0 is the $(\alpha + \beta + ...)$th order rate coefficient of the uncatalyzed component of the total reaction.

For example, if there is catalysis by hydrogen and hydroxide ions, and the rate constant can be expressed in the form

$$k = k_0 + k_{H+}[H^+] + k_{OH^-}[OH^-]$$

then k_{H+} and k_{OH^-} are the catalytic coefficients for H^+ and OH^- respectively. The constant k_0 relates to the uncatalyzed reaction.

PAC 1981, **53**, (763); Gold Book, **57**. PAC 1983, **53**, 1297.

Centrifugal Barrier

In a reaction without an electronic energy barrier, or its reverse, the rotational energy of the transition state gives rise to a reaction barrier, which is known as the centrifugal barrier.

Chain Branching

When in a *chain reaction* there is a net increase in the number of *chain carriers* there is said to be chain branching. A simple example of a chain-propagating reaction leading to chain branching is

$$O + H_2 \rightarrow OH + H$$

in which there is one *chain carrier* (an oxygen atom) on the left and two chain carriers (a hydrogen atom and a hydroxyl radical) on the right.

See also *Degenerate Chain Branching*.

Chain Carrier

A species, such as an atom or free radical, which is involved in *chain-propagating reactions* is known as a chain carrier.

Chain Initiation

The process in a chain reaction that is responsible for the formation of a chain carrier is referred to as chain initiation.

Chain Length, δ

In a *chain reaction* the chain length is defined as the average number of times the closed cycle of reactions (involving the *chain-propagating reactions*) is repeated. It is equal to the rate of the overall reaction divided by the rate of the *initiation reaction*.

PAC 1981, **53**, (762); Gold Book, 61.

Chain-Propagating Reaction

A chain-propagating reaction, or more simply a propagating reaction, is an elementary step in a chain reaction in which one *chain carrier* is converted into another. The conversion can be a unimolecular reaction or a bimolecular reaction with a reactant molecule.

Chain Reaction

A *composite reaction* sometimes includes a cycle of elementary reactions such that certain reaction intermediates consumed in one step are regenerated in another. If such a cycle is repeated more than once the reaction is known as a chain reaction. The reaction intermediates may be atoms, molecules, free radicals or ions.

There are different kinds of chain reactions including: straight chain reactions, branching chain reactions, energetic branching chain reactions, and degenerate branching chain reactions.

See also *Chain Branching, Degenerate Chain Branching*.

PAC 1981, **53**, (762); 1983, **5**, 1297; Gold Book, 61.

Chain-Termination Reaction

An elementary step in a *chain reaction* in which there is a net removal of chain carriers is known as a chain-termination reaction, or simply as a termination reaction or step.

PAC 1983, **55**, 1365; Gold Book, 421.

Channel

Regions of *potential-energy surfaces* where there are valleys are sometimes referred to as arrangement channels. The *reactant* channel or entrance channel is that corresponding to configurations similar to those of the reactants; the *product* channel or exit channel relates to configurations similar to those of the products. In collision theory, the specification of a complete set of quantum numbers in a given arrangement channel is called a channel.

See also *Entrance Channel, Exit Channel.*

Chaperon

A species that facilitates a combination reaction between atoms or radicals, or the reverse process, is known as a chaperon. It is a special case of a *third body*.

Chemical Activation

When some of the energy required for a reaction is provided by a preceding exothermic chemical reaction there is said to be chemical activation. For example, in the scheme

$$A + B \rightarrow X^*$$

$$X^* \rightarrow Y + Z$$

some or all of the energy required for X to decompose is provided by the first reaction.

Chemical Induction (Coupling)

When in a chemical system one reaction accelerates another there is said to be chemical induction or coupling. It is due to an intermediate or *product* of the inducing reaction participating in the second reaction.

Chemical induction is often observed in oxidation-reduction reactions, *chain reactions*, and biological reactions. Sometimes a reaction having $\Delta G^\circ > 0$ is induced by a simultaneous process having $\Delta G^\circ < 0$.

Chemiluminescence

Emission of radiation resulting from a chemical reaction is referred to as chemiluminescence. The emitting species may be a reaction *product* or a species excited by energy transfer from an excited reaction product. The excitation may be electronic, vibrational or rotational; if the luminescence occurs in the infrared the expression infrared chemiluminescence is used.

Col, or Saddle Point

A mountain-pass in a *potential-energy surface* is known as a col or saddle point. It is a point at which the gradient is zero along all coordinates, and the curvature is positive along all but one coordinate, which is the reaction coordinate along which the curvature is negative.

Collinear Reaction

This is a reaction assumed to occur via an *activated complex* in which all of the atoms directly involved in the process lie along a straight line.

Collision Cross Section, σ_c

The area $\pi d_{AA}{}^2$ or $\pi d_{AB}{}^2$ of a circle having a radius equal to the *collision diameter* is known as the collision cross section.

Contrast *Reaction Cross Section*.

Collision Density, (Collision Number), Z_{AA} or Z_{AB}

The collision density (often called *collision number*), Z_{AA} or Z_{AB}, is the total number of collisions of type A–A or A–B per time and volume, in a system containing only gas or solute molecules of type A, or containing molecules of type A and B.

See also *Collision Frequency*.

Collision Diameter, d_{AA} or d_{AB}

In simple collision theory the frequency of bimolecular collisions depend upon the collision diameter, d_{AA} or d_{AB}, which in the simplest form of the theory is the sum of the radii (r_{AA} or r_{AB}) of the colliding molecular entities. The collision cross section, σ, is defined as πd_{AA}^2 or πd_{AB}^2. These expressions are also applied to the equivalent quantities derived from experimental results.

PAC 1981, **53**, (764); Gold Book, 77.

Collision Efficiency, B_c

The collision efficiency, or de-energization efficiency, is defined by

$$k_{-1} = B_c \, k_{-1}^{sc}$$

where k_{-1} is the *rate constant* for a particular substance M when it brings about the de-energization process

$$M + A^* \rightarrow M + A,$$

and k_{-1}^{sc} is the corresponding rate constant for a reference molecule M_r that de-energizes A^* on every collision; that is, the reference molecule M_r undergoes *strong collisions*, and by definition has a collision efficiency B_c of unity. The species A^* is usually in a vibrationally-excited state, and A has energy less than that required for reaction to occur.

Collision, Elastic

A particle (atom or molecule) can undergo a change in its state of excitation as a result of collisions with other particles. In an elastic collision an exchange only of kinetic energy takes place between the colliding species; in an inelastic collision there is an interchange between the kinetic energy and the internal energy of the particle.

PAC 1985, **57**, 1463; Gold Book, 77.

Collision Frequency, z_A

The collision frequency is the number of collisions, z_A, per time experienced by a single molecular entity on collision with molecules of type A. The collision density (also called *collision number*), Z_{AA} or Z_{AB}, is the total number of collisions per time and volume, in a system containing only gas or solute molecules of type A, 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 L 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

$$k = P_{AB} z_{AB} \, e^{-E/RT}$$

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

PAC 1981, **53**, (764); Gold Book, 77.

Collision Frequency Factor, z_{AA} or z_{AB} See under *Collision Frequency.*

Collision Number Now called *Collision Density* (q.v.); see also *Collision Frequency.*

Collision Theory

Various collision theories, dealing with the frequency of collision between *reactant* molecules, have been put forward. In the earliest theories reactant molecules were regarded as hard spheres, and a collision was considered to occur when the distance d between the centres of two molecules was equal to the sum of their radii. For a gas containing only one type of molecule, A, the collision density is given by simple collision theory as

$$Z_{AA} = \tfrac{1}{2}\sqrt{2}\pi\sigma^2 u N_A^2$$

Here N_A is the number density of molecules and u is the mean molecular speed, given by kinetic theory to be $(8k_BT/\pi m)^{1/2}$, where m is the molecular mass, and $\sigma = \pi d_{AA}^2$. Thus

$$Z_{AA} = 2N_A^2\ \sigma^2(\pi k_B T/m)^{1/2}$$

The corresponding expression for the collision density Z_{AB} for two unlike molecules A and B, of masses m_A and m_B is

$$Z_{AB} = N_A N_B\ \sigma^2(\pi k_B T/\mu)^{1/2}$$

where μ is the reduced mass $m_A m_B/(m_A+m_B)$, and $\sigma = \pi d_{AB}^2$.

For the *collision frequency factor* these formulations lead to the following expression:

$$z_{AA} \text{ or } z_{AB} = L\ \sigma^2(8\pi k_B T/\mu)^{1/2}$$

where L is the Avogadro constant.

More advanced collision theories, not involving the assumption that molecules behave as hard spheres, are known as *generalized kinetic theories.*

Competition See *Composite Mechanisms.*

Complex Mechanism

This term is sometimes applied to an *elementary reaction* which proceeds via an intermediate species having a lifetime longer than a few rotational periods, in contrast to a *direct reaction.* However, in view of the danger of confusion with a reaction occurring in more than one step (a *composite reaction*) this usage is not to be recommended; it is better to use the terms complex-mode mechanism or *complex-mode reaction.*

Complex-Mode Reaction

An elementary reaction which proceeds via an intermediate species having a lifetime longer than a few rotational periods is known as a complex-mode reaction, or as an *indirect* reaction.

Contrast *Direct Reaction.*

Complex Reaction See *Composite Mechanism.*

Composite Mechanism

A reaction that involves more than one elementary reaction is said to occur by a composite mechanism. The terms *complex mechanism indirect mechanism*, and *step-wise mechanism* are also commonly used.

There are two main kinds of evidence for a composite mechanism:

(1) The kinetic equation for the reaction does not correspond to its stoichiometry.

(2) There is experimental evidence, direct or indirect, for intermediates of such a nature that it is necessary to conclude that more than one elementary reaction is involved.

There are many types of composite mechanisms, for example:

a. Reactions occurring in parallel, such as

$$\begin{array}{l} A \rightarrow Y \\ A \rightarrow Z \end{array}$$

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

$$\begin{array}{l} A + B \rightarrow Y \\ A + C \rightarrow Z \end{array}$$

where B and C compete with one another for A.

b. Reactions occurring in forward and reverse directions, such as

$$A + B \rightleftarrows Z$$

are called opposing reactions.

c. Reactions occurring in sequence, such as

$$A \rightarrow X \rightarrow Y \rightarrow Z$$

are known as consecutive reactions.

d. 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

$$A \rightarrow X \rightarrow Y \rightarrow Z$$

the intermediate Y may catalyze the reaction $A \rightarrow X$ (positive feedback) or it may inhibit it (negative feedback).

e. *Chain reactions.*

PAC 1981, 53, (760).

Conventional Transition-State Theory See *Transition-State Theory*.

Coupling See *Chemical Induction*.

Critical Energy. or Threshold Energy

A chemical reaction cannot occur, except by *quantum-mechanical tunnelling*, unless the total energy available is greater than a certain energy, which is known as the critical energy, or the threshold energy.

Cross Section See *Collision Cross Section*, and *Reaction Cross Section*.

Crossed Molecular Beams See *Molecular Beams*.

De-Energization Efficiency See *Collision Efficiency*.

Degenerate Chain Branching

Sometimes *chain branching* is brought about by an intermediate which has a long lifetime compared with an ordinary free radical. If this intermediate can break down in different ways, only one of which leads to branching, there may be a relatively slow increase in the number of radicals, and there is said to be degenerate chain branching.

Degree of Activation See under *Activation*.

Degree of Inhibition See under *Inhibition*.

Density of States, N_E

This is the number of quantum states per unit energy range at an energy E. The total number of states in the energy range E to $E+\mathrm{d}E$ is given by $N_E\,\mathrm{d}E$. This definition may involve the specification of vibrational and rotational quantum numbers.

See also *Sum of States*.

Detailed Balance at Equilibrium

The principle of detailed balance at equilibrium states that in a system at equilibrium each collision has an exact counterpart in the reverse direction, and the rate of every chemical process is exactly equal to the rate of the reverse process. This principle is closely related to the principle of *microscopic reversibility at equilibrium*.

The above definition of detailed balance corresponds to that originally given by R.H. Fowler in 1936. However, since many workers interchange the meanings of detailed balance and *microscopic reversibility*, it is probably best now to regard them as synonymous.

Diabatic Coupling

Energy coupling between two potential-energy surfaces is sometimes known as diabatic coupling.

Diffusion Control See *Microscopic Diffusion Control.*

Direct Reaction

A chemical process in which the reactive complex has a lifetime that is shorter than its period of rotation is known as a direct reaction. In a *molecular-beam* experiment the reaction products of a direct reaction are scattered, with reference to the centre of mass of the system, in preferred directions rather than at random.

Some direct reactions are impulsive which means that there is an energy exchange that is very fast compared to the vibrational time scale.

A direct reaction is to be contrasted with an *indirect reaction*, also known as a *complex-mode reaction*.

Dividing Surface

A surface, usually taken to be a hyperplane$_1$ constructed at right angles to the *minimum-energy path* on a *potential-energy surface* is called a dividing surface. In conventional *transition-state theory* it passes through the highest point on the *minimum-energy path*. In generalized versions of *transition-state theory* the dividing surface can be at other positions; in *variational transition-state theory* the position of the dividing surface is varied so as to get a better estimate of the rate constant.

Early-Downhill Surface See *Attractive Surface.*

Elastic Scattering

When in a molecular collision there is no transfer of energy among different degrees of freedom, there is said to be elastic scattering.

Elementary Reaction

A reaction for which there is no evidence that it occurs in more than one step is assumed to occur in one step and is said to be an elementary reaction. It must always be borne in mind that later work may show that the reaction occurs in more than one step (i.e., that the mechanism is composite).

For the type of evidence that shows that a reaction occurs in more than one step, see *Composite Mechanism.*

Encounter

A set of collisions between *reactant* molecules in solids, liquids or dense gases, occurring in rapid succession as a result of the *cage effect*, is known as an encounter. The encounter continues until the reactants separate or react.

Encounter Control See *Microscopic Diffusion Control.*

Endergonic (or Endoergic) Reaction

This is usually taken to be a reaction for which the overall standard Gibbs energy change ΔG° is positive. Some workers use this term with respect to a positive value of ΔH° at the absolute zero of temperature.

Endothermic Reaction

This is a reaction for which the overall standard enthalpy change ΔH° is positive.

Energized Species

In an elementary process an energized species is defined as a species having sufficient energy to become an *activated complex*, but which does not have the structure of the activated complex. If it is not inactivated by collisions, after undergoing vibration it can become an activated complex and pass at once into products.

Energy Profile See *Potential-Energy Profile.*

Energy of Activation See *Activation Energy.*

Enthalpy of Activation, $\Delta^{\ddagger}H^\circ$

The standard enthalpy of activation $\Delta^{\ddagger}H^\circ$ is the enthalpy change that appears in the thermodynamic form of the rate equation obtained from conventional *transition-state theory* *:

$$k = (k_B T / h) \exp(\Delta^{\ddagger}S^\circ/R) \exp(-\Delta^{\ddagger}H^\circ/RT)$$

The quantity $\Delta^{\ddagger}S^\circ$ is the standard *entropy of activation*, and care must be taken with standard states. In this equation k_B is the Boltzmann constant, T the absolute temperature, h the Planck constant, and R the gas constant.

The enthalpy of activation is approximately equal to the *activation energy*; the conversion of one into the other depends on the molecularity.

The enthalpy of activation is always the standard quantity, although the word standard and the superscript $^\circ$ on the symbol are often omitted. The symbol is frequently (but incorrectly) written $\Delta H^{\ddagger}$, where the standard symbol is omitted and the ‡ is placed after the H.

PAC 1983, **55**, 1313; 1981, **53**, (765); Gold Book, 145; Green Book p.56,57.

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* This equation is only dimensionally correct for a first order reaction, for which the rate constant has the dimension reciprocal time. For a second order reaction, for which the rate constant has the dimension (reciprocal time) ×(reciprocal concentration), the left hand side should be read as $k c^\circ$, wnere c° denotes the standard concentration (usually 1 mol dm^{-3}).

Entrance Channel

This expression refers to the region of a potential-energy surface or hypersurface that corresponds to molecular configurations that are closer in geometry to those of the reactants than to those of the products.

Entropy of Activation, $\Delta^{\ddagger}S^{\circ}$

The standard entropy of activation $\Delta^{\ddagger}S^{\circ}$ is the entropy change that appears in the thermodynamic form of the rate equation obtained from conventional transition-state theory; see under *Enthalpy of Activation.*

Equilibrium Reaction

When the reactants in a chemical reaction are initially in a Boltzmann distribution the reaction is referred to as an equilirium reaction.

Contrast *Non-Equilibrium Reaction*

Exergonic (or Exoergic) Reaction

This expression is often applied to a reaction for which the overall standard Gibbs energy change ΔG° is negative. Some workers use this term with reference to a negative value of ΔH° at the absolute zero of temperature.

Exit Channel

This expression refers to the region of a *potential-energy surface* or hypersurface that corresponds to molecular configurations that are closer to those of the *products* than to those of the reactants.

Exothermic Reaction

This is a reaction for which the overall standard enthalpy change ΔH° is negative.

Extent of Reaction (or Extent of Conversion)

If a single reaction occurring in a closed system has known and time-independent *stoichiometry* (i.e. if the stoichiometry remains the same throughout the course of reaction, which requires that intermediates are not formed in significant amounts), the extent of reaction at any time is defined by

$$\xi = (n_B - n_B^{\circ}) / \nu_B$$

where n_B° is the initial amount of the *reactant* or *product* entity B, n_B is the amount at time t, and ν_B is the *stoichiometric number* for that entity in the reaction equation as written. The extent of reaction defined in this way depends on how the reaction equation is written, but it is independent of which entity in the reaction equation is used in the definition. For example, for the general reaction

$$aA + bB + \ldots \rightarrow \ldots . yY + zZ$$

the extent of reaction is the amount n of any product formed divided by its stoichiometric number, and is also equal to the change in the amount of any reactant (a negative quantity) divided by its stoichiometric number (also a negative quantity):

$$\xi = \Delta n_X / x = \Delta n_Z / z = -\Delta n_A / a = -\Delta n_B / b$$

Extent of reaction cannot be specified for a reaction of unknown stoichiometry or for one in which the stoichiometry changes during the course of reaction (i.e. is time-dependent).

PAC 1981, **53**, (756); Gold Book, 153; Green Book p.43.

Feedback See *Composite Reaction.*

Geminate Recombination

This expression refers to the reaction, with each other, of two *transient species* produced from a common precursor in solution. If reaction occurs before any separation by diffusion has occurred, this is termed primary geminate recombination. If the mutually reactive entities have been separated, and come together by diffusion, this is termed secondary geminate recombination. This is illustrated in the reaction diagram below.

See also *Cage.* PAC 1983, **55**, 1316.

$$R{-}N{=}N{-}R \rightarrow [R\cdot + NN + R\cdot]_{\text{solvent cage}}$$

diffusion

primary
geminate recombination

$N_2 + 2R$

secondary
geminate
recombination

$R{-}R + N_2$

Generalized Transition-State Theory

Any form of *transition-state theory*, such as *microcanonical variational TST*, *canonical variational TST*, and *improved canonical variational TST*, in which the transition state is not necessarily located at the saddle point, is referred to as generalized transition-state theory.

Gibbs Energy of Activation, $\Delta^{\ddagger}G^{\circ}$

In *transition-state theory*, the standard Gibbs energy of activation $\Delta^{\ddagger}G^{\circ}$ is a quantity defined by the equation

$$k = (k_B T / h) \exp(-\Delta^{\ddagger}G^{\circ} / RT)$$

where k is the rate constant at a temperature T. The standard Gibbs energy of activation is often called simply the Gibbs energy of activation; it was formerly called the Gibbs free energy of activation, or the free energy of activation. Care must be taken with standard states.

PAC 1981, **53**, (765); *ibid* 1983, **55**, 1317; Green Book, 57

Gibbs Energy Diagram

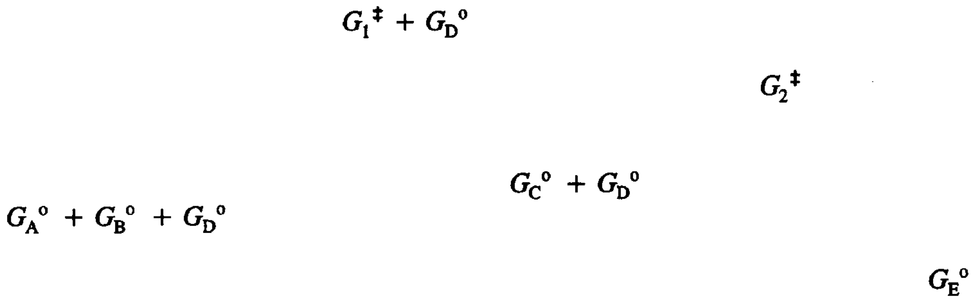
This is a diagram showing the relative standard Gibbs energies of *reactants*, *transition states*, *reaction intermediates*, and *products*, in the same sequence as they occur in a *chemical reaction*. These points are often connected by a smooth curve (a Gibbs energy profile, commonly still referred to as a free energy profile) but experimental observation can provide information on relative standard Gibbs energies only at the maxima and minima and not at configurations between them. The abscissa expresses no more than the sequence of reactants, products, reaction intermediates and transition states.

Contrary to statements in many text books, the highest point on a Gibbs energy diagram does not necessarily correspond to the transition state of the *rate-controlling step*. For example, in a *stepwise reaction* consisting of two reaction steps,

$$(1) \qquad A + B \rightarrow C$$

$$(2) \qquad C + D \rightarrow E$$

one of the transition states of the two reaction steps must (in general) have a higher standard Gibbs energy than the other, whatever the concentration of D in the system. However, the value of that concentration will determine which of the reaction steps is rate-controlling. For a further discussion see Murdoch (1981). An example of a Gibbs energy diagram is shown below.



See also *Potential-energy profile; Potential-energy surface.*

PAC 1983, **55**, 1317.

Gradual and Sudden Potential-Energy Surface

These terms relate to the steepness of the energy rise along the *reaction path* of a *potential-energy surface*.

Half Life, $t_{1/2}$

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 a reactant that is entirely consumed it is the time taken for the reactant concentration to fall to one half its initial value

The half life of a reaction has meaning only in special cases:

(1) For a first-order reaction, the half life of the reactant may be called the half life of the reaction.

(2) For a reaction involving more than one reactant, with the concentrations of the reactants in their stoichiometric ratios, the half life of each reactant is the same, and may be called the half life of the reaction.

If the concentrations of reactants are not in their stoichiometric ratios, there are different half lives for different reactants, and one cannot speak of the half life of the reaction.

PAC 1983, **55**, 1318; 1981, **53**, (758); Gold Book, 181; Green Book p.55

Heat Capacity of Activation, $\Delta^{\ddagger}C_v$

The difference between the heat capacity of the activated complexes and that of the reactants is known as the heat capacity of activation.

If the *modified Arrhenius equation* is employed, the activation energy E_a is given by

$$E_a = E_0 + C_v T$$

where E_0 is the hypothetical value of the activation energy at the absolute zero. The heat capacity of activation is then given by

$$\Delta^{\ddagger}C_v = nR,$$

where R is the gas constant and n the exponent in the *modified Arrhenius equation*.

PAC 1983, **55**, 1319; Gold Book, 184.

Impact Parameter, b

This is the distance of closest approach of the centres of mass of two colliding molecular entities if there were no forces between them and they continued in the directions in which they were moving at the beginning of the trajectory.

PAC 1981, **53**, (767); Gold Book, 196; Green Book p.56

Improved Canonical Variational Transition-State Theory (ICVTST)

This is a modification of *canonical variational transition-state theory* in which, for energies below the *threshold energy*, the position of the *dividing surface* is taken to be that of the microcanonical threshold energy. This forces the contributions to *rate constants* to be zero below the threshold energy. A compromise dividing surface is then chosen so as to minimize the contributions to the rate constant made by *reactants* having higher energies.

Impulsive Reaction See *Direct Reaction*.

Indirect Reaction

A chemical process in which the reactive complex has a lifetime that is longer than its period of rotation is called an indirect reaction (in contrast to a *direct reaction*). In a *molecular-beam* experiment the *products* of such reactions are scattered at random with reference to the centre of mass of the system.

Indirect reactions are also called *complex-mode reactions*. (They are sometimes called complex reactions, but this usage is not recommended in view of the danger of confusion with composite reactions, which occur in more than one step).

PAC 1981, **55**, (767); Gold Book, 239.

Induction Period

With some reaction systems there is an initial period during which very little occurs, followed by a period of more rapid reaction. This initial period is called the induction period. The term *transient phase* is applied to a special type of induction period that occurs prior to the establishment of a *steady state*.

Inelastic Scattering

If in a molecular collision there is transfer of energy among degrees of freedom, but no chemical reaction occurs, there is said to be inelastic scattering.

Information Theory

As applied in reaction dynamics, information theory analyzes the deviations of experimentally-determined energy distributions from predictions made on the basis of equal a priori probabilities for all possible outcomes.

Inhibition

An inhibitor is a substance that diminishes the rate of a chemical reaction, and the process is called inhibition. For polymerization processes, the words retarder and retardation are often used, with the same meaning. The terms negative catalyst and negative catalysis are not recommended.

If a reaction in the absence of an inhibitor proceeds with a rate v_0, and in the presence of an inhibitor with rate v, the degree of inhibition ϵ_i is defined as

$$\epsilon_i = (v_0 - v) / v_0 = 1 - (v / v_0)$$

PAC 1983, **55**, 1323; Gold Book, 199.

Initial and Final State Correlations

These are correlations between the states of the products of a reaction and the initial states of the reactants. The correlations may relate to energy levels, quantum numbers, and symmetries.

Initiation Reaction

When a reaction occurs by a *composite mechanism*, the elementary step responsible for forming reaction *intermediates* is called the initiation reaction. This term is used particularly for *chain reactions*, the reaction that produces the *chain carriers* (e.g., atoms or free radicals) being the initiation reaction.

PAC 1976, **46**, 74; Gold Book, 199.

Initiator

A substance introduced into a reaction system in order to bring about an *initiation reaction* is known as an initiator.

PAC 1976, **46**, 74; Gold Book, 199.

Intermediate

Any reaction species that is neither an initial *reactant* nor a final *product* is referred to as an intermediate.

PAC 1983, **55**, 1323; Gold Book, 341.

Intrinsic Activation Energy, $E_{a,i}$

If $E_{a,1}$ and $E_{a,-1}$ are the *activation energies* for a reaction in forward and reverse directions, the lesser of the two is sometimes called the intrinsic activation energy. It is the activation energy for the reaction in the exothermic direction.

Isotope Effects

If an atom in a reactant molecule is replaced by one of its isotopes, both the equilibrium constant and the rate constant are in general altered. The term equilibrium isotope effect refers to changes in equilibrium constants and the term kinetic isotope effect to changes in rate constants.

An equilibrium isotope effect is usually expressed in terms of the ratio of equilibrium constants K_{light}/K_{heavy}; by convention the equilibrium constant with the lighter isotope is in the numerator. Similarly a kinetic isotope effect is usually expressed as the ratio of rate constants k_{light}/k_{heavy}. A kinetic isotope effect is referred to as 'normal' or 'inverse' according to whether this ratio is larger or smaller than unity.

Isotope effects, both equilibrium and kinetic, are said to be primary if the isotope substitution is at the end of a bond that is broken or formed during the reaction. The effect is smaller, and is said to be secondary, if the substitution is not at such a bond.

When a reaction occurs by a *composite mechanism* a primary kinetic isotope effect may be observed for the overall rate if there is a primary effect on the *rate-controlling step*, or on an equilibrium constant for a *pre-equilibrium* which precedes the rate-controlling step. When neither of these effects applies, a primary kinetic isotope effect on an equilibrium or a rate constant will be observed only as a secondary effect on the overall rate.

PAC 1983, **55**, 1327; Gold Book, 222.

Kinematics

The study of the properties of motion that are independent of the nature of the forces is known as kinematics.

In *reaction dynamics* the term is often applied in particular to effects that occur when atomic masses are changed, the forces remaining the same.

Kinetic Activity Factor

This is a factor involving activity coefficients that appears as a multiplier in the rate equation. For a bimolecular reaction the factor is $y_A y_B / y_\ddagger$, where y_A, y_B and $y_\ddagger$ are the activity coefficients for the reactants A and B and the *activated complex*, respectively. For a unimolecular reaction the factor is $y_A / y_\ddagger$, and for a trimolecular reaction it is $y_A y_B y_c / y_\ddagger$.

Kinetic Theory of Collisions See *Collision Theory*.

Langmuir-Hinshelwood Mechanism

A mechanism for surface catalysis in which the reaction occurs between species that are adsorbed on the surface is often known as a Langmuir-Hinshelwood mechanism.

Langmuir-Rideal Mechanism or Rideal-Eley Mechanism

This is a mechanism for surface catalysis in which the reaction occurs between a reactant molecule in the gas phase and one that is adsorbed on the surface.

Light-Atom Anomaly

This is a dynamical effect that arises for a process $A + B\text{-}C \rightarrow A\text{-}B + C$ when the species A is light (e.g. a hydrogen atom) compared to B and C. The vibrational excitation of the product A-B is low, since the light atom A approaches to within the bonding distance of BC before the C atom retreats. The energy of reaction is therefore released as repulsion between A-B and C, with the result that there is translational excitation of the products.

Line-of-Centres Model

This is a form of the collision theory of chemical reactions in which the assumption is made that reaction can only occur if on collision the component of energy along the line of centres of the masses of the colliding species is greater than a particular threshold energy.

London-Eyring-Polanyi (LEP) Method

This is a semiempirical method of calculating a *potential-energy surface*, based on a simplified quantum-mechanical equation (the London equation).

London-Eyring-Polanyi-Sato (LEPS) Method

This is a modification of the *London-Eyring-Polanyi* method proposed in 1955 by S. Sato.

Macroscopic Diffusion Control This terminology is not recommended. See *Mixing Control*.

Macroscopic Kinetics

This term is applied to a kinetic study in which the interest is in the behaviour of bulk systems, e.g. in changes in concentrations of reactants and products.

Marcus-Coltrin Path

This is a path (*trajectory*) over a *potential-energy surface* which corresponds to the outermost vibrational turning points for the molecular species involved. This path was suggested as a device for calculating the probability of quantum-mechanical *tunnelling*: the trajectory for the system is considered to follow this path.

Michaelis-Menten Equation

An enzyme-catalyzed reaction involving a substrate A is said to follow the Michaelis-Menten equation, or to exhibit Michaelis-Menten kinetics, if the rate equation is of the form

$$v = V[\mathrm{A}]/(K_\mathrm{m} + [A])$$

where V (the limiting rate) and K_m (the Michaelis constant) are independent of [A].

If two substrates A and B are involved the reaction is said to exhibit Michaelis-Menten kinetics if the above type of equation is obeyed when one substrate concentration is held constant.

PAC 1983, **55**, 1335.

Michaelis-Menten Mechanism

The Michaelis-Menten mechanism is the simplest mechanism that will explain *Michaelis-Menten kinetics*. According to the mechanism, a substrate A first combines with a molecule of enzyme E, and this process is followed by a step in which the enzyme-substrate complex EA breaks down (sometimes with the participation of the solvent) into enzyme and reaction products:

$$\mathrm{E} + \mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{EA}$$

$$\mathrm{EA} \xrightarrow{k_2} \mathrm{E} + \text{products}$$

If, as is usual, the substrate A is present in great excess of the enzyme it can be shown that steady-state conditions apply, and that the rate equation is

$$v = \frac{k_2\,[\mathrm{E}]_0\,[\mathrm{A}]}{(k_{-1} + k_1)/k_1 + [\mathrm{A}]}$$

where $[\mathrm{E}]_0$ is the total concentration of enzyme. This equation is of the form of the *Michaelis-Menten equation*.

Other, more complicated, mechanisms lead to the Michaelis-Menten equation, adherence to which does not therefore require that the Michaelis-Menten mechanism applies.

Microcanonical Rate Constant

This is a rate constant calculated by *microcanonical variational transition-state theory*, and therefore a rate constant that relates to a fixed energy.

Microcanonical Variational Transition-State Theory (μVTST)

This is a development of *transition-state theory* in which the *dividing surface* is varied so as to minimize the rate calculated for a fixed energy.

The rate expressions obtained in a microcanonical treatment can be integrated over the energy, taking into account the statistical distribution over energy states, so as to give the canonical, or thermal, rates.

Microscopic Diffusion Control (Encounter Control)

When the rate of a rapid reaction in solution is fully or partially dependent on the microscopic rates with which the reactant species come together there is said to be microscopic diffusion control, or encounter control.

If, hypothetically, a bimolecular reaction in a homogeneous medium occurred instantaneously when two molecular entities made an encounter, the rate of the reaction would be determined solely by the rates of diffusion of the reactants. According to a simple but useful treatment given in 1917 by M.V. Smoluchowski, the rate constant in such a situation would be given by

$$k_D = 4\pi N_A(D_A + D_B)d_{AB}$$

where D_A and D_B are the diffusion coefficients for the reactants A and B and d_{AB} is the distance between the centres of A and B when the encounter occurs; N_A is the Avogadro constant. The expression *full microscopic diffusion control* can be used to describe this situation.

If the rate of a reaction is not entirely determined by the diffusion process, the rate of the chemical process also having some effect on the overall rate, there is said to be 'partial microscopic diffusion control'. This situation arises when the chemical and diffusion rates are comparable. It is difficult in practice to determine with any precision the degree of microscopic diffusion control.

Contrast *Mixing Control.*

Microscopic Kinetics

This term applies to a kinetic study in which the emphasis is on the interpretation of the behaviour in terms of elementary reactions.

Contrast *Macroscopic Kinetics* and *Molecular Kinetics.*

Microscopic Reversibility at Equilibrium

The principle of microscopic reversibility at equilibrium states that, in a system at equilibrium, any molecular process and the reverse of that process occur, on the average, at the same rate.

This definition corresponds to the statement of the principle that was given by R.C. Tolman in 1924. However, many workers have interchanged the meanings of microscopic reversibility and *detailed balance*, and it seems best now to regard the two, which are closely related, as synonymous.

Minimum-Energy Reaction Path

This is the path corresponding to the steepest descent from the *col* of a *potential-energy surface* into the two valleys. The reaction coordinate corresponds to this minimal path.

Some workers refer to the minimum-energy reaction path as simply the reaction path but this is not recommended as it leads to confusion.

Minimum Density of States Criterion

This is a criterion used in *Rice-Ramsperger Kassel-Marcus (RRKM) theory* for locating the transition state. The reaction coordinate r at the transition state, according to this criterion, is given by $\partial N(\epsilon_r) / \partial r = 0$, where $N(\epsilon_r)$ is the density of states at an internal energy ϵ_r.

Mixed Energy Release

This is an effect found in a process A + BC when the attacking species A is heavy. Because A is heavy the A-B distance continues to decrease while the repulsive energy of B-C is being released.

Mixing Control

For a rapid reaction in a homogeneous medium or at an interface, the rate of reaction may depend on the rate of mixing, and one then speaks of mixing control. A distinction, although not a sharp one, can be made between micromixing, involving length scales of the order of micrometres, and macromixing, involving greater distances.

Mixing control is often referred to as 'macroscopic diffusion control', and this usage is recommended in the Gold Book. However, we do not recommend this terminology, since it wrongly implies that diffusion is the only process involved in mixing control. In fact, mixing also involves laminar mixing due to convective motion, turbulent mixing, and chaotic mixing.

See also *Microscopic Diffusion Control.*

Modified Arrhenius Equation

This is an extension of the simple *Arrhenius equation* in which the *pre-exponential factor* is proportional to T^n where T is the temperature and n a constant:

$$k = BT^n \exp(-E_a/RT)$$

B is a temperature-independent constant.

Molecular Beams

A molecular beam is produced by allowing a gas at higher pressure to expand through a small orifice into a container at lower pressure. The result is a beam of particles (atoms, free radicals, molecules or ions) moving at approximately equal velocities, with few collisions occurring between them.

In a crossed molecular-beam experiment a reaction is studied using collimated beams of reactant molecules. For a bimolecular reaction, beams of the two reactants are caused to impinge on one another, often at an angle of 90°.

In a beam-gas scattering experiment a collimated beam is introduced into a gas, and the scattering patterns are observed.

Molecular Dynamics

This term is synonymous with *Reaction Dynamics.*

Molecular Kinetics

This term is applied to a kinetic study in which there is emphasis on the behaviour of the system at the molecular level.

Contrast *Macroscopic Kinetics.*

Molecularity

The number of reactant particles (atoms, molecules, free radicals or ions) that are present in the transition state is referred to as the molecularity.

This term is applicable only to an *elementary reaction.*

Newton Diagram

This is a vector diagram used to show the relationship between initial and final velocities or momenta in a two-particle scattering process. It is commonly used to relate laboratory and centre-of-mass coordinates.

Nonadiabatic See under *Adiabatic.*

Nonadiabatic Coupling

This is momentum coupling between two adiabatic potential-energy surfaces.

See also *Adiabatic.*

Non-Equilibrium Reaction

If the reactants in a chemical reaction are not initially present in a Boltzmann distribution the reaction is referred to as a non-equilibrium reaction.

Contrast *Equilibrium Reaction*

Order of Reaction

Sometimes the rate of a reaction occurring in a closed system can be expressed empirically by an equation of the form

$$v = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}\ldots$$

where k is the *rate constant*, [A] and [B] are reactant concentrations, and α and β are independent of concentrations and of time. The exponents α, β, etc. are defined by the equations

$$\alpha = (\partial \ln v / \partial \ln [\mathrm{A}])_{[\mathrm{B}],\ldots,T,p}$$

$$\beta = (\partial \ln v / \partial \ln [\mathrm{B}])_{[\mathrm{A}],\ldots,T,p}$$

The exponent α is the order of reaction with respect to A, and can be called a partial order. The partial order β is the order with respect to B. The sum of all the partial orders,

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

is called the overall order of the reaction.

PAC 1981, **53**, (757); 1983, **55**, 1341; Gold Book, 282-3; Green Book p.55

Oscillating Reaction

A reaction is said to be oscillating if the concentration of one or more *intermediates* does not vary monotonically, but passes through maximum and minimum values.

Phase-Space Theory

This is a theory applied to unimolecular or bimolecular reactions proceeding through long-lived complexes. The probability of reaction is assumed to be proportional to the number of states available to a particular product *channel* divided by the number of states corresponding to all product channels. The theory is used to predict rates, product energy distributions, product velocity distributions, and product angular momentum distributions.

Photochemical Equivalence

According to the principle of photochemical equivalence, there is a one-to-one relationship between the number of photons absorbed by a system and the number of excited species produced. The principle often fails for light of high intensity (e.g. laser beams), when molecules may absorb more than one photon.

Potential-Energy Profile

A potential-energy profile is a curve describing the variation of the potential energy of the system of atoms that makes up the reactants and products of a reaction, as a function of one geometric co-ordinate, and corresponding to the energetically easiest passage from reactants to products (i.e. along the line produced by joining the paths of steepest descent from the *transition state* to the reactants and to the products). For an *elementary reaction* the relevant geometric coordinate is the *reaction coordinate*; for a *stepwise reaction* it is the succession of reaction coordinates for the successive individual *reaction steps*. (The reaction co-ordinate is sometimes approximated by a quasi-chemical index of reaction progress, such as degree of atom transfer or bond order of some specified bond.)

See also *Potential-Energy Surface*; *Gibbs Energy Diagram.*

PAC 1983, **55**, 1346; see also 1981, **53**, (764); Gold Book, 309.

Potential-Energy Surface or Hypersurface

This is a surface or hypersurface on which the potential energy of a set of reactants is plotted as a function of the co-ordinates representing the molecular geometry of the system. For simple systems two such co-ordinates (characterizing two variables that change during the progress from reactants to products) can be selected, and the potential energy plotted as a contour map.

For simple *elementary reactions*, e.g. A-B + C → A + B-C, the surface can show the potential energy for all values of the A, B, C geometry, provided that the ABC angle is fixed.

For more complicated reactions a different choice of two coordinates is sometimes preferred, e.g. the *bond orders* of two different *bonds*. Such a diagram is often arranged so that reactants are located at the bottom left corner and products at the top right. If the trace of the representative point characterizing the route from reactants to products follows two adjacent edges of the diagram, the changes represented by the two coordinates take place in distinct succession; if the trace leaves the edges and crosses the interior of the diagram, the two changes are *concerted*. In many qualitative applications it is convenient (although not strictly equivalent) for the third co-ordinate to represent standard Gibbs energy rather than potential energy. (Some reservations concerning the diagrammatic use of Gibbs energies are noted under *Gibbs energy diagram*).

The energetically easiest route from reactants to products on the potential-energy contour map defines the *potential-energy profile.*

See also *Reaction coordinate.*

PAC 1983, **55**, 1346; see also 1981, **53**, 764; Gold Book, 309-310.

Pre-Equilibrium or Prior Equilibrium

The mechanism of a reaction may involve two or more consecutive reactions:

$$A \rightarrow B \rightarrow \ldots \rightarrow X \rightarrow Y \rightarrow Z$$

If any step except the first is *rate-controlling*, those steps that precede it are essentially at equilibrium, and there is said to be a pre-equilibrium, or a prior equilibrium; for example

$$\underset{\text{pre-equilibrium}}{A \rightleftharpoons B \rightleftharpoons X} \underset{\substack{\Uparrow \\ \text{rate-controlling step}}}{\rightarrow} Y \rightarrow \ldots\ldots$$

Pre-exponential Factor, A

If the rate constant k of a reaction is expressed as

$$k = A \exp(-E_a/RT)$$

where E_a is the activation energy, the quantity A is called the pre-exponential factor.

Green Book p.56

Prior Distribution, P_0

This is a product state distribution calculated on the basis of some physical model for the reaction. The distribution usually referred to is that of the *products* at the instant of their formation.

Product

A substance that is formed during a chemical reaction is known as a product.

Contrast *Reactant.*

Product State Distribution

This expression refers to the distribution of available energy among the vibrational, rotational and translation degrees of freedom in the product molecules. The distribution usually referred to is that of the products at the instant of their formation.

Pseudo Rate Constant

This term is sometimes used for a rate coefficient. For example, if the rate equation is

$$v = k[\mathrm{A}][\mathrm{B}]$$

the function k[A] is the pseudo first-order rate constant (or first-order rate coefficient) with respect to B. Similarly, k[B] is the pseudo first order rate constant (or first-order rate coefficient) with respect to A.

The term pseudo *rate constant* is particularly useful when the concentration of one reactant is much greater than that of another.

See also *Rate Coefficient.*

PAC 1981, **53**, (758)1983, **55**, 1349.

Quantum-Mechanical Tunnelling See *Tunnelling.*

Quantum Yield, ϕ

For a photochemical reaction the quantum yield is defined by

$$\phi = (\text{rate of conversion}) / (\text{rate of photons absorbed})$$

$$= (\mathrm{d}\xi/dt) / (\mathrm{d}n_\gamma/\mathrm{d}t)$$

A more general definition is

$$\phi = (\text{number of defined events}) / (\text{number of photons absorbed})$$

PAC 1988, **60**, 1055; Green Book, 57.

Quasiclassical Trajectory (QCT) Method

This is a procedure for calculating trajectories in which the quantization of the reactants is taken into account, but in which the course of the reaction is treated classically.

Quasi-Equilibrium

In conventional *transition-state theory* it is assumed that *activated complexes* are formed in a state of equilibrium with the reactants. They are not in classical equilibrium with the reactants; if they were, addition of more activated complexes to the system would cause the equilibrium to shift in favour of the reactants. This would not occur for an activated complex, and the term quasi-equilibrium is used to denote this special type of equilibrium.

Rate Coefficient

If the rate of a reaction occurring in a closed system is expressible by an equation of the form

$$v = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}\ldots.$$

the constant k is known as the rate coefficient or the rate constant for the reaction. It is recommended that the latter term, rate constant, be confined to reactions that are believed to be *elementary reactions*.

When a rate coefficient relates to a reaction occurring by a composite mechanism it may vary with concentrations of reactants. For example, in the case of a unimolecular gas reaction the rate at sufficiently high pressures is given by

$$v = k[\mathrm{A}]$$

while at low pressures the rate expression is

$$v = k'[\mathrm{A}]^2$$

The constant k, which varies with the concentration [A], is called the first-order rate coefficient for the reaction. It is sometimes called the pseudo first-order rate constant.

Gold Book, 283; PAC 1981, **53**, (758); 1983, **55**, 1350; Green Book, 55.

Rate Constant

This name is frequently used for the *rate coefficient*. As noted under *rate coefficient*, the term rate constant is best confined to a reaction which is believed to be elementary. In contrast to a rate coefficient, a rate constant should be independent of concentration (but does, of course, in general vary with temperature).

Gold Book, 283; PAC 1981, **53**, (758); 1983, **55**, 1350; Green Book, 55.

Rate of Consumption, $v_{\mathrm{n,B}}$ or $v_{\mathrm{c,B}}$

The rate of consumption of a specified reactant may be defined in two ways:

(1) As the negative of the time derivative of the amount of reactant; thus for a reactant B, present at any time in amount n_{B}, the rate of its consumption $v(n_{\mathrm{B}})$ may be defined as*

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* See footnote on next page

$$v(n_B) \;=\; -(\mathrm{d}n_B\,/\,\mathrm{d}t)$$

This definition is particularly appropriate for open systems.

(2) For kinetics in closed systems it is more usual to define a rate of consumption per unit volume; thus for a reactant B the rate of consumption $v(c_B)$ is given by

$$v(c_B) \;=\; -(1/V)\,(\mathrm{d}n_B\,/\,\mathrm{d}t)$$

When the volume V is constant this reduces to

$$v(c_B) \;=\; -(\mathrm{d}[B]\,/\,\mathrm{d}t)$$

When the volume is not constant the relationship $n_B = [B]V$ may be differentiated to give

$$\mathrm{d}c_B \;=\; V\mathrm{d}[B] \;+\; [B]\mathrm{d}V$$

and therefore

$$v(c_B) \;=\; -(\mathrm{d}[B]\,/\,\mathrm{d}t) \;-\; ([B]/V)(\mathrm{d}V/\mathrm{d}t)$$

In contrast to the rate of conversion and the rate of reaction, the rate of consumption of a reactant may be specified even for a reaction of time-dependent *stoichiometry* or of unknown stoichiometry.

The rate of consumption of a reactant is often called its rate of disappearance. However, the former expression is to be preferred since the word disappearance is not appropriately translatable into certain languages. When English is used the word disappearance might be reserved for cases where the reactant is almost completely removed.

Green Book, 55.

Rate of Conversion

The rate of conversion for a reaction occurring in a closed system is defined as the time derivative of the extent of reaction,

$$\dot{\xi} \;=\; \mathrm{d}\xi\,/\,\mathrm{d}t$$

In view of the definition of *extent of reaction* it follows that with reference to any species in a reaction showing time-independent *stoichiometry*,

$$\dot{\xi} \;=\; \mathrm{d}\xi\,/\,\mathrm{d}t \;=\; (1/v_i)(\mathrm{d}n_i/\mathrm{d}t)$$

where n_i is the amount of the ith species at any time and v_i is its *stoichiometric coefficient.*

Green Book, 55.

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* Here and elsewhere, when a rate is defined in terms of a time derivative, it must be understood that the definition relates to the process occurring in isolation. In a flow system there may be no actual changes with time, and the time derivative must be inferred. Such an inference is also required for a reaction occurring by a composite mechanism.

Rate of Formation, $v_{n,y}$ or $v_{c,y}$

Like the *rate of consumption*, the rate of formation of a specified product may be defined in two ways:

(1) As the time derivative of the amount of a product. Thus for a product Y, present at any time in amount n_Y, the rate of its formation $v(n_Y)$ may be given by

$$v(n_Y) = (dn_Y/dt)$$

This definition is particularly appropriate for open systems.

(2) For kinetics is closed systems it is more usual to define a rate of formation per unit volume, denoted $v(c_Y)$,

$$v(c_Y) = (1/V)(dn_Y/dt)$$

When the volume is constant this reduces to

$$v(c_Y) = (1/V)(dn_Y/dt) = (d[Y]/dt)$$

When the volume is not constant the relation $n_Y = [Y]V$ may be differentiated to give

$$dn_Y = Vd[Y] + [Y]dV$$

and the rate of formation becomes

$$v(c_Y) = (d[Y]/dt) + ([Y]/V)(dV/dt)$$

A rate of formation may be specified even for a reaction of time-dependent *stoichiometry* or of unknown stoichiometry.

Rate of Reaction, v_r

The rate of reaction can only be expressed for a reaction of known and time-independent *stoichiometry*. For a closed homogeneous system the rate of reaction is the *rate of conversion* per unit volume:

$$v_r = \dot{\xi}/V = (1/V)(d\xi/dt)$$

For a species B the rate of reaction is thus given by

$$v_r = (1/\nu_B V)(dn_B/dt)$$

For the general reaction

$$aA + bB + \ldots \rightarrow \ldots + yY + zZ$$

the rate of reaction can be expressed with reference to the various reactants and products as

$$v_r = -(1/aV)(dn_A/dt) = -(1/bV)(dn_B/dt) = -(1/yV)(dn_Y/dt) = -(1/zV)(dn_Z/dt)$$

If the volume does not change during the course of reaction the rate of reaction may be expressed in terms of concentrations as , for example,

$$v_r = -(1/\nu_B)(d[B]/dt)$$

If the volume is not constant, we differentiate the relationship $n_B = [B]V$ and obtain

$$dn_B = Vd[B] + [B]dV$$

and thus obtain

$$v_r = -(1/\nu_B)(d[B]/dt) - ([B]/\nu_B V)(dV/dt)$$

In certain circumstances it may be convenient to define a rate of reaction in a different way, for example by relating the rate of conversion to other quantities such as mass and surface area.

PAC 1981, **53**, (756); Green Book, 55.

Rate-Controlling Step

A rate-controlling (rate-determining or rate-limiting) step in a reaction occurring by a composite mechanism is an *elementary reaction* the *rate constant* for which exerts a dominant effect on the overall rate. It is recommended that the expressions rate-controlling, rate-determining and rate-limiting be regarded as synonymous, but some special meanings sometimes given to the last two expressions are considered under a separate heading.

A rate-controlling step defined in the way recommended here has the advantage that it is directly related to the interpretation of *kinetic-isotope effects*.

It is to be emphasized that there are difficulties with the identification of a rate-controlling step, and that great care must be taken. The following points are particularly important:

(1) A rate-controlling step can only be identified with certainty if a reaction mechanism has been established without any doubt, and this is never the case; reaction mechanisms are always tentative, and the identification of a rate-controlling step is thus also tentative. Aside from this, there must be adequate information about the rates of the elementary reactions that are believed to occur. It is sometimes thought that one can write down a proposed mechanism and identify a rate-controlling step by inspection. For example, the second step in a *Michaelis-Menten mechanism* is sometimes assumed to be the rate-controlling step under all conditions. However, with the definition recommended here (that the rate-controlling step exerts a dominant effect on the overall rate), this second step is only the rate-controlling step in the limit of high substrate concentrations.

(2) The rate-controlling step in general depends on reactant concentrations. In the case of a Michaelis-Menten mechanism, at low substrate concentrations the formation of complexes is rate-controlling, whereas at high substrate concentrations the breakdown of the complex is rate-controlling.

(3) As already emphasized, the study of kinetic isotope effects can never identify, without any doubt, a rate-controlling step; it can do no more than render an identification plausible. It can sometimes show convincingly that a given proposed step is not rate-controlling. There is always some uncertainty about reaction mechanisms, since more complicated schemes can never be excluded.

(4) A rate-controlling step is sometimes said to be the slowest elementary step that is occurring. This is not necessarily the case; if *steady-state* conditions apply, for example, some elementary reactions are occurring at the same rate.

(5) In the case of reactions occurring in sequence, it is sometimes thought that the rate-controlling step will correspond to the highest barrier in the *Gibbs-energy diagram*. This, however, is not the case; the procedure to use in such cases has been described by Murdoch (1981).

It is to be emphasized that there is no need, in a kinetic investigation, to identify a rate-controlling step; many kineticists make no use of the concept. In kinetic-isotope studies, in particular, the concept may be found useful, but great care must be taken with trying to identify the step, and an identification must always be tentative, subject to revision after further investigation.

Since the term rate-controlling has been used in several senses, it is important for it to be defined whenever it is used.

Gold Book, 337

Rate-Determining Step, Rate-Limiting Step

These terms are best regarded as synonymous with rate-controlling step. However, special meanings that have sometimes been applied to them should be mentioned, as it is necessary to be aware of them in order to avoid confusion.

(1) Sometimes the term rate-determining is used as a special case of rate-controlling, being assigned to an initial slow step followed by rapid steps. Such a step imposes an upper limit on the rate, and has also been called rate-limiting.

(2) Sometimes a later step imposes an upper limit on the rate and has been referred to as rate-limiting or rate-determining, even though it may not be rate-controlling in the sense here recommended. For example, the second step in an enzyme-catalyzed reaction proceeding by a Michaelis-Menten mechanism has sometimes been referred to as rate-limiting. It is only, however, rate-controlling (in the sense recommended here) in the limit of high substrate concentrations.

It can hardly be emphasized too strongly, in view of the different definitions used, that the terms rate-controlling, rate-determining, and rate-limiting should always be defined clearly whenever they are used.

Reactant

A substance that is consumed in the course of a chemical reaction is known as a reactant. It is sometimes known, especially in the older literature, as a reagent, but this term is better used in a more specialized sense as a test substance that is added to a system in order to bring about a reaction or to see whether a reaction occurs (e.g. an analytical reagent).

Reaction Barrier

This is the energy barrier to chemical reaction. In vibrationally *adiabatic transition-state theory* its height is the zero-point energy of the *activated complex* minus that of the reactants.

Reaction Coordinate See under *Minimum-Energy Reaction Path.*

Reaction Cross Section, σ_r

This is a quantity used in collision theories of reactions in order to interpret calculated or experimental rates.

In some collision theories the reaction cross section is considered to be related to b_{max}, the maximum value of the *impact parameter* that allows reaction to occur, by

$$\sigma_r = P_r \pi b_{max}^2$$

where P_r is the reaction probability.

Contrast *Collision Cross Section.*

Reaction Dynamics

This is a branch of chemical kinetics that is concerned with the intermolecular and intramolecular motions that occur in the elementary act of chemical change, and with the details of the relationships between the quantum states of the reactant molecules and those of the product molecules. It is also known as molecular dynamics.

Reaction Path

This is a possible path taken by a reaction system over a *potential energy surface or hypersurface.* A reaction path is also called a trajectory.

See also *Minimum-Energy Reaction Path.*

Reaction Path Degeneracy

This is a factor that is introduced into rate theory to take account of the fact that the process may be able to occur in different but equivalent ways. Thus the process

$$Cl + H_2 \rightarrow HCl + H$$

has a reaction path degeneracy of 2 since the chlorine atom can abstract either of the two hydrogen atoms in the hydrogen molecule. The reaction path degeneracy has also been referred to as the statistical factor for the reaction.

Reaction Probability, P_r

The probability that a reaction occurs when two particles undergo a collision is known as the reaction probability. If N_c is the number of collisions occurring in unit time, and N_r the number of reactions occurring in unit time,

$$P_r = N_r/N_c$$

Reactive Complex

This is a species of very short life that occurs as an intermediate in a chemical reaction. An *activated complex* (or transition state) is a special case of a reactive complex.

Reactive Scattering

If in a *molecular-beam* experiment a chemical reaction occurs there is said to be reactive scattering.

Rebound Reaction

If, in a chemical process occurring in a molecular beam, the reaction products are scattered backwards with respect to the moving centre of mass of the system, the reaction is called a rebound reaction.

Relaxation

If a system is disturbed from its state of equilibrium it relaxes to that state, and the process is referred to as relaxation. The branch of kinetics concerned with such processes is known as relaxation kinetics.

Relaxation techniques include *temperature jump* and pressure jump.

Relaxation Time, τ

The relaxation time, τ, is defined as the time it takes for the *extent of reaction* to change by the fraction 1 - (1/e) of the total change during the relaxation process (e is the base of the natural logarithms).

This may be expressed differently in terms of the concentration change of any species involved. Suppose that a concentration deviates at time t from its equilibrium value by Δc, and that when t=O the deviation is Δc_0. The fractional change in concentration at time t is thus

$$(\Delta c_0 - \Delta c) / \Delta c_0 = 1 - (\Delta c / \Delta c_0)$$

and when $t = \tau$ this is equal to $1 - (1/\mathrm{e})$, so that $(\Delta c_0 / \Delta c) = \mathrm{e}$, or $\ln(\Delta c_0 / \Delta c) = 1$.

Repulsive Potential-Energy Surface

This is a surface for an *exergonic reaction* A + BC in which the *col* corresponds to considerable separation between the products A-B + C. The energy barrier in the *potential-energy profile* is in the later stages of the reaction path. On such a surface most of the energy is released after A-B is formed.

Repulsive surfaces are also called late-downhill surfaces, and the barrier in such a surface is called a Type-II barrier.

Retarder

This term, used mainly in polymerization kinetics, refers to a substance that reduces the rate of reaction.

See also *Inhibitor*, which has the same meaning.

Rice-Ramsperger-Kassel (RRK) Theory

This is a theory of unimolecular gas reactions in which the rate with which the energized reactant molecule breaks down is treated as a function of the energy ϵ that it contains. The theory assumes that the rate is proportional to the number of ways of distributing ϵ among the internal degrees of freedom of the reactant molecule, in such a manner that the critical energy ϵ_c is localized in one particular degree of freedom.

Rice-Ramsperger-Kassel Marcus (RRKM) Theory

This is an improved form of *Rice-Ramsperger-Kassel (RRK) theory* in which account is taken of the way in which the various normal-mode vibrations and rotations contribute to reaction, and allowance is made for the zero-point energies. In this theory the energy ϵ^* in an energized molecule is classified as either active, $\epsilon^*_{\text{active}}$, or inactive, $\epsilon^*_{\text{inactive}}$. The rate depends upon $P(\epsilon^*_{\text{active}})/N(\epsilon^*)$, where $N(\epsilon^*)$ is the density of states having energy between ϵ^* and $\epsilon^* + d\epsilon^*$, and $P(\epsilon^*_{\text{active}})$ is the sum of the active quantum states of the activated complex.

This extension of RRK theory brings it in line with *transition-state theory.*

Saddle Point See *Col.*

Salt Effects

For a reaction in solution involving ions, a salt that does not have an ion in common with the reacting ions is called a foreign salt. The kinetic effects of such foreign salts are called salt effects.

Selectivity

This term is used in two different ways:

(1) It sometimes refers to the discrimination shown by a given reactant A when it reacts with two alternative reactants B and C, or in two different ways (e.g. at two different sites) with a reactant B,

(2) The term also sometimes refers to the ratio of products obtained from given reactants. This meaning is of importance for catalysts, which can have a wide range of selectivities. Selectivity is quantitatively expressed by ratios of rate constants for the alternative reactions, or by the decadic logarithms of such ratios.

Separability Assumption

This expression refers to the assumption, essential to conventional *transition-state theory*, that the energy of the system may be expressed as the sum of components associated with different degrees of freedom. In *transition-state theory* it is assumed that the energy of the motion of the system through the *dividing surface* of the *potential-energy surface* is separable into various components. In many practical calculations it is assumed that the energy of the system is separable into electronic, vibrational, rotational and translational energy.

Spectator-Stripping Reaction

This is an extreme type of stripping reaction in which one reaction product has almost the same direction and momentum that one of the reactant molecules had before the reactive collision occurred.

State-to-State Kinetics

This is a branch of chemical kinetics concerned with the dynamics of reactions in which the reactant species are in known quantum states, and in which the quantum states of the products are determined.

Statistical Factor See *Reaction Path Degeneracy.*

Steady State (or Stationary State)

If during the course of a chemical reaction the concentration of an *intermediate* remains constant, the intermediate is said to be in a steady state.

In a static system a reaction intermediate reaches a steady state if the processes leading to its formation and those removing it are approximately in balance. The steady-state hypothesis leads to a great simplification in reaching an expression for the overall rate of a composite reaction in terms of the rate constants for the individual elementary steps. Care must be taken to apply the steady-state hypothesis only to appropriate reaction intermediates. An intermediate such as an atom or a free radical, present at low concentrations, can usually be taken to obey the hypothesis during the main course of the reaction.

In a flow system a steady state may be established even for intermediates present at relatively high concentrations.

Stepwise Reaction See *Composite Reaction.*

Steric Factor

This is a factor introduced into simple versions of the collision theory of reactions to take care of the fact that the reaction probability depends on the mutual orientations of the reactant molecules.

See also *Collision Frequency*

Stoichiometric Number, ν

A chemical reaction of known *stoichiometry* can be written in general as

$$aA + bB + \ldots \rightarrow \ldots + yY + zZ$$

For the reaction products Y and Z the numbers y and z are known as the stoichiometric numbers, ν_Y and ν_Z, for Y and Z respectively. For the reactants the stoichiometric numbers are the negatives of the numbers appearing in the equation; for example the stoichiometric number ν_A for the reactant A is $-a$. In other words, the stoichiometric numbers are positive for products and negative for reactants.

PAC 1981, **53** (754); Green Book, 42.

Stoichiometry

The term stoichiometry refers to the relationship between the amounts of substances that react together in a particular chemical reaction, and the amounts of products that are formed. The general stoichiometric equation

$$aA + bB + \ldots \rightarrow \ldots + yY + zZ$$

provides the information that a moles of A reacts with b moles and B to produce y moles of Y and z moles of Z.

The stoichiometry of a reaction may be unknown, or may be very complex. For example, the thermal decomposition of acetaldehyde yields mainly methane and carbon monoxide, but also a variety of minor products such as ethane, acetone and diacetyl. The stoichiometric equation

$$CH_3CHO \rightarrow CH_4 + CO$$

is therefore only an approximate one.

Even when the overall stoichiometry of a reaction is well defined, it may be time-dependent in that it varies during the course of a reaction. Thus if a reaction occurs by the mechanism

$$A \rightarrow X \rightarrow Y,$$

and X is formed in substantial amounts during the course of the process, the relationship between the amounts of A, X and Y will vary with time, and no one stoichiometric equation can represent the reaction at all times.

Stripping Reaction

A chemical process, studied in a *molecular beam*, in which the reaction products are scattered forward with respect to the moving centre of mass of the system is known as a stripping reaction.

Strong Collision

This is a collision between two molecules in which the amount of energy transferred from one to the other is large compared with k_BT, where k_B is the Boltzmann constant and T the absolute temperature.

Sudden Potential-Energy Surface See under *Gradual and Sudden Potential-Energy Surfaces.*

Sum of States, $P(\epsilon)$

This is the total number of states for a system corresponding to an energy ϵ less than or equal to a specified value.

Surprisal, s

This is a function relating the prior distribution P_0 of product states to an observed or calculated product distribution P. It is defined by

$$s = -\ln(P/P_0)$$

Surprisal Analysis

The study of product state distributions in terms of *surprisals* has been referred to as surprisal analysis.

Symmetry Number, s

The symmetry number of a molecule is obtained by imagining all identical atoms to be labelled, and then counting the number of different but equivalent arrangements that can be obtained by rotating (but not reflecting) the molecule. It is the order of the rotational subgroup of the molecular point group.

In the statistical-mechanical treatment of chemical equilibrium, the partition function for each molecular species must be divided by its symmetry number.

Temperature Jump

This is a relaxation technique in which the temperature of a chemical system is suddenly raised. The system then relaxes to a new state of equilibrium, and analysis of the relaxation processes provides rate constants.

See also *Relaxation Kinetics*

PAC 1981, **53**, (795); 1983, **55**, 1363.

Third Body

This is a species, other than the reactant itself, which brings about the energization of a molecule that can undergo a unimolecular process, or brings about a combination reaction between atoms or radicals. In the latter case a third body is also called a chaperon.

Threshold Energy See *Critical Energy*.

Trajectory

This is a path taken by a reaction system over a *potential-energy surface*, or a diagram or mathematical description that represents that path. A trajectory can also be called a reaction path.

Transient Phase or Induction Period

This expression relates to the period of time that elapses prior to the establishment of a *steady state*. Initially the concentration of a reactive intermediate is zero, and it rises to the steady-state concentration during the transient phase.

Transient Species

A species occurring as a short-lived intermediate in a reaction occurring by a composite mechanism is known as a transient species.

Transition Species

This is any intermediate species in an *elementary reaction*. An *activated complex* is an example of a transition species, but the latter term also includes other intermediate species. Transition species have also been called transition states, but there is then danger of confusion with a true *activated complex*, which is also commonly known as a transition state.

Transition State See *Activated Complex.*

Transition-State Theory

This is a theory of the rates of elementary reactions which assumes a special type of equilibrium, having an equilibrium constant $K^{‡}$, to exist between reactants and activated complexes. According to this theory the rate constant is given by

$$k = (k_{\mathrm{B}}T / h)\, K^{‡}$$

where k_{B} is the Boltzmann constant and h is the Planck constant. The rate constant can also be expressed as

$$k = (k_{\mathrm{B}}T / h) \exp(\Delta^{‡}S^{\circ}/R) \exp(-\Delta^{‡}H^{\circ}/RT)$$

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

$$k = (k_{\mathrm{B}}T / h) \exp(-\Delta^{‡}G^{\circ}/RT)$$

where $\Delta^{‡}G^{\circ}$, known as the *Gibbs energy of activation*, is the standard molar Gibbs energy change for the conversion of reactants into activated complex. 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 the equations above must be multiplied by a transmission coefficient, κ, 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 $\Delta^{‡}S^{\circ}$, $\Delta^{‡}H^{\circ}$ and $\Delta^{‡}G^{\circ}$ occurring in the above equations are not ordinary thermodynamic quantities, since one degree of freedom in the activated complex is ignored.

Transition-state theory has also been known as absolute rate theory, and as activated-complex theory, but these terms are no longer recommended.

Transmission Coefficient See under *Transition-State Theory.*

Variational Transition State Theory

This expression is applied to modifications of conventional *transition state theory* in which the position of the *dividing surface* in the potential-energy surface is varied. The rate is calculated with the surface at various positions, and the lowest rate calculated is taken to be closest to the truth.

Vibrationally Adiabatic Transition-State Theory See *Adiabatic Transition-State Theory.*

Volume of Activation

This is an experimental quantity defined by

$$\Delta V_a = -RT\,(\partial \ln k / \partial p)_T$$

where k is the rate constant and p the hydrostatic pressure.

In *transition-state theory* ΔV_a is identified with the difference between the partial molar volume of the activated complex and the sum of the partial molar volumes of the reactants; it can then be represented by the symbol $\Delta^{\ddagger}V$.

The volume of activation is made up of an intrinsic contribution due to the changes in lengths and angles during the formation of the activated complex, and a solvational contribution related to readjustment of solvent molecules.

Weak Collision

This is a collision between two molecules in which the amount of energy transferred from one to the other is not large compared to k_BT (k_B is the Boltzmann constant and T the absolute temperature). Contrast *Strong Collision*.

References to Official IUPAC Documents

The first two documents listed below are compilations of IUPAC recommendations in book form. The remainder are articles in *Pure and Applied Chemistry*, the official publication of IUPAC. The recommendations in the present Glossary are consistent with previous IUPAC recommendations, except in one case (see under *Mixing Control*). Page numbers given in parenthesis in the text are the pages in the publication where the particular item is considered.

Green Book
Quantities, Units and Symbols in Physical Chemistry, Ed. Ian Mills *et al.*, Blackwell Science 1993.

Gold Book
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PAC 1974, **31**, 499
Manual of Symbols and Terminology for Physicochemical Quantities and Units. Appendix III: Electrochemical Nomenclature.

PAC 1981, **53**, 753
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PAC 1983, **55**, 1281
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ERRATUM

GLOSSARY OF TERMS USED IN CHEMICAL KINETICS, INCLUDING REACTION DYNAMICS

Pure & Applied Chemistry, Vol. 68, No.1, pp. 149–192, 1996

These recommendations were unfortunately incorrectly attributed on the title page, p. 149 of the reference given above. The title page of the article should have read as follows overleaf

Pure & Appl. Chem., Vol. 68, No. 1, pp. 149–192, 1996.
Printed in Great Britain.

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION
COMMISSION ON CHEMICAL KINETICS

GLOSSARY OF TERMS USED IN CHEMICAL KINETICS, INCLUDING REACTION DYNAMICS

(IUPAC Recommendations 1991)

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for the Commission on Chemical Kinetics of the Physical Chemistry Division of IUPAC

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A glossary of terms used in chemical kinetics, including reaction dynamics (IUPAC Recommendations 1996)

Synopsis

This Glossary is a compilation of terminology recommendations in the field of chemical kinetics. Every effort has been made to include what appear to be the most commonly accepted definitions. Is is hoped that the Glossary will be a helpful guide to those who are writing books and articles in the field. The reader is warned, however, that alternative definitions of some of the terms, such as Adiabatic and Rate-Controlling Step, are frequently to be found in the scientific literature.

Expressions shown in *italics* are to be found as separate items in this glossary.

Acid-Base Catalysis. General

Catalysis by acids or bases in solution is said to be general when it is possible to detect *catalysis* brought about by species other than the ions formed from the solvent itself (e.g., when water is the solvent, by species other than H^+ and OH^- ions).

See *Catalysis*.

Acid-Base Catalysis, Specific

Catalysis by acids or bases in solution is said to be specific when the only observable catalytic effects are those due to the ions formed from the solvent itself (e.g., if when water is the solvent the only observable *catalysis* is that due to the H^+ and OH^- ions).

See *Catalysis*.

Activated Complex

An activated complex is defined as a species corresponding to an arbitrary infinitesimally small region at or near the col (saddle-point) of a *potential-energy surface*. The term 'transition state' is synonymous with activated complex. The superscript ‡ is used to denote an activated complex.

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