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Fundamental chemical kinetics: the first step to reaction modelling and reaction engineering

E. Santacesaria[1]

Dipartimento di Chimica, Università di Napoli Federico II, Via Mezzocannone 4, 80134, Napoli, Italy

Abstract

In the present paper the relation existing between chemical kinetics, reaction mechanisms and reactor modelling is briefly examined by reporting examples of both homogeneous and heterogeneous catalytic reactions. The scope is to give an introductory insight into the more general topic of "Kinetics and Modelling of Catalytic reactions from the laboratory to industrial reactor". © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The scope of chemical kinetics is to define the evolution with time of a reacting system. The information which can be acquired with this type of studies can usefully be applied in different fields, such as the interpretation of reaction mechanisms and of the molecular behaviour, the interpretation of catalytic phenomena, the optimisation of catalysts formulations, the development of new chemical processes and reactors modelling and simulation. Therefore, the study of chemical reaction kinetics is of interest for both chemists and chemical engineers using and elaborating reaction rates data with different objectives and many books and reviews have been published on the subject [1–12].

Two main difficulties arise in undertaking the kinetic study of a chemical reaction:

1. the development of suitable experimental techniques to collect reliable reaction rates data in different conditions, and
2. the definition of an appropriate strategy of elaboration of the data collected to evaluate the unknown of the problem, that is the kinetic law, a functional relationship, able to simulate all the data collected.

The difficulty increases when few reactants originate many products as a consequence of many reactions taking place. In this case, the first step of the kinetic approach will be the determination of an acceptable scheme for the occurring reactions. Then, the study can be oriented to define the kinetics of each reaction in the pattern.

2. Reaction rate definition, reaction rate in the mass and heat balance of the reactor, kinetic equation

The rate of a chemical reaction can normally be determined by measuring the amount of both the

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[1] Tel.: +39-81-547-6544; fax: +39-81-552-7771
E-mail address: santacesaria@chemna.dichi.unina.it (E. Santacesaria)

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products obtained and the reagents disappeared, at different times, in a reactor normally operating in *ideal* conditions. Such conditions could be related to:

1. the thermal behaviour of the reactor (*isothermal, adiabatic,* etc.),
2. the operating conditions (*batch, semibatch, continuous*), and
3. the regime of the flow for continuous reactors (CSTR=continuous stirred tank reactor, PFR=plug flow reactor).

The measurement of the rate of a reaction corresponds to the evaluation of the performance of the reactor where the reaction occurs and requires the solution of the related material balance equations. When considering, for example, an isothermal reactor, the material balance equation referred to the *i*th component will be:

$$[\text{rate of } i \text{ flow in}] = [\text{rate of } i \text{ flow out}] \pm ([i \text{ produced or consumed}] + [i \text{ accumulation}].$$

The balance can be expressed in moles or mass according to the convenience, considering the stoichiometry of the reaction. When there is no change in the number of the moles of products with respect to the reactants and, hence, in the volumetric flow rates, it is possible to write, for example

$$Fc_i^{\text{in}} = Fc_i^{\text{out}} + Wr_i + \frac{\mathrm{d}c_i}{\mathrm{d}t}, \tag{1}$$

the rate of formation or disappearing of "*i*" expressed as (moles/time × mass of catalyst) is, therefore

$$r_i = \frac{F}{W}\left(c_i^{\text{in}} - c_i^{\text{out}}\right) - \frac{1}{W}\frac{\mathrm{d}c_i}{\mathrm{d}t}. \tag{2}$$

In the case of a continuous well stirred reactor, operating in steady state conditions, the term of accumulation is null. On the contrary, for a batch reactor, the first term is null and consequently

$$r_i = -\frac{1}{W}\frac{\mathrm{d}c_i}{\mathrm{d}t}(\text{batch reactor}),$$
$$r_i = \frac{F}{W}(c_i^{\text{in}} - c_i^{\text{out}})(\text{CSTR reactor}). \tag{3}$$

For a tubular plug flow reactor (PFR), the reaction rate changes along the catalytic bed; therefore, the material balance must be applied to an infinitesimal portion of the sectioned tube. It results therefore

$$r_i = \pm F\frac{\mathrm{d}c_i}{\mathrm{d}W}\ (\text{PFR reactor}). \tag{4}$$

Data about reaction rate can be collected indifferently by using one of the above mentioned reactors and interpreted to determine a *kinetic law equation* of the form:

$$r_i = f\ (\text{composition, temperature}), \tag{5}$$

characteristic for a given reaction in the presence of a well-defined catalyst. An equation of this type is fundamental for reactor modelling and simulation and is very important for the interpretation of the catalytic mechanisms. The determination of the correct form of this equation is the main goal of the kinetic study of a reaction.

When the reactor is not isothermal, together with the material balance an energy balance must be considered, the form of which is similar to that of the material balance.

The reaction rates can be related, according to the convenience, to the amount of catalyst or to the volume of the reactor. The composition of the reacting mixtures can usually be expressed in terms of concentrations or partial pressures. Often, adimensional terms such as the conversion of the reactant or the yields of the products are conveniently introduced in the kinetic law expression. Dimensional units of the kinetic parameters will be adjusted, accordingly.

The experimental evaluation of reaction rates is usually performed in laboratory reactors in *chemical regime* conditions, that is, in conditions not affected by diffusional limitations; otherwise also the influence of diffusion must be taken into account.

3. Relation between kinetic law equation and reaction mechanism

3.1. *Scheme of the reaction, single reaction, elementary reaction step, stoichiometry, reaction mechanism*

Two reactants can frequently give rise to more than one reaction. A kinetic study requires to recognise, first of all, how many reactions occur in a reacting system, that is, to identify the reaction pattern and the stoichiometry of each reaction of the scheme.

A complex reaction scheme can be seen as a combination of simpler schemes in which equilibrium and competitive or consecutive reactions appear, while the simpler scheme is made of combinations of single reactions. Any single reaction occurs with a proper mechanism to which a kinetic equation corresponds. The reaction mechanism is a sequence of different steps called "*elementary reactions*" often involving unstable and undetectable molecular species. The kinetic law equation can easily be written for each elementary step, because it can directly be derived from the stoichiometry of the reaction. As a matter of fact, the "*order of the reaction*", with respect to each reactant, which is the power to be given to the reactant concentration in the kinetic law equation, coincides with the stoichiometry coefficient, as in the following examples:

$$A \rightarrow B + C \; r = k\,[A] \quad \text{Unimolecular process} \tag{6}$$

$$2A \rightarrow B + C \; r = k\,[A]^2 \quad \text{Bimolecular process}$$

$$A + B \rightarrow C + D \; r = k\,[A][B] \quad \text{Bimolecular process}$$

$$A + 2B \rightarrow C + D \; r = k\,[A][B]^2 \quad \text{Trimolecular process}$$

Elementary reactions have normally a very simple stoichiometry. A trimolecular process, for example, has a very low probability to occur, as it requires the simultaneous collision of three molecules.

On the other hand, our objective is to find a kinetic law equation being a function of measurable properties, able to reproduce the evolution with time of reactants and products appearing in the experimentally observed stoichiometry. In the reaction of ammonia synthesis, for example

$$N_2 + 3H_2 \Leftrightarrow 2NH_3 \tag{7}$$

the stoichiometry of the reaction suggests only that hydrogen will disappear three times faster than nitrogen and that ammonia will be formed with a rate twice that of disappearing nitrogen. That is, $r = -r_{N_2} = -r_{H_2}/3 = r_{NH_3}/2$.

The problem is to give a mathematical form to the rate law and this information cannot be derived from the stoichiometric equation. It can be derived only from the mechanism of the reaction.

3.2. *Determination of the kinetic law equation through the assumption of two useful hypotheses*

Kinetic data collected, for example, in an isothermal reactor for a generic reaction of the type

$$A + B \rightarrow C + D \tag{8}$$

can be interpreted by initially considering a power law kinetic equation of the type

$$r = k p_A^{\alpha} p_B^{\beta} p_C^{\gamma} p_D^{\delta}, \tag{9}$$

where α, β, γ, δ, the apparent reaction orders, will be small whole, fractional, positive, negative or null numbers. The apparent reaction orders and the kinetic constant can be determined by the mathematical regression analysis of the experimental kinetic data. The values found for α, β, γ, and δ give useful suggestions on the form that should be assigned to the true kinetic law equation. For this purpose, a reasonable mechanism must be formulated in which the products are formed as a consequence of a sequence of elementary reaction steps. The definition of the mechanism can normally be made by the following suggestions derived from literature for both the specific reaction studied and similar reaction. Then, two useful hypotheses can be introduced to evaluate the kinetic law equation on a theoretical basis:

1. the hypothesis of the existence of a rate-controlling step;
2. the assumption of the stationary state approximation for the unstable intermediate appearing in the mechanism.

When one step, in a sequence of different elementary reactions, is very slow, the rate of the entire process can be considered equal to the slow step and this one becomes the rate determining step. For example, in the case of the reaction

$$C_2H_4 + \tfrac{1}{2}O_2 \rightarrow CH_3CHO \tag{10}$$

performed through the Wacker process, that is, through the following cycle of reactions

$$Pd^{++} + C_2H_4 + H_2O \rightarrow Pd^0 + CH_3CHO + 2H^+ \tag{11}$$

$$Pd^0 + 2Cu^{++} \rightarrow Pd^{++} + 2Cu^+ \tag{12}$$

$$4Cu^+ + O_2 + 4H^+ \rightarrow 4Cu^{++} + 2H_2O \tag{13}$$

the following mechanism has been proposed

$$[\mathrm{PdCl}_4^=] + \mathrm{C_2H_4} \overset{\text{fast}}{\leftrightarrow} [\mathrm{PdCl_3C_2H_4^-}] + \mathrm{Cl^-} \tag{14}$$

$$[\mathrm{PdCl_3C_2H_4^-}] + \mathrm{H_2O} \overset{\text{fast}}{\leftrightarrow} [\mathrm{PdCl_2(H_2O)C_2H_4}] + \mathrm{Cl^-} \tag{15}$$

$$[\mathrm{PdCl_2(H_2O)C_2H_4}] + \mathrm{H_2O} \overset{\text{fast}}{\leftrightarrow} [\mathrm{PdCl_2(OH)C_2H_4^-}] + \mathrm{H_3O^+} \tag{16}$$

$$[\mathrm{PdCl_2(OH)C_2H_4^-}] \rightarrow [\mathrm{HOCH_2CH_2PdCl}] + \mathrm{Cl^-} \tag{17}$$

$$[\mathrm{HOCH_2CH_2PdCl}] \rightarrow \mathrm{CH_3CHO} + \mathrm{Pd} + \mathrm{HCl} \tag{18}$$

By assuming reaction (17) as the rate determining step, we can write

$$r = k\,[\mathrm{PdCl_2(OH)C_2H_4^-}] \tag{19}$$

but the concentration of $[\mathrm{PdCl_2(OH)C_2H_4^-}]$ is not easily measurable and we need to find a correlation among this concentration and those of other more easily measurable species. For this purpose, we can suppose that the steps preceding the rate determining one have approximately reached the equilibrium and we can write consequently

$$K_{\mathrm{e}_1} = [\mathrm{PdCl_3C_2H_4^-}]\,[\mathrm{Cl^-}]/[\mathrm{PdCl_4^-}]\,[\mathrm{C_2H_4}] \tag{20}$$
$$K_{\mathrm{e}_2} = [\mathrm{PdCl_2(H_2O)C_2H_4}]\,[\mathrm{Cl^-}]/[\mathrm{PdCl_3C_2H_4^-}]\,[\mathrm{H_2O}]$$
$$K_{\mathrm{e}_3} = [\mathrm{PdCl_2(OH)C_2H_4^-}]\,[\mathrm{H_3O^+}]/[\mathrm{PdCl_2(H_2O)C_2H_4}]\,[\mathrm{H_2O}]$$

by rearranging $[\mathrm{PdCl_2(OH)C_2H_4^-}]$ in relation (19) we obtain

$$r = k_{\mathrm{app}}([\mathrm{PdCl}_4^=]\,[\mathrm{C_2H_4}]/[\mathrm{Cl^-}]^2\,[\mathrm{H_3O^+}]) \tag{21}$$

which very well agrees with experimental observations.

As it can be seen, the kinetic constant appearing in the derived kinetic expression contains the equilibrium constants K_{e_1}, K_{e_2} and K_{e_3} and is, therefore, only an apparent kinetic constant. It is useful to remember that kinetic and equilibrium constants have a similar dependence on temperature

$$k = k^0 \exp((-E/R)(1/T - 1/T^0)),$$
(Arrhenius law)

$$K_{\mathrm{E}} = K_{\mathrm{E}}^0 \exp((-(H/R)(1/T - 1/T^0)). \tag{22}$$
(Van't Hoff law)

However, the enthalpy change has often an opposite sign with respect to the activation energy, that is always a positive value. Therefore, in this case, also the activation energy will be apparent.

When the rate of a reaction is conditioned by two or more elementary steps, the objective of defining the rate law can be achieved conveniently by introducing the hypothesis of the steady state condition, according to which, excluding the initial conditions, the rate of formation of a definite specie is equal to the rate of its disappearing. For example, the mechanism of the reaction:

$$\mathrm{CH_3OH} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{HCHO} + \mathrm{H_2O} \tag{23}$$

catalysed by solid iron molybdate can be written as:

$$\mathrm{CH_3OH} + \text{S-ox} \xrightarrow{k_1} \mathrm{HCHO} + \mathrm{H_2O} + \mathrm{S} - \mathrm{Red} \tag{24}$$

$$\text{S-Red} + \tfrac{1}{2}\mathrm{O_2} \xrightarrow{k_2} \text{S-Ox} \tag{25}$$

S-Ox and S-Red being the oxidised and reduced catalytic sites, respectively.

The reaction rate is that of the formation of the product, therefore

$$r = k_1\, p_{\mathrm{CH_3OH}}\, \theta_{\mathrm{ox}}. \tag{26}$$

We need again to find an expression giving the concentration of the undetectable species θ_{ox} (fraction of oxidised sites) and to do this we assume this species reacting with the same rate of formation; therefore

$$\mathrm{d}\theta_{\mathrm{red}}/\mathrm{d}t = \mathrm{d}\theta_{\mathrm{ox}}/\mathrm{d}t = r_{25} - r_{24} = k_2 p_{\mathrm{O_2}}^{(1/2)} \theta_{\mathrm{red}} - k_1 P_{\mathrm{CH_3OH}} \theta_{\mathrm{ox}} \cong 0. \tag{27}$$

Assuming that $\theta_{\mathrm{red}} + \theta_{\mathrm{ox}} = 1$ it is now possible to obtain θ_{ox} and, inserting it in expression (26), to write the rate law equation

$$r = k_1\, k_2\, p_{\mathrm{M}}\, p_{\mathrm{O_2}}^{(1/2)}/k_1\, p_{\mathrm{M}} + k_2\, p_{\mathrm{O_2}}^{(\frac{1}{2})}. \tag{28}$$

Notwithstanding it is now possible to suggest an acceptable mechanism for any kind of reaction, the possible mechanisms being well classified, very seldom the mechanism of a reaction can be considered without uncertainty. Moreover, it is useful to observe that a reliable kinetic expression is not enough to accredit a reaction mechanism; on the other hand the kinetic expression cannot be in contrast with the mechanism directly deriving therefrom.

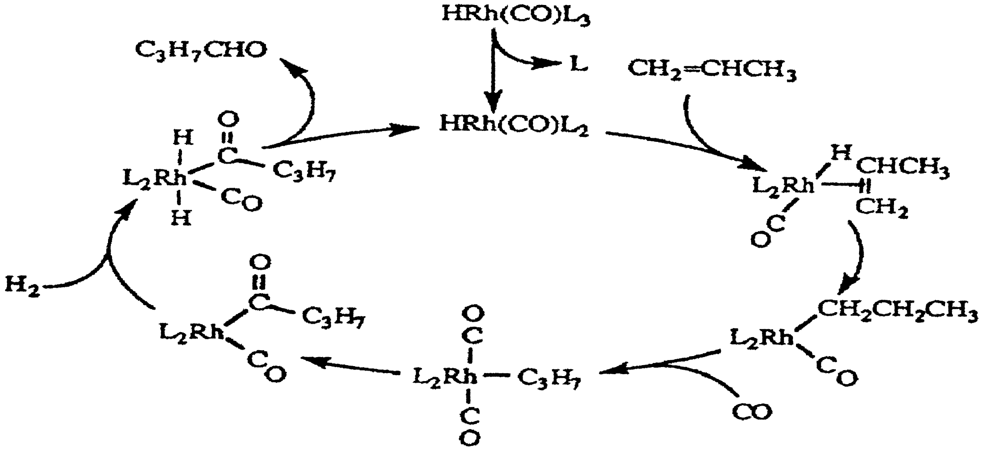
3.3. Kinetics and mechanism for homogeneous reactions

In the previous section, we have seen the strict correlation existing between kinetics and reaction mechanisms. The two aspects should be considered always together. In the last decades, the possible reaction mechanisms have been classified in a relatively small number of categories. An example of such classification is reported in Table 1. This classification is based on the simple observation that a reaction occurs with the cleavage of a chemical bond and the formation of another one.

This can be achieved only by two ways: the homolytic and the heterolytic mechanisms, the first involving the formation of free radicals and the second the formation of ionic intermediates. Then, different reaction paths are possible for each of the mentioned mechanisms, as shown in tab.1. The role of catalyst in a reaction is to favour the movement of the electrons involved in both the rupture and the formation of bonds. When the catalysts are complexes of transition metals, other possible mechanisms must be considered, because transition elements have the following prerogatives:

1. the possibility to change their oxidation state,
2. the possibility to give σ and π bonds with d and f internal orbitals, and
3. the property of showing a coordination number always greater than the oxidation one, favouring the contact between potentially reactive molecules bonded to the same metal atom.

Considering that a transition metal tends towards an external electronic configuration with 18 electrons (saturated configuration), the mechanism of the reactions catalysed by transition metal complexes can be considered as a sequence of many possible elementary steps such as those reported in Table 2. In said reactions either the oxidation or the coordination number can change and, consequently, the spatial geometry of the metal complex can change too. Many industrial processes of great practical importance occur in the homogeneous phase and are catalysed by transition metal complexes, such as, for example, olefine hydroformylation, methanol carbonylation, ethylene oxidation to acetaldehyde (Wacker process), etc. We report here, as an example, the catalytic cycle (an impressive way to represent the mechanism of the reaction) of hydroformylation catalysed by the Wilkinson complex $HRh(CO)L_3$ [13,14]:

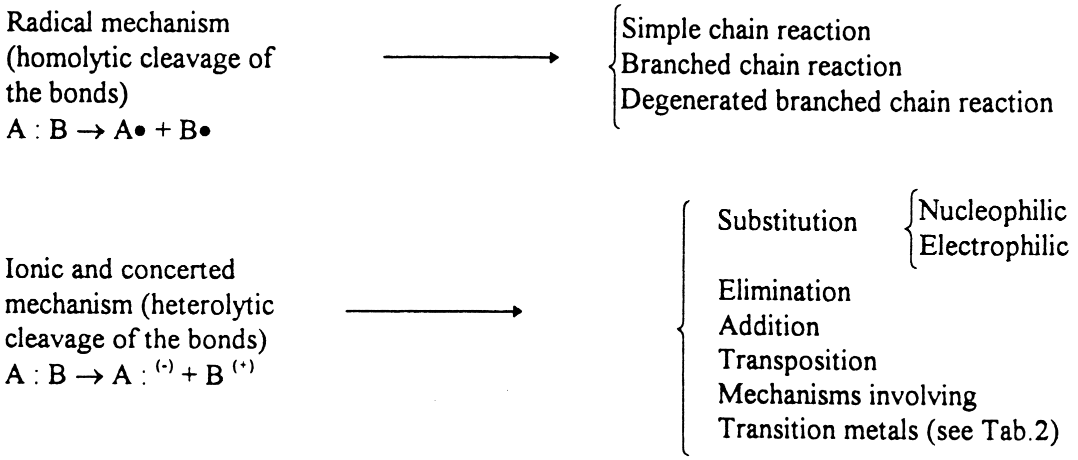


The mechanism of hydroformylation catalyzed by the Wilkinson complex.

The insertion step is normally considered as rate determining and on this basis the kinetic equation can be derived.

An example of the opportunity of interpreting the kinetic law through the study of the reaction mechan-

Table 1
Classification of the mechanisms for a homogeneous reaction



Radical mechanism (homolytic cleavage of the bonds) $A:B \rightarrow A\bullet + B\bullet$ → Simple chain reaction; Branched chain reaction; Degenerated branched chain reaction

Ionic and concerted mechanism (heterolytic cleavage of the bonds) $A:B \rightarrow A:^{(-)} + B^{(+)}$ → Substitution (Nucleophilic; Electrophilic); Elimination; Addition; Transposition; Mechanisms involving Transition metals (see Tab.2)

ism can be derived, as an example, from reactions such as the oxidation of hydrogen or other molecules (CO, CS_2, PH_3) with molecular oxygen. The mechanism is that of a radical chain branched reaction. The following is a simplified scheme

$$1/2\,R_2 + \cdots \rightarrow R^{\bullet} \text{ Initiation } r_{\mathrm{I}} = f_{\mathrm{I}}, \tag{29}$$

$$R^{\bullet} + \cdots \rightarrow \alpha R^{\bullet} \text{ Propagation } r_{\mathrm{II}} = f_{\mathrm{II}}\,[R^{\bullet}], \tag{30}$$

$$R^{\bullet} + \cdots \rightarrow \text{Products propagation } r_{\mathrm{III}} = f_{\mathrm{III}}\,[R^{\bullet}], \tag{31}$$

$$R^{\bullet} + \text{wall} \rightarrow 1/2\,R_2 \text{ Termination } r_{\mathrm{IV}} = f_{\mathrm{p}}\,[R^{\bullet}], \tag{32}$$

$$R^{\bullet} + \text{gas} \rightarrow 1/2\,R_2 \text{ Termination } r_{\mathrm{V}} = f_{\mathrm{g}}\,[R^{\bullet}]. \tag{33}$$

By applying the steady state assumption to $[R^{\bullet}]$ we will have for an isothermal batch reactor

$$\frac{\mathrm{d}[R^{\bullet}]}{\mathrm{d}t} = f_{\mathrm{I}} + \alpha f_{\mathrm{II}}\,[R^{\bullet}] - f_{\mathrm{II}}\,[R^{\bullet}] - f_{\mathrm{p}}\,[R^{\bullet}] - f_{\mathrm{g}}\,[R^{\bullet}] = 0 \tag{34}$$

Table 2
Possible elementary steps in the mechanisms of the reaction catalysed by a complex of transition metals

(a)	Reactions giving coordinatively unsaturated complexes
(b)	Reactions giving coordinatively saturated complexes
(c)	Reactions of insertion
(d)	Oxidative addition reactions
(e)	Reductive elimination reactions

from which,

$$[R^{\bullet}] = \frac{f_{\mathrm{I}}}{(f_{\mathrm{p}} + f_{\mathrm{g}}) - f_{\mathrm{II}}(\alpha - 1)}. \tag{35}$$

The reaction rate is the rate of product formation, therefore

$$r = r_{\mathrm{III}} = f_{\mathrm{III}}\,[R^{\bullet}] = \frac{f_{\mathrm{I}} f_{\mathrm{III}}}{(f_{\mathrm{p}} + f_{\mathrm{g}}) - f_{\mathrm{II}}(\alpha - 1)}. \tag{36}$$

As it can be observed, the reaction rate becomes extremely fast when $(f_{\mathrm{p}}+f_{\mathrm{g}}) \approx f_{\mathrm{II}}(\alpha-1)$ and the consequence is an ‘‘explosion’’. The event can be originated only by changing pressure, because it can change both f_{p} and f_{g} and it is possible to individuate a range of pressure in which the chemical explosion occurs.

It is obvious that an empirical kinetic law equation such as a power law equation cannot reproduce the explosive behaviour and the extrapolation of this inadequate kinetic law to unexplored conditions could be dangerous. This example has been reported in order to stress the importance of the reaction mechanism in determining the form of the kinetic equation.

3.4. *Kinetics and mechanism of heterogeneous reactions*

Reactions occurring in the heterogeneous phase, for example on the surface of a solid catalyst, always require the rupture of a bond of a molecule, followed by the formation of a new bond, but in this case, the molecules are previously chemisorbed on the catalyst surface. The reactions occurring between the molecules and the coordinatively unsaturated atoms called "active sites" existing on the solid surface (*chemisorption*) can be considered elementary steps of the reaction mechanism.

The approximations introduced in the previous sections, that is, the "rate determining step" and the "steady state", can still be employed to construct the rate law equation. Let us consider, for example, the simplest reaction occurring in the heterogeneous phase

$$A \rightarrow B. \tag{37}$$

We can suggest a reasonable mechanism of the type

$$A + \Theta_V \Leftrightarrow \Theta_A \text{ Adsorption reaction of A,} \tag{38}$$

$$\Theta_A \Leftrightarrow \Theta_B \text{ Surface reaction,} \tag{39}$$

$$\Theta_B \Leftrightarrow B + \Theta_V \text{ Desorption reaction of B,} \tag{40}$$

where Θ_V being the fraction of empty sites and Θ_A and Θ_B the fraction of sites occupied by A and B, respectively (*Adsorption Coverage Degree*). Therefore, $\Theta_A+\Theta_B+\Theta_V=1$. The surface reaction may be characterised by a sequence of many elementary steps instead of only one as indicated here, but again we can solve the problem by considering only the rate determining step. For a slow surface reaction, the adsorption and desorption steps can be considered nearly at equilibrium and the chemisorption equilibrium can well be described by the Langmuir isotherm, according to which

$$\theta_A = \frac{b_A p_A}{1 + b_A p_A + b_B p_B}, \quad \theta_B = \frac{b_B p_B}{1 + b_A p_A + b_B p_B}. \tag{41}$$

The reaction rate, that is the rate of the slow step, will be

$$r = r_s = k\theta_A = \frac{k b_A p_A}{1 + b_A p_A + b_B p_B}. \tag{42}$$

A first observation about this kinetic law equation is that A and B compete in the adsorption on the empty sites and the Langmuir isotherm is able to account for this competition. Consequently, both A and B have deactivating effects on the reaction, appearing at the denominator and their apparent reaction order in an experimentally determined "power law" of the type $r = k p_A^{\alpha} p_B^{\beta}$ will be respectively: $0<\alpha<1$ and $\beta<0$. This kinetic model is currently known as Langmuir–Hinshelwood mechanism. If adsorption or desorption rates are determining steps, it is easy to derive therefrom the corresponding kinetic equations which are, respectively:

$$r = r_A = k_A\left(p_A - \frac{p_B}{K_p}\right) \Big/ \left(1 + \frac{p_B}{K_p} + \frac{p_B}{b_B}\right) \text{ (Adsorption),} \tag{43}$$

$$r = r_B = k_B K_s\left(p_A - \frac{p_B}{K_p}\right) \Big/ p_A(1 + K_s) \text{ (Desorption),} \tag{44}$$

where K_p being the equilibrium constant of the reaction A⇔B in the gas phase and K_s the equilibrium constant of the surface reaction $\Theta_A \Leftrightarrow \Theta_B$; this last can be set in a group with the other kinetic constants to have the smallest number of parameters to be evaluated. We report here, as an example, the procedure followed to obtain the kinetic law Eq. (43) valid when adsorption is the rate determining step. The rates corresponding to adsorption, surface reaction and desorption, respectively, are

$$r = r_A = k_A\left(p_A\theta_v - \frac{\theta_A}{b_A}\right), \quad r_s = k_s\left(\theta_A - \frac{\theta_B}{K_s}\right),$$
$$r_B = k_B\left(\theta_B - \frac{p_B\theta_v}{b_B}\right). \tag{45}$$

Superficial and desorption reactions can be considered nearly at equilibrium, that is $r_s=r_B=0$. As a consequence:

$$\frac{r_B}{k_B} = \frac{r_s}{K_s} \cong 0 \quad \text{and} \quad \theta_B = \theta_V\frac{p_B}{b_B}, \ \theta_A = \frac{\theta_B}{K_s} = \frac{\theta_V p_B}{b_B K_s}. \tag{46}$$

By substituting in the expression, we obtain

$$r_A = k_A\,\theta_V\left(p_A - \frac{p_B}{b_B K_s b_A}\right) = k_A\,\theta_V\left(p_A - \frac{p_B}{K_p}\right), \tag{47}$$

being $K_P=b_B K_s b_A$ the equilibrium constant of the reaction A⇔B in the gas phase. Remembering that $\Theta_A+\Theta_B+\Theta_V=1$,

$$\theta_V = \frac{1}{(1 + (p_B/K_p) + (p_B/b_B))}. \tag{48}$$

Substituting Θ_V in the relation (47), we obtain the already reported final expression (43).

When the reaction considered is more complicated than that reported, A→B, say for example,

$$A + B \Leftrightarrow C + D \tag{49}$$

the approach is similar and for a surface reaction controlling rate, we obtain

$$r = r_s = k_A\,\theta_A\,\theta_B - k_{-r}\,\theta_c\,\theta_B,$$

$$r = r_s = k_r\left(\theta_A\,\theta_A - \frac{\theta_C\,\theta_D}{K_s}\right). \tag{50}$$

$$\text{Considering that}: \ K_s = \left(\frac{\theta_c\,\theta_D}{\theta_A\,\theta_B}\right) = \left(\frac{b_C\,p_c\,b_B\,p_D}{b_A\,p_A\,b_B\,p_B}\right) = K_p\frac{b_C\,b_D}{b_A\,b_B} \quad \text{and that}: \theta_i = \frac{b_i\,p_i}{1+\sum_j b_j\,p_j} \tag{51}$$

it results

$$r = k_r\frac{b_A\,b_B(p_A\,p_B - (p_C\,p_D/K_p))}{(1 + b_A\,p_A + b_B\,p_B + b_C\,p_C + b_D\,p_D)^2}. \tag{52}$$

In practice, some terms of the denominator are often very small and can be neglected and the relations can greatly be simplified.

When two sites intervene in the adsorption of a molecule before the occurrence of the surface reaction and the adsorption on the second adjacent site is a rate determining step, we have

$$A\sigma + \sigma \rightarrow A\sigma_2. \tag{53}$$

The reaction rate in this case is

$$r = k_r\,\theta_A\,\theta_V = k\,\theta_A(1-\theta_A), \quad r = k_r\frac{b_A\,p_A}{(1+b_A\,p_A)^2}. \tag{54}$$

This mechanism is called "*dual site*" mechanism. Another possibility is that a chemisorbed molecule reacts with a molecule coming from the fluid phase ("*Rideal-Eley mechanism*"), that is,

$$A\sigma + B \rightarrow \text{products in this case}: r = k_r\,\theta_A\,p_B = k_r\frac{b_A\,p_A\,p_B}{1+b_A\,p_A}. \tag{55}$$

In all the mechanisms considered we have introduced the approximation of the rate controlling step. On the contrary, in the "redox" or "Mars–Krevelen" mechanism the "steady state" hypothesis is normally adopted, as we have seen in the above described example (23)–(28).

Reconsidering that example, if one or more species are adsorbed on the catalytic sites, we get $\Theta_{ox}+\Theta_{red}+\Theta_{occ}=1$, the mechanism becomes a mixed one (Redox–Langmuir–Hinshelwood) and the reaction rate expression will be

$$r_1 = \frac{k_1\,p_A}{[1+(k_1/k_2)(p_A/P^n_{O_2})]\left(1+\sum_i b_i\,p_i\right)}. \tag{56}$$

All the considerations reported in this section start from the assumption that the catalytic sites on the surface are uniform, that is, the enthalpy change for the adsorption of a molecule is the same for all the types of sites. In practice, the enthalpy change, as a function of the surface coverage degree, normally shows a declining trend. The conclusion is that surfaces are not homogeneous and sites are not uniform. Another constraint of the Langmuir adsorption model that could be not respected in the actual case is that molecules should not have lateral interactions. Despite these adverse observations, the Langmuir–Hinshelwood model is almost universally applied and with few exceptions it performs quite well. This is due to the fact that normally only a small portion of the catalytic sites are active in the adopted conditions and these working sites can be considered uniform and not interacting.

When the Langmuir isotherm is not suitable to describe the adsorption of a molecule on a solid surface, other isotherms can be introduced. A detailed description of the non-uniformity of the catalytic sites can be made by introducing a distribution function of the heats of adsorption $\rho(Q_{ads})$ such that $\rho(Q_{ads})\,dQ_{ads}$ gives the fraction of sites having adsorption heat in the range Q_{ads} and $Q_{ads}+dQ_{ads}$ and

$$\int_{Q_{ads1}}^{Q_{ads2}} \rho(Q_{ads})\,dQ_{ads} = 1. \tag{57}$$

Different forms can be assigned to the function $\rho(Q_{ads})$, for example $\rho(Q_{ads})$=constant, that is, the sites with different heat of adsorption have the same probability to exist. The resulting isotherm is the Temkin one and it can be used only for the intermediate adsorption coverage degree, losing the physical meaning at the low and high coverage, respectively.

If we assume $\rho(Q_{\mathrm{ads}}) = \alpha \times \mathrm{e}^{\beta Q_{\mathrm{ads}}}$, i.e. a Gaussian distribution, the Freundlich isotherm can be derived,- which is useful at low and intermediate coverage degrees. Again losing the physical meaning for the high adsorption coverage degree. The non-uniformity of the catalytic sites has other consequences on the kinetic behaviour of the catalysts being responsible for the correlation often observed between the two kinetic parameters: the preexponential factor and the activation energy, respectively (compensation effect or theta rule). The correlation observed is an almost linear trend for log A_{d} (the logarithm of the preexponential factor) and E (the activation energy) for different catalysts of the same kind on the same reaction.

This correlation is due to the fact that, according to the operating conditions, a small number of very active sites of low activation energies or alternatively a large number of less active sites characterised by high activation energies can be involved.

Another consequence of surface dishomogeneity is the change of selectivity with the dispersion of the active part of the catalyst on an inert support of a high interphase area. The atoms of a dispersed catalyst, for example of a dispersed metal, can be geometrically located at one vertex, edge, plane, at one step, in a hole with different characteristics of unsaturation in the coordination. The number of each type of atom can strongly change with dispersion. When a reaction requires a particular type of site, the rate of this reaction changes with the dispersion (structure sensitive-reactions or demanding-reactions). On the contrary, reactions not requiring a particular degree of unsaturation and of geometrical disposition of sites (structure-insensitive or facile-reactions) do not change activities with dispersion.

Other kinetic aspects peculiar to heterogeneous catalysis are deactivation phenomena, normally occurring by poisoning or sintering. Empirical correlations are commonly used to describe the deactivating effects of both poisoning and sintering, when these phenomena are very slow compared with the contact time of the reactants in the reactor. When poisoning occurs very fast and the catalyst must be regenerated before a new cycle of utilisation, more rigorous kinetic models are necessary to accurately simulate the reaction occurring together with catalyst poisoning.

4. Physical meaning and constraints of kinetic parameters

The kinetic parameters appearing in the kinetic law equations must have a physical meaning. For example, the preexponential factor of a true kinetic constant, that is, the kinetic constant of an elementary step performed in the gas phase should be lower than collision frequency of the molecules.

Similarly, for a gas–solid catalytic process, the same parameter should be lower than the collision frequency of the reacting molecules on the surface.

The activation energy must be a positive number greater than 5 kcal/mol and lower than 50 kcal/mol, that is in the order of magnitude of the energy necessary for the chemical bond breaking.

Adsorption parameters are equilibrium parameters and,consequently, we can write

$$b = [\exp(\Delta S_{\mathrm{ads}}/R)][\exp(-\Delta H_{\mathrm{ads}}/RT)]. \tag{58}$$

The constraints of these parameters are quite rigid. The absolute value of ΔS_{ads}, for example, must be greater than the translational entropy of the adsorbed molecule and lower than the total entropy

$$S^{\circ}_{\mathrm{trans}} < \Delta S_{\mathrm{ads}} < S^{\circ}_{\mathrm{tot}} \tag{59}$$

being
$S^{\circ}_{\mathrm{trans}} = (3/2)R\ln M + (5/2)R\ln P - 2.2298$ (e.u.).

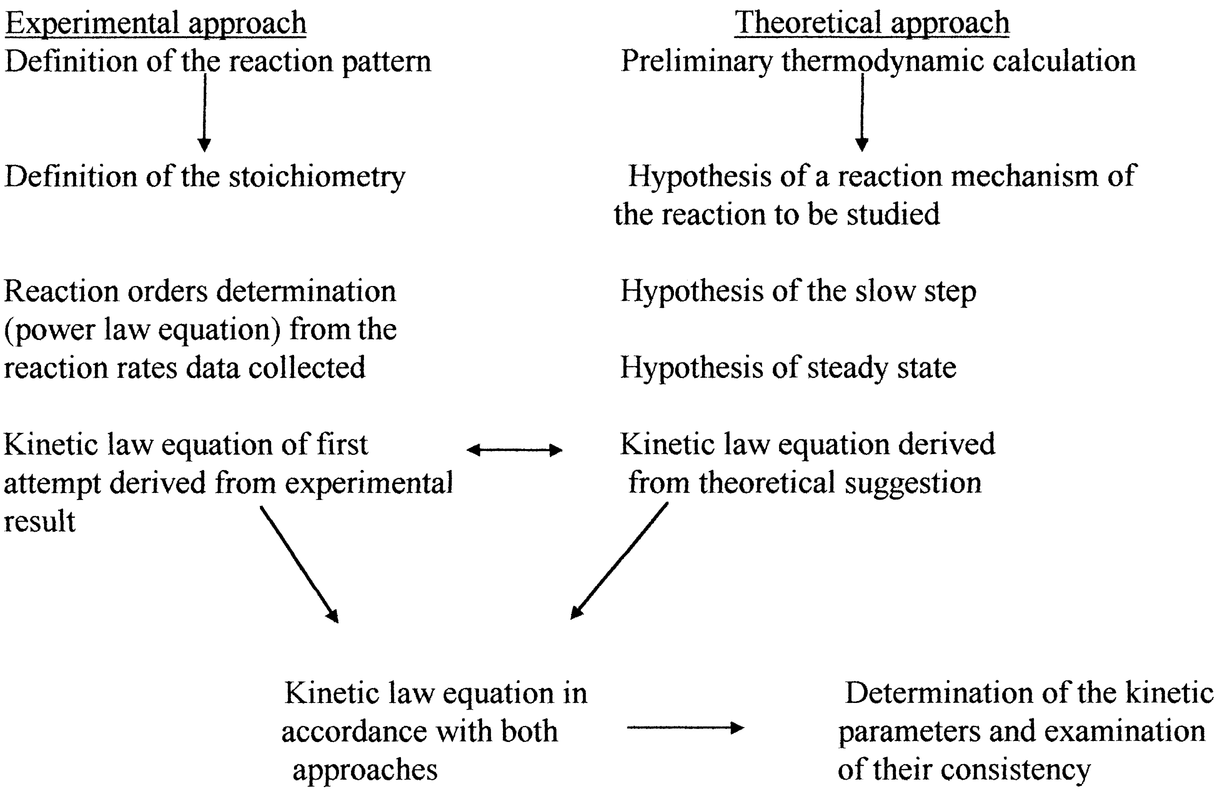
The enthalpy change in adsorption is usually a negative number falling in the range

$$-50.000 < \Delta H_{\mathrm{ads}} < -5.000.$$

Another important constraint is imposed by the thermodynamic equilibrium. The direct and inverse reactions must be kinetically congruent. This means that when for example the kinetic law equation for a direct reaction shows fractional orders, the reverse reaction will have fractional order too, and by assuming r=0 the expression of the equilibrium constant must be obtained.

This fact can usefully be exploited in kinetic studies, because it is possible to study the kinetics of a reverse reaction, when this is easier, in order to define the kinetic law equation of the corresponding direct reaction.

Table 3
Scheme of the phases occurring in the kinetic study of a reaction



5. Concluding remarks

We have seen that the evaluation of the kinetic law equation for a chemical reaction requires the combination of both the experimental and theoretical approach occurring in different phases, as summarised in Table 3.

6. Nomenclature

b_i	Equilibrium constant for i adsorption
c_i	Molar i concentration
F	Molar flow rate
H_{ads}	Adsorption enthalpy
k	Kinetic constant at temperature T
k°	Kinetic constant at temperature T°
K_{e}	Equilibrium constant at temperature T
K_{e}°	Equilibrium constant at temperature T°
M	Molecular weight
P	Pressure
P_i	Partial pressure of i
Q_{ads}	Adsorption heat
R	Constant of gases
r_i	Rate of i appearing or disappearing
S_{ads}	Adsorption entropy
T	Time
W	Weight of catalyst

Greek letters

θ_i	Fraction of active sites occupied by i
θ_{V}	Fraction of empty sites
ρ	Distribution function

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