

INTERNATIONAL UNION OF PURE  
AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON COLLOID AND SURFACE CHEMISTRY

MANUAL OF SYMBOLS AND  
TERMINOLOGY FOR  
PHYSICOCHEMICAL QUANTITIES  
AND UNITS—APPENDIX II

Definitions, Terminology and Symbols in Colloid and Surface Chemistry

PART II: HETEROGENEOUS CATALYSIS

Adopted by the IUPAC Council at Madrid, Spain, on 9 September 1975

Prepared for publication by

ROBERT L. BURWELL, JR.

PERGAMON PRESS  
OXFORD · NEW YORK · PARIS · FRANKFURT

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COLLOID AND SURFACE CHEMISTRY

PART II: HETEROGENEOUS CATALYSIS  
(RULES APPROVED 1975)

PREFACE

This Part II of Appendix II† to the *Manual of Symbols and Terminology for Physicochemical Quantities and Units*‡ (hereinafter referred to as the *Manual*) has been prepared by the Commission on Colloid and Surface Chemistry of the Division of Physical Chemistry of the International Union of Pure and Applied Chemistry. It is the outcome of extensive discussions within the Commission§ and its Task Force headed by Professor Burwell, with other IUPAC Commissions, and with persons outside IUPAC during the period 1970–1975. Among the latter, special mention must be made to Professors M. Boudart (USA), J. B. Butt (USA), and F. S. Stone (UK). A tentative version of these proposals was issued as Appendix 39 (August 1974) on Tentative Nomenclature, Symbols, Units and Standards to IUPAC *Information Bulletin*. The text has been revised in the light of the criticisms, comments, and suggestions which were received, and the present version was prepared by the Commission and formally adopted by the IUPAC Council at its meeting in Madrid, Spain, in September 1975.

It was felt that the use of unambiguous terminology would promote communication and avoid misunderstandings among workers in heterogeneous catalysis and that a list of preferred symbols would be useful in many

respects. Heterogeneous catalysis is primarily a branch of physical chemistry but it has substantial overlap with organic and inorganic chemistry and with chemical engineering. The Commission agreed that no term or symbol should be used in heterogeneous catalysis in a sense different from that in physical chemistry in general or, as far as possible, in a sense different from that in other branches of chemistry.

The present proposals are based on the same principles as those used in the *Manual*‡ and in Part I of this Appendix and are consistent with them. The most pertinent definitions of Part I are summarized and quoted in sections 1.2.1 and 1.2.2.

Historical and common usage of terms has been retained as far as is compatible with the above principles.

Since the present proposals should be considered as one of the sub-sets of the set of terms and symbols of physical chemistry, the general principles are not repeated here. Attention must be called, however to one point, namely the restriction of the term "specific" to the meaning, divided by mass. This necessitates either the repetitive use of "per unit area" or the introduction of a new term having this meaning. After careful consideration the Commission recommends that the term *areal*, meaning divided by area, be used. This is, however, at this time, a provisional recommendation subject to a decision on this and related terms by ICSU, the International Council of Scientific Unions.

†Part I of Appendix II, *Definitions, Terminology and Symbols in Colloid and Surface Chemistry*, prepared for publication by D. H. Everett, *Pure Appl. Chem.*, 31, 579–638 (1972).

‡*Manual of Symbols and Terminology for Physicochemical Quantities and Units* (1973 Edn.), prepared for publication by M. L. McGlashan and M. A. Paul, Butterworths, London (1975).

§The membership of the Commission during this period was as follows:

*Chairman*: –1973 D. H. Everett (UK); 1973–K. J. Mysels (USA)

*Secretary*: H. van Olphen (USA)

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*Observer*: –1971 Sir Eric Rideal (UK).

*National Representatives*: 1972–K. Morikawa (Japan); 1971–1974 Sir Eric Rideal (UK) (deceased); 1975 W. Schirmer (DDR).

La Jolla, California  
29 December 1975

KAROL J. MYSELS  
Chairman  
Commission on Colloid  
and Surface Chemistry

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## SECTION 1. DEFINITIONS AND TERMINOLOGY

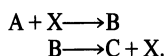
### 1.1 *Catalysis and catalysts*

*Catalysis* is the phenomenon in which a relatively small amount of a foreign material, called a *catalyst*, augments the rate of a chemical reaction without itself being consumed. Cases occur with certain reactants in which the addition of a substance reduces the rate of a particular reaction, for example, the addition of an inhibitor in a chain reaction or a poison in a catalytic reaction. The term "negative catalysis" has been used for these phenomena but this usage is not recommended; terms such as inhibition or poisoning are preferred.

A catalyst provides for sets of *elementary processes* (often called *elementary steps*) which link reactants and products and which do not occur in the absence of the catalyst. For example, suppose the reaction



to proceed at some rate which might be measurable but might be essentially zero. The addition of X might now provide a new pathway involving the intermediate B,



If reaction by this pathway proceeds at a rate significant with respect to the uncatalysed rate such that the total rate is increased, X is a catalyst. In this sense, a *catalytic reaction* is a closed sequence of elementary steps similar to the propagation steps of a gas-phase chain reaction.

The catalyst enters into reaction but is regenerated at the end of each reaction cycle. Thus, one unit of catalyst results in the conversion of many units of reactants (but see §1.7).

A catalyst, of course, may catalyse only one or some of several thermodynamically possible reactions.

It is difficult to separate Nature into water-tight

compartments and probably no operational definition of catalysis can be entirely satisfactory. Thus, water might facilitate the reaction between two solids by dissolving them. This phenomenon might appear to constitute an example of catalysis but such solvent effects are not, in general, considered to fall within the scope of catalysis. The kinetic salt effect in solution is also usually excluded. Further, a catalyst must be material and, although an input of heat into a system usually augments the rate of a reaction, heat is not called a catalyst, nor is light a catalyst in leading to reaction between chlorine and hydrogen.

A catalyst should be distinguished from an *initiator*. An initiator starts a chain reaction, for example, di-*t*-butylperoxide in the polymerization of styrene, but the initiator is consumed in the reaction. It is not a catalyst.

In *homogeneous catalysis*, all reactants and the catalyst are molecularly dispersed in one phase.

In *heterogeneous catalysis*, the catalyst constitutes a separate phase. In the usual case, the catalyst is a crystalline or amorphous solid, the reactants and products being in one or more fluid phases. The catalytic reaction occurs at the surface of the solid and, ideally, its rate is proportional to the area of the catalyst. However, in practical cases, transport processes may restrict the rate (see §1.6).

Most examples of catalysis can be readily characterized as homogeneous or heterogeneous but there are examples of catalysis which overlap the two types. Consider a system in which intermediates are formed at the surface and then are desorbed into the gas phase and react there. Such intermediates might generate a chain reaction in the gas phase, i.e. chain initiation and chain termination occur at the surface but chain propagation occurs in the gas phase.

*Enzyme catalysis* may share some of the characteristics of homogeneous and heterogeneous catalysis, as when the catalyst is a macromolecule small enough to be molecularly dispersed in one phase with all reactants but large enough so that one may speak of active sites on its surface.

This manual deals with heterogeneous catalysis. Other types of catalysis will receive no further attention.

### 1.2 *Adsorption*

#### 1.2.1 *General terms*

Although adsorption exists as a subject of scientific investigation independent of its role in heterogeneous catalysis, it requires particular attention here because of its central role in heterogeneous catalysis. Most or all catalytic reactions involve the adsorption of at least one of the reactants. Many terms related to adsorption have already been defined in Appendix II, Part I, §1.1. These include *surface*, *interface*, *area of surface or interface*, and *specific surface area*. Appendix II, Part I, recommends *A* or *S* and *a* or *s* as symbols for area and specific area, respectively. *A<sub>s</sub>* and *a<sub>s</sub>* may be used to avoid confusion with Helmholtz energy *A* or entropy *S* where necessary.

Other terms are *sorption*, *sorptive*, *sorbate* [a distinction being made between a species in its sorbed state (sorbate) and a substance in the fluid phase which is capable of being sorbed (sorptive)], *absorption*, *absorptive*, *absorbate*, *absorbent*; and *adsorption*, *adsorptive*, *adsorbate*, *adsorbent*.† The term *adsorption complex* is used to denote the entity constituted by the adsorbate and the part of the adsorbent to which it is bound.

Appendix II, Part I, § 1.1.5, treats the adsorbent/fluid‡ interface as follows.

†The use of *substrate* for adsorbent or support is to be discouraged because of its general use in enzyme chemistry to designate a reactant.

‡Appendix II, Part I, recommends: The use of a solidus to separate the names of bulk phases is preferred to the use of a hyphen which can lead to ambiguities.

"It is often useful to consider the adsorbent/fluid interface as comprising two regions. The region of the fluid phase (i.e. liquid or gas) forming part of the adsorbent/fluid interface may be called the *adsorption space*, while the portion of the adsorbent included in the interface is called the *surface layer of the adsorbent*."

When used to denote the process in which molecules† or dissociated molecules accumulate in the adsorption space or in the surface layer of the adsorbent, adsorption has as its counterpart the term *desorption* which denotes the converse process (see Appendix II, Part I, §1.1.4). Adsorption is also used to denote the result of the process of adsorption, i.e. the presence of adsorbate on an adsorbent. The adsorbed state may or may not be in equilibrium with the adsorptive (see §1.2.2(c)).

Adsorption and desorption may also be used to indicate the direction from which equilibrium has been approached, e.g. adsorption curve (point), desorption curve (point).

### 1.2.2 Chemisorption and physisorption

For convenience, the relevant portions of §§1.1.6 and 1.1.7 of Appendix II, Part I, are reproduced here.

#### *Chemisorption and physisorption*

*Chemisorption* (or *Chemical Adsorption*) is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds. The problem of distinguishing between chemisorption and physisorption (see below) is basically the same as that of distinguishing between chemical and physical interaction in general. No absolutely sharp distinction can be made and intermediate cases exist, for example, adsorption involving strong hydrogen bonds or weak charge-transfer.

Some features which are useful in recognising chemisorption include:

- (a) the phenomenon is characterised by chemical specificity;
- (b) changes in the electronic state may be detectable by suitable physical means (e.g. u.v., infrared or microwave spectroscopy, electrical conductivity, magnetic susceptibility);
- (c) the chemical nature of the adsorptive(s) may be altered by surface dissociation or reaction in such a way that on desorption the original species cannot be recovered; in this sense chemisorption may not be reversible;
- (d) the energy of chemisorption is of the same order of magnitude as the energy change in a chemical reaction between a solid and a fluid: thus chemisorption, like chemical reactions in general, may be exothermic or endothermic and the magnitudes of the energy changes may range from very small to very large;
- (e) the elementary step in chemisorption often involves an activation energy;
- (f) where the activation energy for adsorption is large (*activated adsorption*), true equilibrium may be achieved slowly or in practice not at all. For example, in the adsorption of gases by solids the observed extent of adsorption, at a constant gas pressure after a fixed time, may in certain ranges of temperature increase with rise in temperature. In addition, where the activation energy for desorption is large, removal of the chemisorbed species from the surface may be

possible only under extreme conditions of temperature or high vacuum, or by some suitable chemical treatment of the surface;

- (g) since the adsorbed molecules are linked to the surface by valence bonds, they will usually occupy certain *adsorption sites* on the surface and only one layer of chemisorbed molecules is formed (monolayer adsorption).

*Physisorption* (or *Physical Adsorption*) is adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved. The term *van der Waals adsorption* is synonymous with physical adsorption, but its use is not recommended.

Some features which are useful in recognising physisorption include:

- (a') the phenomenon is a general one and occurs in any solid/fluid system, although certain specific molecular interactions may occur, arising from particular geometrical or electronic properties of the adsorbent and/or adsorptive;
- (b') evidence for the perturbation of the electronic states of adsorbent and adsorbate is minimal;
- (c') the adsorbed species are chemically identical with those in the fluid phase, so that the chemical nature of the fluid is not altered by adsorption and subsequent desorption;
- (d') the energy of interaction between the molecules of adsorbate and the adsorbent is of the same order of magnitude as, but is usually greater than, the energy of condensation of the adsorptive;
- (e') the elementary step in physical adsorption does not involve an activation energy. Slow, temperature dependent, equilibration may however result from rate-determining transport processes;
- (f') in physical adsorption, equilibrium is established between the adsorbate and the fluid phase. In solid/gas systems at not too high pressures the extent of physical adsorption increases with increase in gas pressure and usually decreases with increasing temperature. In the case of systems showing hysteresis the equilibrium may be metastable.
- (g') under appropriate conditions of pressure and temperature, molecules from the gas phase can be adsorbed in excess of those in direct contact with the surface (multilayer adsorption or filling of micropores).

#### *Monolayer and multilayer adsorption, micropore filling and capillary condensation*

In *monolayer adsorption* all the adsorbed molecules are in contact with the surface layer of the adsorbent.

In *multilayer adsorption* the adsorption space accommodates more than one layer of molecules and not all adsorbed molecules are in contact with the surface layer of the adsorbent.

The *monolayer capacity* is defined, for chemisorption, as the amount of adsorbate which is needed to occupy all adsorption sites as determined by the structure of the adsorbent and by the chemical nature of the adsorptive; and, for physisorption, as the amount needed to cover the surface with a complete monolayer of molecules in close-packed array, the kind of close-packing having to be stated explicitly when necessary. Quantities relating to monolayer capacity may be denoted by subscript *m*.

The *surface coverage* ( $\theta$ ) for both monolayer and

†The term molecules is used in the general sense to denote any molecular species: atom, ion, neutral molecule or radical.

multilayer adsorption is defined as the ratio of the amount of adsorbed substance to the monolayer capacity.

The area occupied by a molecule in a complete monolayer is denoted by  $a_m$ ; for example, for nitrogen molecules  $a_m(N_2)$ .

*Micropore filling* is the process in which molecules are adsorbed in the adsorption space within micropores.

The *micropore volume* is conventionally measured by the volume of the adsorbed material which completely fills the micropores, expressed in terms of bulk liquid at atmospheric pressure and at the temperature of measurement.

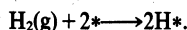
In certain cases (e.g. porous crystals) the micropore volume can be determined from structural data.

*Capillary condensation* is said to occur when, in porous solids, multilayer adsorption from a vapour proceeds to the point at which pore spaces are filled with liquid separated from the gas phase by menisci.

The concept of capillary condensation loses its sense when the dimensions of the pores are so small that the term meniscus ceases to have a physical significance. Capillary condensation is often accompanied by hysteresis."

### 1.2.3 Types of chemisorption

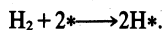
*Non-dissociative, dissociative.* If a molecule is adsorbed without fragmentation, the adsorption process is *non-dissociative*. Adsorption of carbon monoxide is frequently of this type. If a molecule is adsorbed with dissociation into two or more fragments both or all of which are bound to the surface of the adsorbent, the process is *dissociative*. Chemisorption of hydrogen is commonly of this type.



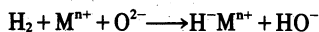
The asterisk represents a surface site.

*Homolytic and heterolytic* relate in the usual sense to the formal nature of the cleavage of a single bond. If the electron pair in the bond of the adsorptive A:B is divided in the course of its dissociative adsorption, the adsorption is *homolytic dissociative adsorption*. If A or B retains the electron pair, the adsorption is *heterolytic dissociative adsorption*. Examples follow.

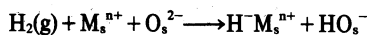
(a) Homolytic dissociative adsorption of hydrogen on the surface of a metal:



(b) Heterolytic dissociative adsorption of hydrogen at the surface of an oxide where the surface sites  $M^{n+}$  and  $O^{2-}$  are surface sites in which the ions are of lower coordination than the ions in the bulk phase:



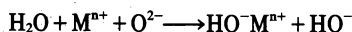
Where clarity requires it, the equation may be written



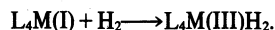
where the subscript s indicates that the species indicated are part of the surface.

The notation  $H^-M^{n+}$  is used, as in conventional inorganic terminology, to indicate that the oxidation number of M has not changed.

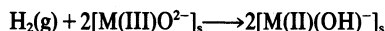
(c) Heterolytic dissociative adsorption of water at the same pair of sites as in (b):



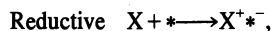
*Reductive and oxidative dissociative adsorption* involve usage analogous to that in coordination chemistry in which one speaks of the following reaction as an oxidative addition



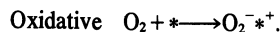
Here, M represents a transition metal atom and L a ligand. H as a ligand is given an oxidation number of -1. If reductive, the electron pair which constitutes the bond in the sorptive, A:B, is transferred to surface species; if oxidative, a pair of electrons is removed from surface species. One would say that dissociative adsorption of  $Cl_2$  on a metal is oxidative if chlorine forms  $Cl^-$  ions on the surface of the adsorbent. A dissociative adsorption would be reductive if, for example, it occurred thus (note that  $H_2 \rightarrow 2H^+ + 2e$  here),



*Charge transfer adsorption* represents oxidative or reductive chemisorption where reductive and oxidative refer to electron gain or loss on species in the solid. In simple cases it is non-dissociative, i.e. there is a mere transfer of charge between adsorptive and adsorbent in forming the adsorbate. Two examples follow.



where X represents an aromatic molecule of low ionization potential such as anthracene or triphenylamine and \* a site on silica-alumina.



The term, charge transfer adsorption, has also been applied to adsorption which resembles the charge transfer complexes of Mulliken.

*Immobile, mobile.* These terms are used to describe the freedom of the molecules of adsorbate to move about the surface. Adsorption is immobile when  $kT$  is small compared to  $\Delta E$ , the energy barrier separating adjacent sites. The adsorbate has little chance of migrating to neighbouring sites and such adsorption is necessarily *localized*. Mobility of the adsorbate will increase with temperature and mobile adsorption may be either *localized* or *non-localized*. In localized mobile adsorption, the adsorbate spends most of the time on the adsorption sites but can migrate or be desorbed and re-adsorbed elsewhere. In non-localized adsorption the mobility is so great that a small fraction of the adsorbed species are on the adsorption sites and a large fraction at other positions on the surface.

In some cases of localized adsorption the adsorbate is ordered into a two-dimensional lattice or *net* in a particular range of surface coverage and temperature. If the net of the ordered adsorbed phase is in registry with the lattice of the adsorbent the structure is called *coherent*, if not it is called *incoherent* (see also §1.2.4).

Each of the various processes of adsorption may have desorptions of the reverse forms, for example, dissociative adsorption may have as its reverse, *associative*

*desorption*. However, the process of chemisorption may not be reversible (§1.2.2(c)). Desorption may lead to species other than that adsorbed, for example, ethane dissociatively adsorbed on clean nickel gives little or no ethane upon desorption, 1-butene dissociatively adsorbed to methylallyl and H on zinc oxide gives mainly 2-butenes upon desorption, and some  $\text{WO}_3$  may evaporate from tungsten covered with adsorbed oxygen.

*Photoadsorption, photodesorption*. Irradiation by light (usually visible or ultraviolet) may affect adsorption. In a system containing adsorptive and adsorbent exposure to light may lead to increased adsorption (*photoadsorption*) or it may lead to desorption of an adsorbate (*photodesorption*).

#### 1.2.4 Sites for chemisorption

Sites may be classified according to their chemical nature in usual chemical terminology. The following terms are simple extensions of ordinary chemical usage: *basic sites*, *acidic sites*, *Lewis acid sites*, *proton* or *Brønsted acid sites*, *electron accepting sites* and *electron donating sites* (possible examples of the last two appear under *charge transfer adsorption*).

It is often useful to consider that sites for chemisorption result from *surface coordinative unsaturation*, i.e. that atoms at the surface have a lower coordination number than those in bulk. Thus, for example a chromium ion at the surface of chromium oxide has a coordination number less than that of a chromium ion in the bulk. The chromium ion will tend to bind a suitable adsorptive so as to restore its coordination number. An atom in the (100) surface of a face-centered cubic metal has a coordination number of 8 vs 12 for an atom in bulk; this, too, represents surface coordinative unsaturation. However, of course, there are sites to which the concept of surface coordinative unsaturation does not apply, for example, *Brønsted acid sites*.

One is rarely sure as to the exact identity and structure of sites in adsorption and heterogeneous catalysis. However, some symbolism is needed for theoretical discussion of possible sites. On the one hand one may wish to use a description which is general and non-specific. For this \* and (ads) are recommended as, for example,  $\text{H}^*$  and  $\text{H}(\text{ads})$ . Or, one may wish to use a symbolism which is as specific as possible. General chemical symbols may be useful in this case. A symbolism useful for metals involves the specification of  $\text{C}_j$  and  $\text{B}_n$ , where  $\text{C}_j$  denotes a surface atom with  $j$  nearest neighbours and  $\text{B}_n$  denotes an ensemble of  $n$  surface atoms which together constitute an adsorption site, for example, the adsorption site lying above the centre of three surface atoms constituting the corners of an equilateral triangle is a  $\text{B}_3$  site (for details see van Hardeveld and Hartog, *Surface Sci.* 15, 189 (1969)).

Cases of chemisorption are known in which at high coverages the net (two-dimensional lattice) of the adsorbate is not in registry with the lattice of the adsorbent. In such situations, the concept of sites of precise location and fixed number may not be applicable. Similar difficulties about the definition of sites will occur if surface reconstruction takes place upon interaction of adsorbate and adsorbent.

Because of various difficulties which often appear in knowing the identity of surface sites, it is frequently convenient, particularly for metals, to define the surface coverage  $\theta$  as the ratio of the number of adsorbed atoms or groups to the number of surface atoms (c.f. §1.2.2).

#### 1.2.5 Uniformity of sites

Variations in the nature of the sites for adsorption or catalysis can occur even with pure metals where there is no question of differences in chemical composition between one part of the surface and another. These variations arise not only because of defects in the metal surfaces but also because the nature of a site depends on the structure of the surface. *Uniform sites* are more likely to be encountered when adsorption or catalysis is studied on an individual face of a single crystal, but even individual faces may present more than one kind of site. *Non-uniform sites* will normally occur with specimens of metal exposing more than one type of crystal face. There are two main kinds of non-uniformities. *Intrinsic non-uniformity* is a variation due solely to the nature of the adsorbent. *Induced non-uniformity* arises when the presence of an adsorbate molecule on one site leads to a variation in the strength of adsorption at a neighbouring site. Thus, a set of uniform sites on an individual crystal face may become non-uniform if the surface is partially covered with a chemisorbed species.

When the catalytic properties of metals are examined, the importance of the non-uniformity of sites depends on the reaction under study. For some reactions, the activity of the metal catalyst depends only on the total number of sites available and these are termed *structure-insensitive reactions*. For other reactions, classified as *structure-sensitive reactions*, activity may be much greater on sites associated with a particular crystal face or even with some type of defect structure. The alternative names of *facile* or *demanding* have been used to describe structure-insensitive or structure-sensitive reactions respectively.

The terms of §1.2.5 have been discussed with reference to metallic surfaces but they can be applied to other adsorbents and catalysts and, in particular, to the pair-sites involved in heterolytic dissociative adsorption.

#### 1.2.6 Active site, active centre

The term *active sites* is often applied to those sites for adsorption which are the effective sites for a particular heterogeneous catalytic reaction. The terms *active site* and *active centre* are often used as synonyms, but *active centre* may also be used to describe an ensemble of sites at which a catalytic reaction takes place.

#### 1.2.7 Adsorption isotherms

An *adsorption isotherm* for a single gaseous adsorptive on a solid is the function which relates at constant temperature the amount of substance adsorbed at equilibrium to the pressure (or concentration) of the adsorptive in the gas phase. The surface excess amount rather than the amount adsorbed is the quantity accessible to experimental measurement, but, at lower pressures, the difference between the two quantities becomes negligible (see Appendix II, Part I, §1.1.11).

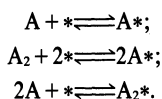
Similarly, when two or more adsorptives adsorb competitively on a surface, the adsorption isotherm for adsorptive  $i$  at a given temperature is a function of the equilibrium partial pressures of all of the adsorptives. In the case of adsorption from a liquid solution, an adsorption isotherm for any preferentially adsorbed solute may be similarly defined in terms of the equilibrium concentration of the respective solution component, but the isotherm usually depends on the nature of the solvent and on the concentrations (mole fractions) of other solute components if present. Individual solute isotherms cannot

be derived from surface excesses except on the basis of an appropriate model of the adsorption layer; when chemisorption occurs it is generally adequate to assume monolayer adsorption. Amounts adsorbed are often expressed in terms of coverages  $\theta_i$ . In chemisorption,  $\theta_i$  is the fraction of sites for adsorption covered by species  $i$ . Types of adsorption isotherms of interest to heterogeneous catalysis follow.

*The linear adsorption isotherm.* The simplest adsorption isotherm is the analogue of Henry's law. For a single adsorptive, it takes the form

$$\theta = Kp \quad \text{or} \quad \theta = Kc,$$

where  $p$  and  $c$  are the pressure and concentration of the adsorptive,  $\theta$  is the coverage by adsorbate and  $K$  the *linear adsorption isotherm equilibrium constant*, or *Henry's law constant*. Most adsorption isotherms reduce to Henry's law when  $p$  or  $c$  becomes small enough provided that simple adsorption occurs, i.e. adsorption is neither dissociative nor associative. That is, at low enough coverages Henry's law usually applies to the first of the following equations but not the second and third.

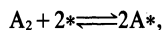


The *Langmuir adsorption isotherm*,

$$\theta = \frac{Kp}{1 + Kp} \quad \text{or} \quad \frac{\theta}{p(1 - \theta)} = K,$$

or the equivalents in terms of concentrations, is commonly taken to result from simple (non-dissociative) adsorption from an ideal gas on a surface with a fixed number of uniform sites which can hold one and only one adsorbate species.  $K$  is called the *Langmuir adsorption equilibrium constant*. Further, the enthalpy of the adsorbed form must be independent of whether or not adjacent sites are occupied and consequently the enthalpy of adsorption is independent of  $\theta$ . The second form of Langmuir's isotherm given above, emphasizes that the constant  $K$  is the equilibrium constant for  $A + * \rightleftharpoons A*$ . Since the constancy of enthalpy with coverage is analogous to the constancy of enthalpy with pressure in an ideal gas, the adsorbed state in a system following Langmuir's isotherm is sometimes called an *ideal adsorbed state*.

If chemisorption is dissociative,



Langmuir's equation takes the form

$$\theta = \frac{K^{1/2} p^{1/2}}{1 + K^{1/2} p^{1/2}} \quad \text{or} \quad K = \frac{\theta^2}{p(1 - \theta)^2}.$$

For simple adsorption of two adsorptives A and B competing for the same sites, Langmuir's isotherm takes the form

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B},$$

where  $K_A$  and  $K_B$  are the equilibrium constants for the separate adsorption of A and B respectively. This

equation can be generalized to cover adsorption of several adsorptives and to allow for dissociative adsorption of one or more adsorptives.

In the *Freundlich adsorption isotherm*, the amount adsorbed is proportional to a fractional power of the pressure of the adsorptive. For a particular system, the fractional power and the constant of proportionality are functions of temperature. In terms of coverage the isotherm assumes the form

$$\theta = ap^{1/n},$$

where  $n$  is a number greater than unity and  $a$  a constant. In the region of validity of the isotherm the (differential) enthalpy of adsorption is a linear function of  $\ln \theta$ .

In the *Temkin adsorption isotherm*, the amount adsorbed is related to the logarithm of the pressure of the adsorptive

$$\theta = A \ln p + B,$$

where  $A$  and  $B$  are constants. In the region of validity of the isotherm the (differential) enthalpy of adsorption is a linear function of  $\theta$ .

The *Brunauer-Emmett-Teller* (or *BET*) *adsorption isotherm* applies only to the physisorption of vapours but it is important to heterogeneous catalysis because of its use for the determination of the surface areas of solids. The isotherm is given by the following equation,

$$\frac{n}{n_m} = \frac{c(p/p^0)}{(1 - p/p^0)(1 + (c - 1)(p/p^0))} = \theta,$$

where  $c$  is a constant which depends upon the temperature, the adsorptive and the adsorbent,  $n$  is the amount adsorbed,  $n_m$  is the monolayer capacity and  $p^0$  is the saturated vapour pressure of the pure, liquid adsorptive at the temperature in question. According to this equation, which is based on a model of multilayer adsorption,  $\theta$  exceeds unity when  $p/p^0$  is sufficiently large.

### 1.2.8 Bifunctional catalysis

Some heterogeneous catalytic reactions proceed by a sequence of elementary processes certain of which occur at one set of sites while others occur at sites which are of a completely different nature. For example, some of the processes in the reforming reactions of hydrocarbons on platinum/alumina occur at the surface of platinum, others at acidic sites on the alumina. Such catalytic reactions are said to represent *bifunctional catalysis*. The two types of sites are ordinarily intermixed on the same primary particles (§1.3.2) but similar reactions may result even when the catalyst is a mixture of particles each containing but one type of site. These ideas could, of course, be extended to create the concept of *polyfunctional catalysis*.

### 1.2.9 Rates of adsorption and desorption

*Sticking coefficient* is the ratio of the rate of adsorption to the rate at which the adsorptive strikes the total surface, i.e. covered and uncovered. It is usually a function of surface coverage, of temperature and of the details of the surface structure of the adsorbent.

*Sticking probability* is often used with the same meaning but in principle it is a microscopic quantity concerned with the individual collision process. Thus the sticking coefficient can be considered as a mean sticking

probability averaged over all angles and energies of the impinging molecules and over the whole surface.

The *mean residence time* of adsorbed molecules is the mean time during which the molecules remain on the surface of the adsorbent, i.e. the mean time interval between impact and desorption. While residing on the surface the molecules may migrate between adsorption sites before desorption. If the residence time of an adsorbed species refers to specified adsorption sites it would be called the *mean life time* of the particular adsorption complex. When the rate of desorption is first order in coverage the residence time is independent of surface coverage and equal to the reciprocal of the rate constant of the desorption process. In this case it can be characterized unambiguously also by a half-life or by some other specified fractional-life of the desorption process. If the desorption process is not first order, e.g. due to mutual interactions of the adsorbed molecules and/or energetic heterogeneity of the surface, the residence time depends upon surface coverage and the operational definition of "residence time" needs to be specified precisely.

*Unactivated and activated adsorption.* If the temperature coefficient of the rate of adsorption is very small, the adsorption process is said to be *unactivated* (i.e. to have a negligible activation energy). In this case the sticking coefficient at low coverages may be near unity particularly for smaller molecules. If the temperature coefficient of the rate of adsorption is substantial, the adsorption process is said to be *activated* (i.e. to have a significant activation energy). In this case, the sticking coefficient is small. In general, the activation energy of activated adsorption is a function of coverage and it usually increases with increasing coverage.

A number of relations between rate of activated adsorption and coverage have been proposed. Of these, one has been particularly frequently used, the *Roginskii-Zeldovich equation* sometimes called the *Elovich equation*,

$$\frac{d\theta}{dt} = a e^{-b\theta}$$

where  $\theta$  is the coverage, and  $a$  and  $b$  are constants characteristic of the system.

### 1.3 Composition, structure and texture of catalysts

#### 1.3.1 General terms

Catalysts may be one-phase or multiphase. In the first case, they may be composed of one substance (for example, alumina or platinum black) or they may be a one phase solution of two or more substances. In this case, the components of the solution should be given and joined by a hyphen (for example, silica-alumina).

*Support.* In multiphase catalysts, the active catalytic material is often present as the minor component dispersed upon a *support* sometimes called a *carrier*. The support may be catalytically inert but it may contribute to the overall catalytic activity. Certain bifunctional catalysts (§1.2.8) constitute an extreme example of this. In naming such a catalyst, the active component should be listed first, the support second and the two words or phrases should be separated by a solidus, for example, platinum/silica or platinum/silica-alumina. The solidus is sometimes replaced by the word "on", for example, platinum on alumina.

*Promoter.* In some cases, a relatively small quantity of one or more substances, the *promoter* or *promoters*, when

added to a catalyst improves the activity, the selectivity, or the useful lifetime of the catalyst. In general, a promoter may either augment a desired reaction or suppress an undesired one. There is no formal system of nomenclature for designating promoted catalysts. One may, however, for example, employ the phrase "iron promoted with alumina and potassium oxide".

A promoter which works by reducing the tendency for sintering and loss of area may be called a *textural promoter* (see §1.7.3).

*Doping.* In the case of semiconducting catalysts, a small amount of foreign material dissolved in the original catalyst may modify the rate of a particular reaction. This phenomenon is sometimes called *doping* by analogy with the effect of similar materials upon semiconductivity.

#### 1.3.2 Porosity and texture

Many but not all catalysts are porous materials in which most of the surface area is internal. It is sometimes convenient to speak of the *structure* and *texture* of such materials. The *structure* is defined by the distribution in space of the atoms or ions in the material part of the catalyst and, in particular, by the distribution at the surface. The *texture* is defined by the detailed geometry of the void space in the particles of catalyst. *Porosity* is a concept related to texture and refers to the pore space in a material. With zeolites, however, much of the porosity is determined by the crystal structure.

An exact description of the texture of a porous catalyst would require the specification of a very large number of parameters. The following averaged properties are often used.

With respect to porous solids, the surface associated with pores may be called the *internal surface*. Because the accessibility of pores may depend on the size of the fluid molecules, the extent of the accessible internal surface may depend on the size of the molecules comprising the fluid, and may be different for the various components of a fluid mixture (*molecular sieve effect*).

When a porous solid consists of discrete particles, it is convenient to describe the outer boundary of the particles as *external surface*.

It is expedient to classify pores according to their sizes†

- (i) pores with widths exceeding about 0.05  $\mu\text{m}$  or 50 nm (500 Å) are called *macropores*;
- (ii) pores with widths not exceeding about 2.0 nm (20 Å) are called *micropores*;
- (iii) pores of intermediate size are called *mesopores*.

The terms *intermediate* or *transitional* pores, which have been used in the past, are not recommended.

In the case of micropores, the whole of their accessible volume may be regarded as adsorption space.

The above limits are to some extent arbitrary. In some circumstances it may prove convenient to choose somewhat different values.

*Pore size distribution* is the distribution of pore volume with respect to pore size; alternatively, it may be defined by the related distribution of pore area with respect to pore size. It is an important factor for the kinetic behaviour of a porous catalyst and thus an essential property for its characterization (see §1.6).

The computation of such a distribution involves arbitrary assumptions and a pore-size distribution should always be accompanied by an indication as to the method used in its determination. The methods usually involve either or both of the following (i) adsorption-desorption isotherms of nitrogen or other adsorptives in conjunction with a particular model for conversion of the isotherm

†See Appendix II, Part I, §1.1.5.



into a pore-size distribution, (ii) data obtained by the mercury porosimeter. The isotherm gives a pore-size distribution for mesopores. The mercury porosimeter gives a distribution covering macropores and larger mesopores. In both cases what is measured is, strictly speaking, not the exact volume of pores having a given pore size, but the volume of pores accessible through pores of a given size. The relationship between these two functions depends on the geometrical nature of the pore system.

The *specific pore volume* is the total internal void volume per unit mass of adsorbent. Some of the pore volume may be completely enclosed, and thus inaccessible to molecules participating in a catalytic reaction.

The total accessible pore volume may be measured by the amount of adsorbate at the saturation pressure of the adsorptive, calculated as liquid volume, provided the adsorption on the external surface can be neglected or can be evaluated. The accessible pore volume may be different for molecules of different sizes. A method which is not subject to the effect of the external surface is the determination of the dead space by means of a non-sorbable gas (normally helium) in conjunction with the determination of the bulk volume of the adsorbent by means of a non-wetting liquid or by geometrical measurements.

*Primary particles.* Certain materials widely used as catalysts or supports consist of spheroids of about 10 nm (100 Å) in diameter loosely cemented into granules or pellets. The texture of these resembles that of a cemented, loose gravel bed. The 10 nm (100 Å) particles may be called *primary particles*.

*Percentage exposed* in metallic catalysts. The accessibility of the atoms of metal in metallic catalysts, supported or unsupported, depends upon the percentage of the total atoms of metal which are surface atoms. It is recommended that the term *percentage exposed* be employed for this quantity rather than the term *dispersion* which has been frequently employed.

*Pretreatment and activation.* Following the preparation of a catalyst or following its insertion into a catalytic reactor, a catalyst is often subjected to various treatments before the start of a catalytic run. The term *pretreatment* may, in general, be applied to this set of treatments. In some cases the word *activation* is used. It implies that the material is converted into a catalyst or into a very much more effective one by the pretreatment. *Outgassing* is a form of pretreatment in which a catalyst is heated *in vacuo* to remove adsorbed or dissolved gas. *Calcination* is a term which means heating in air or oxygen and is most likely to be applied to a step in the preparation of a catalyst.

#### 1.4 Catalytic reactors

The vessel in which a catalytic reaction is carried out is called a *reactor*. Many different arrangements can be adopted for introducing the reactants and removing the products.

In a *batch reactor* the reactants and the catalyst are placed in the reactor which is then closed to transport of matter and the reaction is allowed to proceed for a given time whereupon the mixture of unreacted material together with the products is withdrawn. Provision for mixing may be required.

In a *flow reactor*, the reactants pass through the reactor while the catalysis is in progress. Many variations are possible.

The catalyst may be held in a *packed bed* and the reactants passed over the catalyst. A packed bed flow reactor is commonly called a *fixed bed reactor* and the term *plug-flow* is also used to indicate that no attempt is made to back-mix the reaction mixture as it passes through the catalyst bed. The main modes of operation of a flow reactor are *differential* involving a small amount of reaction so that the composition of the mixture is approximately constant throughout the catalyst bed, or *integral* involving a more substantial amount of reaction such that the composition of material in contact with the final section of the catalyst bed is different from that entering the bed.

In a *pulse reactor*, a carrier gas, which may be inert or possibly one of the reactants, flows over the catalyst and small amounts of the other reactant or reactants are injected into the carrier gas at intervals. A pulse reactor is useful for exploratory work but kinetic results apply to a transient rather than to the steady state conditions of the catalyst.

Several alternative modes of operation may be used to avoid the complications of the changing concentrations along the catalyst bed associated with integral flow reactors and each of these has a special name. In a *stirred flow reactor*, effective mixing is achieved within the reactor often by placing the catalyst in a rapidly-rotating basket. If the mixing achieved in this way is efficient, the composition of the mixture in the reactor will be close to that of the exit gases. The same result can be reached by *recirculation* of the gas around a loop containing a fixed bed of catalyst, provided that the rate of recirculation is considerably larger than the rate of flow in and out of the loop. Under these circumstances, a substantial conversion to products can be obtained even though conditions in the bed correspond more closely to those associated with a differential rather than with an integral reactor. Another mode of operation involves a *fluidized bed* in which the flow of gases is sufficient to cause the bed of finely divided particles of catalyst to behave like a fluid. In a fluidized bed, the temperature is uniform throughout, although mixing of gas and solid is usually incomplete. It has special applications in cases where the catalyst has to be regenerated, e.g. by oxidation, after a short period of use. Continuous transfer of catalyst between two vessels (one used as reactor and the other for catalyst regeneration) is possible with a fluidized system. The stirred flow and the recirculation reactors are characterized ideally by very small concentration and temperature gradients within the catalyst region. The term, *gradientless reactor*, may be used to include both types.

All reactors, batch or flow, may be operated in three main ways in regard to temperature. These are *isothermal*, *adiabatic* and *temperature-programmed*. For the last, in a batch reactor the variation of temperature with time may be programmed, or in a fixed bed reactor the variation of temperature along the length of the bed may be controlled.

When reactors are operated isothermally the batch reactor is characterized by adsorbate concentrations and other aspects of the state of the surface which are constant in space (i.e. uniform within the catalyst mass) but which change with time. In the integral flow reactor with the catalyst at steady state activity, the surface conditions are constant with time but change along the bed. In the gradientless reactor at steady state, the surface conditions are constant in space and, if the catalyst is at a steady state, with time. In the pulse reactor, the catalyst is

often not in a condition of steady state, concentrations change as the pulse moves through the bed, and there may be chromatographic separation of reactants and products.

In general, if heterogeneous catalytic reactions are to be conducted isothermally, the reactor design must provide for heat flow to or from the particles of catalyst so as to keep the thermal gradients small. Otherwise, temperatures within the catalyst bed will be non-uniform. The differential reactor and the various forms of the gradient-less reactors are advantageous in this regard.

The types of reactors described above can, in principle, be extended to reactions in the liquid phase although the pulse reactor has been little used in such cases.

Reactions in which one reactant is gaseous, the other is in a liquid phase, and the catalyst is dispersed in the liquid phase, constitute a special but not unusual case, for example, the hydrogenation of a liquid alkene catalysed by platinum. A batch reactor is most commonly employed for laboratory scale studies of such reactions. Mass transport from the gaseous to the liquid phase may reduce the rate of such a catalytic reaction unless the contact between the gas and the liquid is excellent (see §1.6).

### 1.5 Kinetics of heterogeneous catalytic reactions

#### 1.5.1 General terms

Consider a chemical reaction

$$0 = \sum_B \nu_B B,$$

where  $\nu_B$  is the stoichiometric coefficient (plus for products, minus for reactants) of any product or reactant B. The *extent of reaction*  $\xi$  is defined (see §11.1 of the Manual)

$$d\xi = \nu_B^{-1} dn_B,$$

where  $n_B$  is the amount of the substance B.

If *rate of reaction* is to have an unambiguous meaning, it should be defined as the rate of increase of the extent of reaction

$$\dot{\xi} = d\xi/dt = \nu_B^{-1} dn_B/dt$$

whereas the quantity  $dn_B/dt$  may be called the *rate of formation* (or *consumption*) of B.

To facilitate the comparison of the results of different investigators, the rates of heterogeneous catalytic reactions should be suitably expressed and the conditions under which they have been measured should be specified in sufficient detail. If the rate of the uncatalyzed reaction is negligible, the rate of the *catalyzed* reaction may be given as

$$r = \frac{1}{Q} d\xi/dt.$$

If  $Q$ , the *quantity of catalyst*, is in mass,

$$r = r_m = \frac{1}{m} d\xi/dt$$

and  $r_m$  is the *specific rate of reaction* which may be called the *specific activity of the catalyst* under the specified conditions. If  $Q$  is in volume,

$$r = r_v = \frac{1}{V} d\xi/dt.$$

The volume should be that of the catalyst granules

excluding the intergranular space. If  $Q$  is in area,

$$r = r_a = \frac{1}{A} d\xi/dt$$

where  $r_a$  is the *areal† rate of reaction*. If the *total surface area* of the catalyst is used, it should be preferably a BET nitrogen area. However, other types of specified areas may be employed, for example, the exposed metal area of a supported metallic catalyst. The exposed metal area is often estimated by selective chemisorption of a suitable sorptive, e.g. hydrogen or carbon monoxide.

The *turnover frequency*,  $N$ , (commonly called the *turnover number*) defined, as in enzyme catalysis, as molecules reacting per active site in unit time, can be a useful concept if employed with care. In view of the problems in measuring the number of active sites discussed in §1.2.4, it is important to specify exactly the means used to express  $Q$  in terms of active sites. A realistic measure of such sites may be the number of surface metal atoms on a supported catalyst but in other cases estimation on the basis of a BET surface area may be the only readily available method. Of course, turnover numbers (like rates) must be reported at specified conditions of temperature, initial concentration or initial partial pressures, and extent of reaction.

In comparing various catalysts for a given reaction or in comparing various reactions on a given catalyst, it may be inconvenient or impracticable to compare rates at a specified temperature since rates must be measured at temperatures at which they have convenient values. Therefore, it may be expedient to compare the temperatures at which the rates have a specified value.

In reactors in which the concentrations of reactants and products are uniform in space, the rate is the same on all parts of the catalyst surface at any specified time. In integral flow reactors, however, the rate on each element of the catalyst bed varies along the bed.

#### 1.5.2 Selectivity

The term *selectivity*  $S$  is used to describe the relative rates of two or more competing reactions on a catalyst. Such competition includes cases of different reactants undergoing simultaneous reactions or of a single reactant taking part in two or more reactions. For the latter case,  $S$  may be defined in two ways. The first of these defines a *fractional selectivity*  $S_F$  for each product by the equation

$$S_F = \dot{\xi}_i / \sum \dot{\xi}_i.$$

The second defines *relative selectivities*,  $S_R$ , for each pair of products by:

$$S_R = \dot{\xi}_i / \dot{\xi}_j.$$

In *shape selectivity*, which may be observed in catalysts with very small pores, the selectivity is largely determined by the bulk or size of one or more reactants. On zeolites, for example, the rate of reaction of alkanes with linear carbon chains may be much greater than that of those with branched chains.

#### 1.5.3 Rate equations

Gaseous systems in which all concentrations are uniform in space and in which the reaction is irreversible will be considered first.

†The term *areal* meaning per unit area is tentative (see Preface).

The rate  $\dot{\xi}$ , besides being proportional to the quantity of catalyst,  $Q$ , is also in general a function of temperature  $T$  and the concentrations  $c_i$  or partial pressures  $p_i$  of reactants, products and other substances if present:

$$r = \frac{\dot{\xi}}{Q} = f(T, c_i) \quad \text{or} \quad r = f(T, p_i).$$

The statement of this equation is commonly called the *rate equation* or the *rate law*. Frequently, in heterogeneous catalysis, the function  $f$  is of the form

$$r = k \prod_i c_i^{a_i}$$

where  $k$  is the rate constant which is a function of temperature but not of concentrations and  $a_i$  (integral or fractional; positive, negative or zero) is the *order of the reaction* with respect to component  $i$ . This form of the rate law is called a *power rate law*. Often, however, a rate expression of different form is used. For example, for a reaction  $A + B \rightarrow$  products, the rate equation might be

$$r = \frac{kK_A K_B c_A c_B}{(1 + K_A c_A + K_B c_B + \sum_n K_n c_n)^2}$$

This equation can be interpreted in terms of Langmuir adsorption isotherms. It is assumed (see §1.5.4) that both reactants must be adsorbed in order to react and that  $K_A$  and  $K_B$  are the respective Langmuir adsorption equilibrium constants. The denominator allows for competition for sites between reactants and other substances (diluent, poisons and products) present in the system at concentrations  $c_n$  with related adsorption equilibrium constants  $K_n$ . A rate law of this type is appropriately called a *Langmuir rate law* although it was made popular by Hinshelwood, Schwab, Hougen, Watson and others. Such rate laws are frequently used for systems in which the adsorptions may not obey the Langmuir adsorption isotherm. Under these circumstances, the rate laws can still provide a useful means of correlating experimental results but the values of the derived constants must be interpreted with caution.

For a single elementary process,

$$k = A \exp(-E/RT),$$

where  $A$  is the *frequency factor* and  $E$  the *activation energy*. Even though heterogeneous catalytic reactions rarely if ever proceed by a single elementary process, the same relation often applies to the overall rate constant. In such a case, however,  $A$  is not a frequency factor but should be called the *pre-exponential factor* and  $E$  should be called the *apparent activation energy*.

Sometimes  $A$  and  $E$  exhibit *compensation*, i.e. they change in the same direction with change in catalyst for a given reaction or with change in reaction for a given catalyst. A special case of compensation called the  $\theta$ -rule occurs when, at least approximately,

$$\ln A = \text{const} + \frac{E}{RT_\theta},$$

where  $T_\theta$  is the *isokinetic temperature*, the temperature at which all  $k$ 's would be identical.

These considerations can be extended to reversible

processes. They also apply to single phase, liquid systems. For the case, rather common in heterogeneous catalysis, in which one reactant is in a gas phase and the others and the products are in a liquid phase, application of the principles given above is straightforward provided that there is mass transfer equilibrium between gas phase and liquid phase, i.e. the fugacity of the reactant in the gas phase is identical with its fugacity in the liquid phase. In such case, a power rate law for an irreversible reaction of the form

$$\dot{\xi} = k p_g^{a_g} \prod_i c_i^{a_i}$$

may apply where the quantities have the same significance as before except that the gaseous reactant  $g$  is omitted from the  $c_i$ 's and entered as a pressure term with order  $a_g$ .

The determination of rate of reaction in a flow system requires knowledge both of the feed rate,  $v$ , of a given reactant and of the *fraction converted*,  $x$ . The definition of feed rate as the amount of reactant fed per unit time to the inlet of the reactor is consistent with 1.5.1. The rate of reaction is then given by

$$\frac{d\xi}{dt} = v \frac{x}{\nu_B}$$

where  $\nu_B$  is the stoichiometric coefficient of the reactant of which the fraction  $x$  is converted. Alternatively, one may proceed from  $r_m$ ,  $r_v$ , and  $r_a$  rather than  $d\xi/dt$  by defining the *space velocities*,  $v_m$ ,  $v_v$ , and  $v_a$  where the  $v_i$ 's represent the rate of feed of the given reactant fed per unit mass, volume or surface area of the catalyst. The relation,

$$r_m = v_m \frac{x}{\nu_B}$$

gives the *specific rate of reaction* or, under specified conditions, the *specific activity of the catalyst*. Substitution of  $v_a$  or  $v_v$  gives the *areal rate of reaction* or the rate divided by volume of the catalyst, respectively. Alternatively, *space times*,  $\tau_m$ ,  $\tau_a$ , and  $\tau_v$ , the reciprocals of the space velocities, may be used. "Contact time" and "residence time" are terms which may be misleading for flow systems in heterogeneous catalysis and should be avoided.

#### 1.5.4 Kinetic aspects of mechanism

Of general convenience in the treatment of mechanisms are the notions of *rate determining process* or *step* and *most abundant surface intermediate*. The rate determining process is defined, as is usual in kinetics in general, as that single elementary process in the catalytic sequence which is not in equilibrium when the overall reaction is significantly displaced from equilibrium. If the surface of a catalyst has one set of catalytic sites, a particular intermediate is said to be the most abundant surface intermediate if the fractional coverage by that intermediate is much larger than coverages by the other intermediates. Of course, there is no guarantee that either a rate determining process or a most abundant surface intermediate will exist for any particular reaction under a particular set of conditions.

The term *reaction centre* may be used to include both vacant and occupied catalytic sites. The sum of the *surface concentrations of reaction centres* on the surface of a catalyst is a constant  $L$ . Thus, if species  $m$  at a surface

concentration  $L_m$  is the most abundant surface intermediate,  $L_m + L_v \approx L$ , where  $L_v$  is the surface concentration of vacant reaction centres.

*Langmuir-Hinshelwood mechanism.* This represents a somewhat anomalous use of the term mechanism to specify relative magnitudes of rate constants. In a Langmuir-Hinshelwood mechanism, all adsorption-desorption steps are essentially at equilibrium and a *surface step* is rate determining. Such a surface step may involve the unimolecular reaction of a single adsorbate molecule or the reaction of two or more molecules on adjacent sites with each other. Where the adsorption processes follow Langmuir adsorption isotherms, the overall reaction will follow some kind of a Langmuir rate law (§1.5.3). However, the term Langmuir-Hinshelwood mechanism may cover situations in which Langmuir adsorption isotherms do not apply.

### 1.5.5 Non-uniformity of catalytic sites

A characteristic of a catalytic surface is that its sites may differ in their thermodynamic and kinetic properties. In the kinetic description of catalytic reactions on non-uniform surfaces, a parameter  $\alpha$  is frequently used to connect changes in the activation energy of activated adsorption with the enthalpy of the adsorption

$$E_{\text{ads}} - E_{\text{ads}}^0 = \alpha(q - q^0),$$

where  $E_{\text{ads}}^0$  is the energy of activation and  $-q^0$  is the enthalpy of adsorption on the uncovered surface.  $E_{\text{ads}}$  and  $q$  apply to the surface with the same value of  $\theta$ . In practice the equation may apply only over a restricted range of  $\theta$ . Sometimes  $\alpha$  is defined as in the equation above but in terms of Gibbs energies of activation and adsorption respectively. The name *transfer coefficient* has been used by electrochemists to represent  $\alpha$  in another related situation.

### 1.6 Transport phenomena in heterogeneous catalysis

This section will not attempt to cover the more technical aspects of chemical reactor engineering.

A unique feature of heterogeneous catalytic reactions is the ease with which chemical kinetic laws are disguised by various transport phenomena connected with the existence of concentration and/or temperature gradients in the hydrodynamic boundary layer surrounding the catalyst particles (*external gradients*) or in the porous texture of the catalyst particles themselves (*internal gradients*). Additional difficulties arise in batch reactors and in stirred flow reactors if agitation is inadequate to maintain uniform concentrations in the fluid phase. Agitation is particularly critical where one of the reactants is a gas and the catalyst and other reactants and products are in condensed phases for example, in the hydrogenation of a liquid alkene. Here the agitation must be adequate to maintain the fugacity of the dissolved gaseous reactant equal to that in the gaseous phase.

When external gradients correspond to substantial differences in concentration or temperature between the bulk of the fluid and the external surface of the catalyst particle, the rate of reaction at the surface is significantly different from that which would prevail if the concentration or temperature at the surface were equal to that in the bulk of the fluid. The catalytic reaction is then said to be influenced by external mass or heat transfer respectively, and, when this influence is the dominant one, the rate corresponds to a *regime of external mass or heat transfer*.

Similarly, when internal gradients correspond to differences in concentration or temperature between the external surface of the catalyst particle and its centre, the rate in the particle is substantially different from that which would prevail if the concentration or temperature were the same throughout the particle. The catalytic reaction is then said to be influenced by internal mass or heat transfer, and, when this influence is the dominant one, the rate corresponds to a *regime of internal mass or heat transfer*.

Terms such as *diffusion limited* or *diffusion controlled* are undesirable because a rate may be larger in regimes of heat or mass transfer than in the *kinetic regime* of operation, i.e. when gradients are negligible.

## 1.7 Loss of catalytic activity

### 1.7.1 Poisoning and inhibition

Traces of impurities in the fluid to which the catalyst is exposed can adsorb at the active sites and reduce or eliminate catalytic activity. This is called *poisoning* and the effective impurity is called a *poison*. If adsorption of poison is strong and not readily reversed, the poisoning is called *permanent*. If the adsorption of the poison is weaker and reversible, removal of the poison from the fluid phase results in restoration of the original catalytic activity. Such poisoning is called *temporary*. If adsorption of the poison is still weaker and not greatly preferred to adsorption of reactant, the reduction in rate occasioned by the poison may be called *competitive inhibition* or *inhibition*. Here, of course, the poison may be present in much larger than trace amounts. There are, of course, no sharp boundaries in the sequence permanent poisoning, temporary poisoning, competitive inhibition.

In *selective poisoning* or *selective inhibition*, a poison retards the rate of one catalysed reaction more than that of another or it may retard only one of the reactions. For example, there are poisons which retard the hydrogenation of olefins much more than the hydrogenation of acetylenes or dienes. Also, traces of sulphur compounds appear selectively to inhibit hydrogenolysis of hydrocarbons during catalytic reforming.

A product of a reaction may cause poisoning or inhibition. The phenomenon is called *self-poisoning* or *autopointing*.

### 1.7.2 Deactivation—general

The conversion in a catalytic reaction performed under constant conditions of reaction often decreases with *time of run* or *time on stream*. This phenomenon is called *catalyst deactivation* or *catalyst decay*. If it is possible to determine the kinetic form of the reaction and, thus, to measure the rate constant for the catalytic reaction  $k$ , it is sometimes possible to express the rate of deactivation by an empirical equation such as

$$-dk/dt = Bk^n,$$

where  $t$  is the time on stream,  $n$  is some positive constant, and  $B$  remains constant during a run but depends upon the temperature and other conditions of the reaction. Alternatively, the decline in  $k$  may be assumed to result from elimination of active sites and  $L$  may be substituted for  $k$  in the preceding equation where  $L$  is considered to be the effective concentration of surface centers. It is then common practice to define a *time of deactivation* (or *decay time*) as the time on stream during which  $k$  falls to a specified fraction of its original value, often 0.5. Times of

deactivation may vary from minutes as in catalytic cracking to years as in hydrodesulphurization.

Catalytic deactivation can sometimes be reversed and the original catalytic activity restored by some special operation called *regeneration*. For example, coked cracking catalyst is regenerated by burning off the coke (see §§1.7.3, 1.9).

If the catalytic reaction is a network of various processes, deactivation can lead to a change in the distribution of products. In such cases, the deactivation not only reduces the overall rate but it changes the selectivity.

### 1.7.3 Types of deactivation

Catalyst deactivation can result from deactivation of catalytic sites by poisoning either by impurities or by products of the catalytic reaction (§1.7.1). Many reactions involving hydrocarbons and particularly those run at higher temperatures lead to the deposition on the catalyst of high molecular weight compounds of carbon and hydrogen which deactivate the catalyst. This phenomenon is called *coking* or *fouling*. Catalysts so deactivated can often be regenerated.

Catalyst deactivation may also result from changes in the structure or in the texture of the catalyst. Changes of this kind are usually irreversible and the catalyst cannot be regenerated. This type of deactivation is often called *catalyst ageing*.

*Sintering and recrystallization.* Catalysts often suffer during use from a gradual increase in the average size of the crystallites or growth of the primary particles. This is usually called *sintering*. The occurrence of sintering leads to a decrease in surface area and, therefore, to a decrease in the number of catalytic sites. In some cases, sintering leads to a change in the catalytic properties of the sites, for example, for catalysts consisting of highly dispersed metals on supports, catalytic properties may change on sintering due to a change in the relative exposure of different crystal planes of the metallic component of the catalyst or for other reasons. Thus sintering leads to a decrease in rate and perhaps also to a change in selectivity. Similar phenomena can occur in oxide catalysts as used in catalytic oxidation. The crystal size increases, or the initial structure of the crystals changes. For example, a binary solid compound may decompose into its components or an amorphous mass may crystallize. These processes may be called *recrystallization*. In some cases the terms sintering and recrystallization may refer to the same process. The removal of surface defects may accompany these processes.

In some cases, as for example in catalytic cracking on silica-alumina, processes similar to those involved in sintering and recrystallization can lead to a change in the texture of the catalyst. Surface areas are diminished and the pore-size distribution is changed.

## 1.8 Mechanism of catalytic reactions

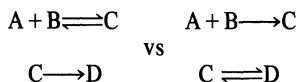
### 1.8.1 General

A chemical reaction proceeds by a set of elementary processes (the Manual, §11.3) which are in series and perhaps also in parallel. These processes start and terminate at species of minimum free energy (reactants, intermediates and products) and each elementary process passes through a state of maximum free energy (the transition state). To specify the mechanism, one must specify the elementary processes. This specifies the intermediates. One must also give the nature (energetics,

structure, charge distribution) of the transition state. So much is true for chemistry in general. The special features of mechanism in heterogeneous catalysis are those which involve reactions between sorptives and active sites, reactions among adsorbates, and processes which regenerate active sites to give a type of chain reaction.

In general, only partial approaches to the specification of mechanism as given above have been possible.

Mechanism is sometimes used in different senses. For example, consider the two situations.



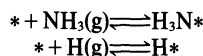
It may be said that the two situations have different mechanisms or that they are two variants of the same mechanism.

### 1.8.2 Elementary processes in heterogeneous catalysis

There are many more types of elementary processes in heterogeneous catalysis than in gas phase reactions. In heterogeneous catalysis the elementary processes are broadly classified as either adsorption-desorption or surface reaction, i.e. elementary processes which involve reaction of adsorbed species. Free surface sites and molecules from the fluid phase may or may not participate in surface reaction steps.

There is no generally accepted classification of elementary processes in heterogeneous catalysis. However, names for a few types of elementary processes are generally accepted and terminology for a partial classification (see M. Boudart, *Kinetics of Chemical Processes*. Chap. 2 (1968)) has received some currency. The particular reactions used below to exemplify this terminology are ones which have been proposed in the literature but some have not been securely established as occurring in nature at any important rate.

*Adsorption-desorption.* This includes the process of physical adsorption as well as non-dissociative chemisorption.

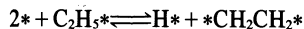


*Dissociative adsorption* and its reverse, *associative desorption*.



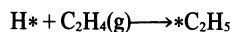
The methane might be supposed to react either from the gas phase or from a physisorbed state.

*Dissociative surface reaction* and its reverse, *associative surface reaction*.



This involves 'dissociative adsorption' in an adsorbate.

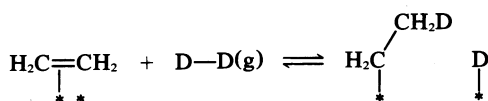
*Sorptive insertion.* This is analogous to the process of ligand insertion in coordination chemistry.



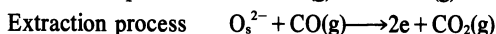
This reaction might also be imagined to proceed by adsorption of  $\text{C}_2\text{H}_4$  followed by ligand migration (an associative surface reaction).

*Reactive adsorption* and its reverse, *reactive desorp-*

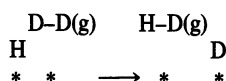
tion. This resembles dissociative adsorption but one fragment adds to an adsorbate rather than to a surface site.



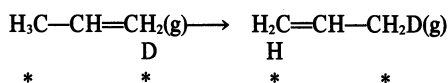
In *abstraction* and *extraction* processes, an adsorptive or adsorbate species extracts an adsorbed atom or a lattice atom respectively.



The following elementary process occurring either on one site or, as shown, on two sites is called a *Rideal* or a *Rideal-Eley mechanism*:



D<sub>2</sub> may also be considered to be in some kind of a weakly adsorbed state. It will be noted that one D atom is never bonded to the surface in any minimum Gibbs energy intermediate. It is recommended that the term *Rideal* or *Rideal-Eley mechanism* be reserved for this particular elementary process. However, the term has been used for analogous processes in which there is a reactant molecule and a product molecule of nearly the same energy in the fluid phase or in some weakly adsorbed state and in which one or more atoms are never bonded to the surface. An example is the following elementary process



which has been called a *switch* process. The term might well be used generically for similar processes. The term *Rideal* or *Rideal-Eley mechanism* has been further extended to include all elementary processes in which a molecule reacts from the fluid phase or from some weakly adsorbed state. Even the sorptive insertion process and the abstraction process illustrated above fall within this extended definition.

### 1.8.3 Nomenclature of surface intermediates

Surface intermediates should be named in ways compatible in so far as possible with chemical nomenclature in general.

Adsorbed species may be treated as surface compounds analogous to molecular compounds. For example, \*H may be called surface hydride, \*=C=O may be called a linear surface carbonyl and

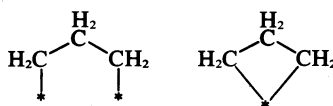


may be called a bridged surface carbonyl. H<sub>2</sub>N\* may be called a surface amide and H<sub>3</sub>C\*, a surface methyl or a surface  $\sigma$ -alkyl.

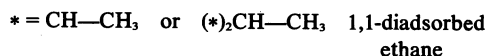
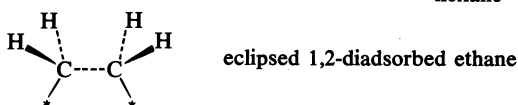
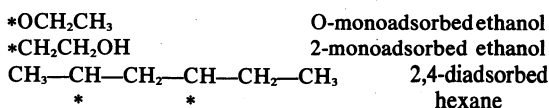
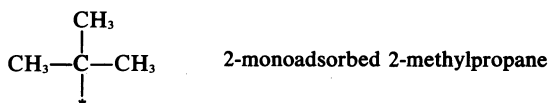
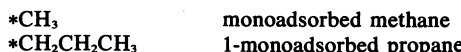
The species \*H may also be called an adsorbed hydrogen atom and \*CO, adsorbed carbon monoxide.

Organic adsorbates pose a particular problem because quite particular structures of some complexity are

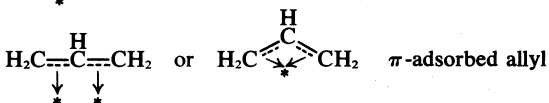
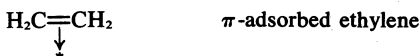
regularly discussed. A nomenclature is recommended in which the surface is treated as a substituent which replaces one or more hydrogen atoms. The degree of substitution is indicated by *monoadsorbed*, *diadsorbed*, etc. This terminology does not specify the nature of the chemical bonding to the surface nor does it restrict, *a priori*, the valency of the surface site \*. Thus, both of the following species



are named 1,3-di-adsorbed propane. Other examples are:



Species adsorbed as  $\pi$ -complexes are described as  $\pi$ -adsorbed:



The substitution system of nomenclature should be viewed as showing only how atoms are connected and not as indicating the precise electronic structure. Thus  $\pi$ -adsorbed ethylene is one representation of 1,2-diadsorbed ethane.

Nomenclature based upon the process of formation of a particular adsorbate is to be discouraged. Thus, H\* may be 'dissociatively adsorbed hydrogen' but the same species is formed in dissociative adsorption of CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O.

### 1.9 Nomenclature of catalytic reactions

In general, a catalytic reaction may be named by adding the adjective "catalytic" to the standard chemical term for the reaction, for example, *catalytic hydrogenation* (or, if clarity demands, *heterogeneous catalytic hydrogenation*), *catalytic hydrodesulphurization*, *catalytic oxidative dehydrogenation*, *catalytic stereospecific polymerization*.

In general, special terminology for reactions is to be discouraged. However, certain catalytic processes of

technological interest have special names in common use. Where such processes involve the simultaneous occurrence of two or more different chemical reactions, special names for the processes are probably inevitable. Some important examples of such processes of technological interest are:

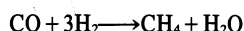
**Catalytic cracking.** In this process, a higher boiling cut of petroleum, for example, gas oil, is converted substantially into a lower boiling material of high octane number. Among the processes which appear to be involved are skeletal isomerization of alkanes followed by their cleavage into alkane and olefin, and hydrogen transfer reactions which reduce the amount of olefin formed and which lead to coke and aromatic hydrocarbons.

**Catalytic hydrocracking.** This is similar to catalytic cracking in its industrial purpose but it is effected under hydrogen pressure and on a catalyst containing an ingredient with a hydrogenating function.

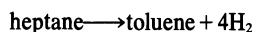
**Catalytic reforming.** Catalytic reforming is a process for increasing the octane number of naphthas. It involves isomerization of alkanes, dehydrogenation of cyclohexanes to aromatic hydrocarbons, isomerization and dehydrogenation of alkylcyclopentanes, and dehydrocyclization of alkanes.

The following reactions may be mentioned because they are rare except as heterogeneous catalytic reactions and have somewhat specialized meanings in catalysis.

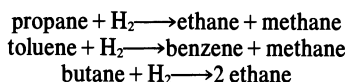
**Catalytic methanation.** This is a process for removing carbon monoxide from gas streams or for producing methane by the reaction



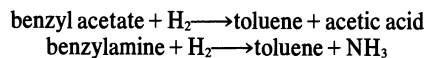
**Catalytic dehydrocyclization.** This is a reaction in which an alkane is converted into an aromatic hydrocarbon and hydrogen, for example,



**Catalytic hydrogenolysis.** This is ordinarily used for reactions in which  $\equiv\text{C}-\text{C}\equiv + \text{H}_2$  gives  $\equiv\text{CH} + \text{HC}\equiv$ , for example,



However, it may also be used for cleavage of bonds other than  $\equiv\text{C}-\text{C}\equiv$ , for example,



**Catalytic hydrodesulphurization.** This is a process in which, in the presence of hydrogen, sulphur is removed as hydrogen sulphide.

## SECTION 2. LIST OF SYMBOLS AND ABBREVIATIONS

### 2.1 Catalysis and catalysts

#### 2.2 Adsorption

Area of surface	$A, A_s, S$
Specific surface area	$a, a_s, s$
Surface coverage	$\theta$
Area per molecule in complete monolayer of substance $i$	$a_m(i)$

Surface site	*
Ion $M^{n+}$ (or atom $M$ ) of adsorbent or catalyst at the surface	$M_s^{n+}$ (or $M_s$ )
Constant in Henry's law	$K$
Constant in Langmuir's adsorption isotherms	$K$
Constant in Langmuir's adsorption isotherms for substance $i$	$K_i$
Constants in Freundlich isotherms	$a, n$
Constants in Temkin isotherms	$A, B$
Constant in BET isotherms	$c$
Monolayer capacity	$n_m$
Constants of Roginskii-Zeldovich equation	$a, b$
2.3 Composition, structure and texture of catalysts	
2.4 Catalytic reactors	
2.5 Kinetics of heterogeneous catalytic reactors	
Stoichiometric coefficient of substance B	$\nu_B$
Extent of reaction	$\xi$
Rate of catalysed reaction	$\dot{\xi}$
Quantity of catalyst	$Q$
Specific rate of reaction	$r_m$
Specific activity of the catalyst	$r_m$
Rate of reaction per unit volume of catalyst	$r_v$
Areal rate of reaction	$r_a$
Turnover frequency (turnover number)	$N$
Selectivity	$S, S_F, S_R$
Rate constant	$k$
Order of the reaction	$a_i$
Frequency factor	$A$
Activation energy	$E$
Isokinetic temperature (Kelvin scale)	$T_\theta$
Fraction converted	$x$
Feed rate	$v$
Space velocities	$v_m, v_v, v_a$
Space times	$\tau_m, \tau_v, \tau_a$
Sum of surface concentrations of reaction centres	$L$
Surface concentration of surface intermediate $m$	$L_m$
Surface concentration of vacant reaction centres	$L_v$
Energy of activation for activated adsorption	$E_{ads}$
Energy of activation for activated adsorption on uncovered surface	$E_{ads}^0$

(Differential) enthalpy of adsorption	$-q$	BET adsorption isotherm	1.2.7
(Differential) enthalpy of adsorption on uncovered surface	$-q^0$	bifunctional catalysis	1.2.8
Transfer coefficient	$\alpha$	Brønsted acid site	1.2.4
2.6 <i>Transport phenomena in heterogeneous catalysis</i>		Brunauer–Emmett–Teller adsorption isotherm	1.2.7
2.7 <i>Loss of catalytic activity</i>		calcination	1.3.2
Constants in equation for rate of deactivation	$B, n$	capillary condensation	1.2.2
Time of run (on stream)	$t$	carrier catalysis	1.3.1
2.8 <i>Mechanism</i>		catalyst	1.1
2.9 <i>Nomenclature of catalytic reactions</i>		catalyst ageing	1.7.3
		catalytic cracking	1.9
		catalyst deactivation (decay)	1.7.2
		catalytic dehydrocyclization	1.9
		catalytic hydrodesulphurization	1.9
		catalytic hydrocracking	1.9
		catalytic hydrogenation	1.9
		catalytic hydrogenolysis	1.9
		catalytic methanation	1.9
		catalytic oxidative dehydrogenation	1.9
		catalytic reaction	1.1
		catalytic reactors	1.4
		catalytic reforming	1.9
		catalytic stereospecific polymerization	1.9
		charge transfer adsorption	1.2.3, 1.2.4
		chemical adsorption	1.2.2
		chemisorption	1.2.2, 1.2.3, 1.2.4
		coherent structure	1.2.3
		coking	1.7.3
		compensation	1.5.3
		competitive inhibition	1.7.1
		composition of catalyst	1.3
		contact time	1.5.3
		coverage	1.2.2, 1.2.4, 1.2.7
		deactivation	1.7.2
		decay time	1.7.2
		demanding reaction	1.2.5
		desorption	1.2.1, 1.2.3
		diadsorbed	1.8.3
		differential flow reactor	1.4
		diffusion limited (controlled)	1.6
		dispersion	1.3.2
		dissociative	
SECTION 3. ALPHABETICAL INDEX			
<i>Symbol</i>	<i>Term</i>	<i>Section</i>	
	adsorbate	1.2.1	
	absorbent	1.2.1	
	absorption	1.2.1	
	absorptive	1.2.1	
	abstraction process	1.8.2	
	accessible pore volume	1.3.2	
	acid site	1.2.4	
	activated adsorption	1.2.2, 1.2.9, 1.5.5	
	activation	1.3.2	
$E, E_{ads}$	activation energy	1.5.3, 1.5.5	
	active centre	1.2.6	
$*, (ads)$	active site	1.2.2, 1.2.6	
	adiabatic reactor	1.4	
	adsorbate	1.2.1	
	adsorbed state	1.2.1	
	adsorbent	1.2.1	
	adsorption	1.2.1	
	adsorption–desorption process	1.8.2	
	adsorption complex	1.2.1	
	adsorption isotherm	1.2.7	
$*, (ads)$	adsorption site	1.2.2	
	adsorption space	1.2.1	
	adsorptive	1.2.1	
	ageing	1.7.3	
$E$	apparent activation energy	1.5.3	
$a_m$	area occupied by molecule in complete monolayer	1.2.2	
$A, A_s, s$	area of interface	1.2.1	$\theta, \theta_i$
$A, A_s, s$	area of surface	1.2.1	
	areal	preface	
$r_a$	areal rate of reaction	1.5.1	
	associative desorption	1.2.3, 1.8.2	
	associative surface reaction	1.8.2	
	autopoisoning	1.7.1	
	basic site	1.2.4	
	batch reactor	1.4	



	adsorption			intrinsic	
	(chemisorption)	1.2.3, 1.8.2		non-uniformity	1.2.5
	dissociative		$T_0$	isokinetic	
	surface reaction	1.8.2		temperature	1.5.3
	doping	1.3.1		isothermal	
	eclipsed			reactor	1.4
	diadsorbed	1.8.3		kinetic aspects	
	electron			of mechanism	1.5.4
	accepting site	1.2.4		kinetics of	
	electron			heterogeneous	
	donating site	1.2.4		catalytic	
	elementary			reactions	1.5
	process	1.1, 1.8.2		kinetic regime	1.6
	elementary step	1.1	$K, K_i$	Langmuir	
	Elovich equation	1.2.9		adsorption	
	enzyme catalysis	1.1		equilibrium	
$\xi$	extent of reaction	1.5.1		constant	1.2.7, 1.5.3
	external gradient	1.6		Langmuir	
	external surface	1.3.2		adsorption	
	extraction			isotherm	1.2.7
	process	1.8.2		Langmuir rate	
	facile reaction	1.2.5		law	1.5.3
$v$	feed rate	1.5.3		Langmuir-	
	fixed bed reactor	1.4		Hinshelwood	
	flow reactor	1.4		mechanism	1.5.4
	fluidized bed			Lewis acid site	1.2.4
	reactor	1.4		linear adsorption	
	fouling	1.7.3		isotherm	1.2.7
$x$	fraction of		$K$	linear adsorption	
	reactant converted	1.5.3		isotherm	
$A$	frequency factor	1.5.3		equilibrium	
	Freundlich			constant	1.2.7
	adsorption			localized adsorption	1.2.3
	isotherm	1.2.7		loss of catalytic	
				activity	1.7
	gradientless reactor	1.4		macropores	1.3.2
$K$	Henry's law			mean life time	
	constant	1.2.7		of adsorption	
	heterogeneous			complex	1.2.9
	catalytic			mean residence	
	hydrogenation	1.9		time	1.2.9
	heterogeneous			mechanism of	
	catalysis	1.1		catalytic	
	heterolytic			reactions	1.8
	dissociative			mesopores	1.3.2
	adsorption	1.2.3		micropore filling	1.2.2
	homogeneous			micropore volume	1.2.2
	catalysis	1.1		micropores	1.3.2
	homolytic			mobile adsorption	1.2.3
	dissociative			molecular sieve	
	adsorption	1.2.3		effect	1.3.2
	ideal adsorbed			monoadsorbed	1.8.3
	state	1.2.7		monolayer	
	immobile adsorption	1.2.3		adsorption	1.2.2
	incoherent		$n_m^s, n_m, v_m$	monolayer	
	structure	1.2.3		capacity	1.2.2, 1.2.7
	induced			most abundant	
	non-uniformity	1.2.5		surface	
	inhibition	1.7.1		intermediate	1.5.4
	initiator	1.1		multilayer	
	integral flow			adsorption	1.2.2
	reactor	1.4		negative catalysis	1.1
	interface	1.2.1		net	1.2.3
	intermediate			nomenclature of	
	pores	1.3.2		catalytic	
	internal gradient	1.6		reactions	1.9
	internal surface	1.3.2		nomenclature of	

	surface intermediates	1.8.3		reactor recirculation	1.4
	non-dissociative chemisorption	1.2.3		reactor recrystallization	1.4
	non-localized adsorption	1.2.3		regeneration	1.7.3
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