

# **An Introduction to Chemical Kinetics**

**Michel Soustelle**

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Michel Soustelle



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## Preface

This book on chemical kinetics is especially designed for undergraduate or postgraduate students or university students intending to study chemistry, chemistry and physics, materials science, chemical engineering, macromolecular chemistry and combustion.

Part 1, which consists of the first eight chapters, presents the basic concepts of chemical kinetics. Particular importance is given to definitions and the introduction of concepts. This part includes a first approach to kinetic calculations and some information on elementary reactions. All these models are widely adopted and developed in the Part 2, which, in seven chapters (Chapters 9-15), deepens the relationships between reaction mechanisms and kinetic properties.

Part 2 begins with Chapter 9, which presents the different classes of elementary steps, the nature and identification of reaction intermediates and the principles that must be observed to write an elementary step.

Then Chapters 10 and 11 are devoted to the modeling of elementary steps through the activated complex theory that is presented in as complete a manner as possible at this level, bearing in mind students who will then be confronted with molecular dynamics. The theory is presented in gaseous phase as well as in condensed liquid and solid phases.

Then come three chapters that deal with different specific areas (chain reactions, catalysis and heterogeneous reactions). For each area, the application clues of basic concepts are deepened and we introduce the specialized teachings that will be covered at doctorate level.

Finally, Chapter 15 addresses non-pseudo-steady state processes that are encountered in different areas. We place particular emphasis on these modes for combustion and explosion reactions and heterogeneous reactions.

This book is the result of extensive experience teaching this course at this level and fundamental and applied research for over 30 years in chemical kinetics at the highest level. These accumulated experiences have led me to a certain number of significant modifications compared to previously published books that cover this level of study.

First of all, the arrival and growth of computer science that has populated laboratories should be taken into account, which implies not only unprecedented opportunities of computation but, more significantly, changes in attitude towards the ways of tackling problems and therefore how to teach kinetics. Thus, the sacrosanct chapter on formal kinetics has disappeared. Indeed, there is now only the resolution of three or four integrals that are rarely used nowadays because, unlike our predecessors, we possess derivative curves that give the speed, as easily as integral curves; and because modeling always leads to speed expressions (from infinitesimal calculus), the calculation of these few particular integrals is no longer of interest in kinetics.

The book no longer only refers to the famous “quasi-steady state approximation” (QSSA) for several reasons:

– First, this QSSA is about the concentrations of intermediate species, which is only applied to homogeneous systems with constant volumes, which is relatively rare and inadequate for many gas-phase reactions carried out at constant pressure, as is mostly the case. This is the same for reactions where a condensed phase is created.

– Second, this QSSA is always presented as a calculus approximation that is only justified by computations on a small number of specific cases for which it is not even necessary. In fact, the introduction of the concept of a kinetic mode enables us to bond the approximation level of modeling to that of the accuracy and the reproducibility of measurements. Thus, we consider several types of kinetic modes corresponding to multiple types of approximation in the calculation of speeds using various mechanisms.

Among these modes, those called pseudo-steady states are very important because they greatly simplify the calculations. These modes are characterized by the stability of the amounts of the intermediate species and are detected by the experiment (described in Chapter 7). Other regimes termed “with rate-determining steps” are also used, which is still in line with the precision of the measurements.

Even if the notion of reaction order was retained for the elementary steps, for which this notion is closely related with the mechanism, it is no longer used for more complex reactions because the order obtained will not help us to infer the reaction mechanism. On the contrary, the notion of separate variables of speed – concentration, temperature, etc. – is more directly related to the mechanisms and it should be noted that the order with respect to a concentration is only a special case of the separation of this variable in the expression of speed.

Regarding the influence of temperature, a clear distinction is made between the elementary steps, for which Arrhenius' law is always true and leads to an activation energy, and the common reactions (in general non-elementary) for which Arrhenius' law's experimental application leads to a "temperature coefficient". This coefficient can sometimes, but by no means always, be linked to magnitudes related to the mechanism's steps, such as activation energies and/or enthalpies. This temperature coefficient is then called the apparent activation energy.

We retain this distinction between elementary steps to which we attribute a reactivity that follows an order and obeys Arrhenius' law and the multi-step reactions for which the notion of specific speed is retained (volumetric or areal) and whose expression of speed is far from obvious.

The importance given to the relationships between experiment and modeling should also been noted. Very simple methods that enable us to verify, or discount, a certain number of hypotheses are introduced: pseudo-steady state mode; and the separation of variables.

This work has included information from many French and foreign books that cover this subject, some of which are cited at the end of the book, retaining their contributions and originality.

My gratitude goes to all my students who attended my classes on kinetics because their feedback, questions and curiosity compelled me to ask myself real questions and to deepen my reflections. I would also like to thank a number of colleagues – foremost among whom is Françoise Rouquerol – for the discussions, sometimes fierce but always passionate and meaningful, that we have had. This book owes a great deal to these people. Finally, I want to express my gratitude to Ecole des Mines de Saint Etienne, which has for many years given me the means to carry out my work and enabled the achievement of this book.

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May 2011



## PART 1

# Basic Concepts of Chemical Kinetics



# Chapter 1

## Chemical Reaction and Kinetic Quantities

This first chapter devoted to chemical kinetics, should provide us with definitions of specific notions that are the extents and speeds of reactions every time we approach a new field of disciplinary paradigms. This description is particularly important in chemical kinetics because many definitions are intuitively related to the evolution of a reaction system and the speed of this evolution and for which the same word does not always correspond to the same definition according to authors. Thus we encounter many “speeds” of reaction that are not expressed in the same units and are not always linked with each other. The result is such that when starting to read a book – or an article on kinetics – the reader needs to pay particular attention to definitions given by the author if indeed he or she has taken the trouble to explain them. Therefore we specially draw the reader’s attention to this chapter.

### 1.1. The chemical reaction

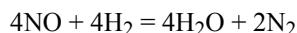
#### 1.1.1. *The chemical equation and stoichiometric coefficients*

A chemical reaction is the phenomenon that turns an unstable chemical species or mixture, *under the conditions of chemical experiment*, into other stable species. A reaction is represented by its chemical equation such as reaction [1.R1], which represents the reaction between nitric oxide and hydrogen, and produces water and nitrogen:



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This chemical equation, besides the chemical species being involved, includes numbers placed in front of each species (e.g. 2 for N<sub>2</sub>) that are called the *arithmetic stoichiometric coefficients*. The set of coefficients belonging to a reaction may be multiplied or divided by the same number without modifying the reaction in any way. For example, the above reaction could also be written by multiplying all the stoichiometric coefficients by two in the following:



These coefficients (integer or fractional) indicate the proportions of species that are involved in the reaction. For example, in reaction [1.R1] if three moles of nitric oxide react with three moles of hydrogen respectively, *in fine*, when the reaction is totally complete it will have produced three moles of water and 1.5 moles of nitrogen.

NOTE 1.1.— During the kinetic study (as for the thermodynamic study) of a reaction, it is recommended we choose a set of stoichiometric coefficients and keep them. It is highly recommended to choose the same series for the kinetic and thermodynamic study that often precedes it.

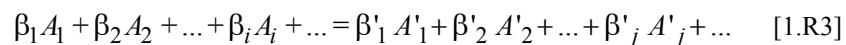
We state that the chemical equation is a “molar” equation and it should be noted that the two members of the equation are separated by the equals sign.

In the case of certain generalizations it is sometimes usual to represent equation [1.R1] as [1.R2], which is obtained by passing all the initial chemical species to the right-hand side through the application of the algebraic rule of change in sign:



The new coefficients 2, 1, -2 and -2 are called *algebraic stoichiometric coefficients*. It should be noted that they are positive for a product of the reaction and negative for a starting compound.

GENERALIZATION.— A reaction between the compounds A<sub>1</sub>, A<sub>2</sub>, [...], A<sub>i</sub>... producing species A'<sub>1</sub>, A'<sub>2</sub> [...], A'<sub>j</sub> will be generally written as [1.R3], with the arithmetic stoichiometric coefficients β<sub>k</sub> or as [1.R4] with the algebraic stoichiometric coefficients ν<sub>k</sub>:



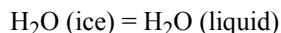
$$0 = \sum_k v_k A_k \quad [1.R4]$$

with the relations:

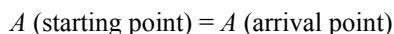
$-v_i = -\beta_i$  for a species that reacts; and

$-v_j = \beta_j$  for a species that is produced.

NOTE 1.2.— Some physical transformations are treated as reactions and can be represented by a chemical equation. For example, let us quote state changes like the fusion of ice in water, which can be written as:



or the diffusion of a species A from one point to another within a solution and that will be represented by:



It should be noted that physical transformations frequently involve stoichiometric coefficients that are equal to one.

### 1.1.2. The reaction components

When a reaction is performed in a vessel called a reactor, at one point the different kinds of substances that are called the components of this reaction may be present in this reactor.

We keep the definition of the thermodynamics of a component as a specific species in a specified phase (solid, liquid, gas or solution). From the viewpoint of the kinetics of reactions, it is common to divide these components into four families:

— *Principal components*: these are the components that are mentioned in the chemical equation and they are subclassified into two categories:

— reactants (or reagents), which are written on the left-hand side in the chemical equation in [1.R3] and are the species introduced into the reactor in order to carry out the reaction (such as nitric oxide and hydrogen in reaction [1.R1]); and

— products, which are written in the right-hand side of the chemical equation and are produced by the reaction, such as water and nitrogen in our example.

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– *Catalysts* or *inhibitors*: these components are intentionally added to the reactor and can be found among the products of the reaction. They influence the speed at which the reaction occurs. This influence can be positive (leading to the reaction's acceleration), these are then catalysts; or negative (slowing down the reaction), these are inhibitors.

– *Inert components* or *diluents*: these compounds are intentionally introduced to the reactor, for example to adjust the concentrations or the total pressure, but they have no chemical effect on the progress of the reaction. For instance, if we introduce argon into reaction [1.R1] occurring in gas phase, the total pressure can be adjusted to one atmosphere with insufficient quantities of gas. We must be cautious before considering a constituent as inert in kinetics and ensure that its presence does not affect the progress of the reaction, etc.

– *Intermediary components* or *intermediates*: these species are not introduced into the reactor and are no longer there when the reaction is complete; they are produced and destroyed during the reaction. Their kinetic role is of the utmost importance in the way the reaction occurs.

### 1.1.3. Reaction zones

We will see (in section 2.1) that many reactions take place in several steps and some of these steps (sort of partial reactions) do not all occur in the reactor's regions.

The *reaction zones* are the regions in space where one part of this reaction occurs.

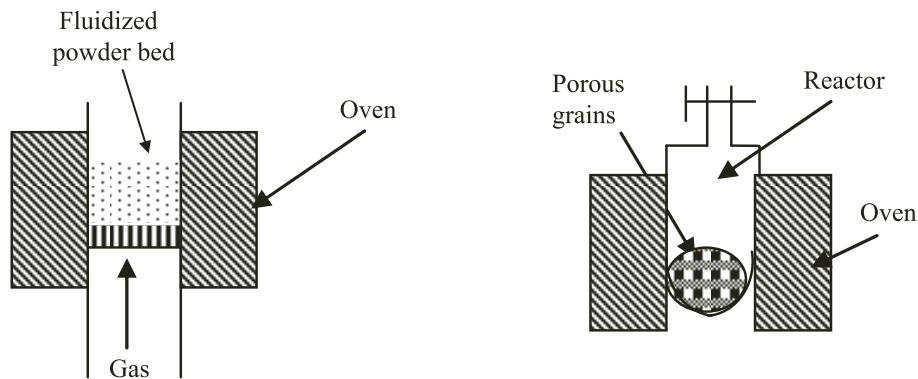
If the entire reaction takes place in one specific region of the reactor, we say that it is a *single zone* or *monozone reaction*. Otherwise it is a *multiple zone* or *multizone reaction*.

Let us reconsider reaction [1.R1] in gas phase. It is a single zone reaction because the entire reaction can take place at any point of the reactor and the reactor is the reaction zone.

Now let us imagine a reaction between gases catalyzed by a solid. This means that the actual reaction only occurs at the surface of the solid. We consider two cases here.

In the first case (see Figure 1.1a) the catalyst is not porous and a fluidized bed reactor is used. The solid is suspended in the gas in motion and the mixture is perfectly stirred. The gas has very easy access to the surface of the solid and the

concentrations of different species far from the catalyst will be the same as those in the vicinity of the surface. We will be dealing with a single zone reaction and the solid surface constitutes the reaction zone.



**Figure 1.1.** Catalytic reactor: a) stirred fluidized with nonporous solid; and b) closed with porous catalyst

Let us now consider the same catalytic reaction but with a porous catalyst in a closed reactor with a static gas (Figure 1.1b). The concentrations of the various gases away from the solid are not the same as those in the vicinity of the surface because of the difficulty that gases have in accessing or moving away from the surface. In this case the reaction will display two reaction zones:

- the catalyst surface where part of the phenomenon occurs; and
- the rest of the reactor (including the pores of the solid), in which the gases will diffuse, constituting a second zone for the overall reaction.

There are frequently more reaction zones in the reactions that involve gases and solids, such as oxygen's reaction on a metal in order to form an oxide.

A reaction zone can be a volume, as in the case of reaction [1.R1] in gas phase, or a surface, as in the case of heterogeneous catalysis. During a reaction, the dimensions of the reaction zones may remain constant or vary due to the reaction. For instance, in the heterogeneous catalysis in [1.R1], the area of the solid's surface is invariable as is the area of the rest of the reactor. Contrary to this, if reaction [1.R1] is carried out under constant pressure in gas phase in a deformable reactor, due to the reaction the volume of this reactor and therefore of the zone will decrease.

## 1.2. Homogeneous and heterogeneous reactions

In kinetics, a distinction is commonly made between *homogeneous reactions*, in which all the components of the reaction belong to the same phase, and *heterogeneous reactions*, where the components of the reaction belong to different phases. Thus, in our previous examples, reaction [1.R1] carried out in gas phase is a homogeneous reaction; while the catalytic reaction in Figures 1.1 is a heterogeneous reaction. As a component of the reaction, the catalyst alone constitutes a solid phase.

This distinction is historic but does not appear to be very useful. In fact, for kinetic studies, experience shows us that it is more appropriate to separate single zone reactions from multizone reactions. We will see that differences appear at this level. Thus, in our previous examples we will classify reaction [1.R1] in gas phase and the catalytic reaction in Figure 1.1a in the same category of single zone reactions; while the reaction presented in Figure 1.1b will be a multizone reaction. In addition to this, it should be noted that the same chemical reaction might occur with a different number of zones depending on the conditions of the experiment.

### 1.2.1. Single zone reaction

There are two broad classes of reactions that involve a single zone:

- homogeneous reactions in which all the components (whether principal or not) belong to the same phase. These are then distinguished as:
  - gas phase reactions,
  - reactions between liquids in which all the liquid components are miscible with each other,
  - reactions in solutions, for which the different components (whether principal or not) are dissolved in the same solvent. This solvent can be a liquid or a solid that does not appear in the writing of the chemical equation;
  - elementary reactions or elementary steps that will be defined in Chapter 2.

### 1.2.2. Multizone reaction

This category gathers together all the heterogeneous reactions that can be divided into two classes:

- heterogeneous catalytic reactions in which all the components belong to the same phase (typically a gas or a solution) with the exception of the catalyst that constitutes a separate solid phase;

– strictly heterogeneous reactions in which at least one condensed phase, usually a solid, is one of the reactants or products of the reaction.

A reaction such as the one shown in Figure 1.1a that we have called a single zone is actually a heterogeneous reaction with several zones rendered to single zone behavior by the experimental conditions (agitation, solid non-porous).

### 1.3. Extent and speed of a reaction

In this section we will discuss reaction [1.R1] written as [1.R2], occurring in gas phase, and will eventually generalize this using reaction [1.R4] exhibiting, unless otherwise stated, one or several zones indifferently.

#### 1.3.1. Stoichiometric abundance of a component in a reaction mixture

The stoichiometric abundance of a constituent  $k$  in a reaction mixture at a given time is the ratio  $\eta$  of the amount of this component to its arithmetic stoichiometric coefficient, which is defined by:

$$\eta_k = \frac{\{A_k\}}{\beta_k} \quad [1.1]$$

Let us reconsider our example of reaction [1.R1] between nitric oxide and hydrogen. We will say that nitric oxide is stoichiometrically more abundant than hydrogen if:

$$\eta_{NO} = \frac{\{NO\}}{2} > \eta_{H_2} = \frac{\{H_2\}}{2}$$

Similarly for the products, nitrogen will be more abundant than water if we have:

$$\eta_{N_2} = \frac{\{N_2\}}{1} > \eta_{H_2O} = \frac{\{H_2O\}}{2}$$

#### 1.3.2. Extent of a reaction

If for a short time interval  $dt$ , we perform reaction [1.R1], some of the reactants will be consumed and some of the products will be produced. We will consume, for example,  $d\{NO\}$  moles of nitric oxide and  $d\{H_2\}$  moles of hydrogen in order to

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produce  $d\{H_2O\}$  moles of water and  $d\{N_2\}$  moles of nitrogen. If we consider the stoichiometry ratios between these quantities<sup>1</sup> we must have:

$$\frac{d\{NO\}}{-2} = \frac{d\{H_2\}}{-2} = \frac{d\{H_2O\}}{2} = \frac{d\{N_2\}}{1}$$

We will say that during  $dt$  all of these variations of stoichiometric abundances are in fact the variation  $d\xi$  of a certain function  $\xi$  that we will call the *extent of reaction* [1.R1], and therefore:

$$\frac{d\{NO\}}{-2} = \frac{d\{H_2\}}{-2} = \frac{d\{H_2O\}}{2} = \frac{d\{N_2\}}{1} = d\xi$$

If we posit that this function is zero when the environment contains only the reactants, the extent of the reaction at a time  $t$  is:

$$\xi = \int_0^t d\xi \quad [1.2]$$

The extent is expressed in amounts of substance, i.e. it is given in moles.

If we generalize this definition to reaction [1.R3] written as [1.R4], for any reactant or product in a closed system with respect to this component we will have:

$$\frac{d\xi}{dt} = \frac{d\{A_k\}}{v_k dt} \quad [1.3]$$

At any time  $t$ , if  $\{A_k\}_0$  is the amount of component  $A_k$  at a time  $t_0$ , applying [1.2] to the amount of component  $A_k$  at a time  $t$  gives:

$$\{A_k\} = \{A_k\}_0 + v_k \int_{t_0}^t d\xi = \{A_k\}_0 + v_k (\xi - \xi_0) \quad [1.4]$$

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<sup>1</sup> We will see later (in Chapter 5, section 5.2 and Chapter 7, section 7.1.2) that this condition is not as obvious as it seems and is not always met.

NOTE 1.3.– We consider that the extent is zero when at least one of the reaction's products is not present in the mixture. This means that starting at the initial instant  $t_0$  of a mixture containing all reactants and products, the initial advancement is  $\xi_0$ .

Let us reconsider the example of reaction [1.R1] and mix at initial instant  $t_0$  the components of the reaction: 2 moles of nitric oxide, 2 moles of hydrogen, 2 moles of water and 2 moles of nitrogen. We want to calculate  $\xi_0$ .

First let us determine the least abundant product of the reaction. It is clear that:

$$(\eta_{N_2})_0 = \frac{\{N_2\}_0}{1} = 2 > (\eta_{H_2O})_0 = \frac{\{H_2O\}_0}{2} = \frac{2}{2} = 1$$

We will then calculate the initial extent using the stoichiometric abundance of water, which is the lowest, and therefore:

$$\xi_0 = \frac{\{H_2O\}_0}{2} = 1 \text{ mole}$$

We can now calculate the composition of the mixture when the reactor does not contain water by applying equation [1.4]:

$$\begin{aligned} \{NO\} &= 2 + 2 = 4 \text{ moles} ; \{H_2\} = 2 + 2 = 4 \text{ moles} \\ \{N_2\} &= 2 - 1 = 1 \text{ mole} \end{aligned}$$

The variation of the amount of  $A_k$  in the open system is due on one hand to the reaction and on the other hand to the algebraic sum of the currents  $q_A$  (input and output) of the constituent:

$$\frac{d\{A_k\}}{dt} = v_k \frac{d\xi}{dt} + \sum_{input} q_A - \sum_{output} q_A \quad [1.5]$$

### 1.3.3. Speed of a reaction

The speed of a reaction ( $v_a$ ), sometimes called the *absolute speed*, is the derivative in relation to time of the extent of this reaction, so we will write:

$$v_a = v_a(t) = \frac{d\xi}{dt} \quad [1.6]$$

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A reaction speed is measured in moles per second.

The application of relation [1.2] immediately leads to the extent at time  $t$ :

$$\xi - \xi_0 = \int_{t_0}^t v_a(t) dt \quad [1.7]$$

Through [1.4] we obtain the amount of any principal component of the reaction at the same time in a closed zone:

$$\{A_k\} = \{A_k\}_0 + v_k \int_{t_0}^t v_a(t) dt \quad [1.8]$$

The exchange of the components between the zone and the exterior must be taken into account in the open zone, and therefore:

$$\{A_k\} = \{A_k\}_0 + v_k \int_{t_0}^t v_a(t) dt + \int_{t_0}^t q_k(t) dt \quad [1.9]$$

### 1.4. Volumetric and areal speed of a monozone reaction

The reaction speed in a monozone reaction is proportional at each moment to the volume (or surface in the case of a surface zone) of the zone concerned at this instant. For instance, for the gas phase of reaction [1.R1], the reaction volume is the volume of the reactor that contains the gaseous constituents of the reaction.

In the case of a surface zone (a 2D zone), the reaction volume is given by the product of its area with the thickness of this zone. The latter has the same order of magnitude as the molecule's sizes and is not likely to change during the reaction. To characterize the dimension of the zone we will define a reaction surface in this case. In the case of the catalytic reaction in Figure 1.1a, the reaction surface is the area of the total surface of the grains of the catalyst solid.

An *expansion coefficient* ( $z$ ) of a product B with respect to a reactant A is the ratio of the volume of B at any time to the volume of A that has produced it:

$$z = \frac{\beta_B V_{mB}}{\beta_A V_{mA}} \quad [1.10]$$

Here  $V_{mA}$  and  $V_{mB}$  are the molar volumes of A and B, and  $\beta_A$  and  $\beta_B$  are the arithmetic stoichiometric coefficients of A and B in the reaction being studied.

This ratio does not vary with the extent of the reaction. This ratio is not useful for gaseous phases because all the gases have the same molar volume. It is interesting, however, in the case of solid–solid reactions such as, for example, the expansion coefficient of an oxide with respect to its metal.

The *volumetric speed of a single-zone reaction* is the speed of the reaction per unit of volume (the areal speed will be used for 2D zones). We emphasize that this notion is only defined for reactions with a single reaction zone, which includes all homogeneous reactions, in other words that occur entirely in one phase:

$$v_a = v/V \text{ or} \quad [1.11a]$$

$$v_a = v/S \quad [1.11b]$$

The volumetric speed (areal speed) is thus expressed in moles per second and  $\text{m}^3$  (moles per second and  $\text{m}^2$ ). This magnitude is *a priori* based on the extent of the reaction (among others like temperature, concentration of the reactants, etc.) and therefore time, but is independent of the volume (or the surface) of the zone.

Considering equations [1.3] and [1.11a] (or [1.11b]), we obtain:

– in a closed zone:

$$v = \frac{1}{Vv_k} \frac{d\{A_k\}}{dt} \quad [1.12a]$$

or:

$$v = \frac{1}{Sv_k} \frac{d\{A_k\}}{dt} \quad [1.12b]$$

– in open zone for the component concerned:

$$v = \frac{1}{V} \left( \frac{1}{v_k} \frac{d\{A_k\}}{dt} + \sum_{input} q_A - \sum_{output} q_A \right) \quad [1.13]$$

## 1.5. Fractional extent and rate of a reaction

### 1.5.1. The fractional extent of a reaction

The fractional extent of a reaction is a very practical notion because it defines a dimensionless quantity. The definition of the notion of fractional extent leads us to consider three cases.

#### 1.5.1.1. Closed reactors *with respect to the principal components of the reaction*

Such a reactor does not exchange any substance with its surroundings. At the initial moment it contains a certain amount of reactants and the stoichiometrically least abundant reactant in reaction [1.R3] is the constituent denoted  $A_1$ .

The *fractional extent* ( $\alpha$ ) of the reaction is the ratio of the actual extent to the initial amount of the stoichiometrically less abundant reactant:

$$\alpha = \frac{\xi}{\{A_1\}_0} \quad [1.14]$$

For example, let us reconsider reaction [1.R1] with 4 moles of nitric oxide and 6 moles of hydrogen at the start. The stoichiometrically least abundant compound is the nitric oxide, as  $4/2$  is less than  $6/2$ . According to [1.11], the fractional extent will be:

$$\alpha = \frac{\xi}{\{\text{NO}\}_0} = \frac{\xi}{4}$$

Through a combination of equations [1.4] and [1.14] in a closed zone we obtain:

$$\{A_k\}_0 = \{A_k\}_0 + v_k \{A_1\}_0 (\alpha - \alpha_0) \quad [1.15]$$

The difference  $\{A_k\}_0 - \{A_k\}$  is the lost quantity of a reactant and its opposite is the amount of a product produced.

$\alpha_0 = 0$  is mostly chosen if at least one of the products formed by the reaction is missing.

The application of equation [1.15] to the components of reaction [1.R1] gives:

$$\{\text{NO}\} = \{\text{NO}\}_0 - 2\{\text{NO}\}_0 \alpha = \{\text{NO}\}_0 (1 - 2\alpha) = 4(1 - 2\alpha)$$

$$\{H_2\} = \{H_2\}_0 - 2\{NO\}_0 \alpha = 6 - 8\alpha$$

$$\{H_2O\} = \{H_2O\}_0 + 2\{NO\}_0 \alpha = 2\{NO\}_0 \alpha = 8\alpha$$

$$\{N_2\} = \{N_2\}_0 + \{NO\}_0 \alpha = \{NO\}_0 \alpha = 4\alpha$$

From this we can see that the fractional extent is zero if only the reactants are present and is one when the reaction is terminated by the complete disappearance of the least abundant reactant. Therefore, this dimensionless number varies at most between zero and one in a closed reactor.

If the reaction is balanced, it means that the equilibrium corresponds to a certain fractional extent  $\alpha_e$  and that if we apply the mass-action law, we can write:

$$\prod_k [A_k]^{v_k} = K_c = \prod_k ([A_k]_0 + v_k [A_l]_0 \alpha_e)^{v_k}$$

NOTE 1.4.— If we apply equation [1.15] to the reference reactant  $A_1$ , we get:

$$\alpha = \frac{1}{v_1} \frac{\{A_1\} - \{A_1\}_0}{\{A_1\}_0} \quad [1.16]$$

We note from equation [1.16] that the fractional extent represents the portion of the reference reactant that has reacted if its stoichiometric coefficient is one (which can often be chosen). Hence the name “fractional conversion” is sometimes used to refer to the fractional extent of a reaction.

#### 1.5.1.2. Closed reactors with respect to one or more reactants of the reaction

If the reactor is closed or partially closed with respect to one or more components, the stoichiometrically least abundant component will be chosen. We can again apply definition [1.14] and equation [1.15] in order to calculate the quantities of different species lost or produced when the system is closed to the fractional extent  $\alpha$ .

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### 1.5.1.3. Completely open reactors

The concept of the initial amount of a reactant is meaningless in an open system. In order to maintain the dimensionless character of a fractional extent, it will be defined from a random amount of substance  $n_1^0$  of one of the components  $A_1$ . So, instead of [1.14] and [1.15], we will get the expressions:

$$\alpha = \frac{\xi}{n_1^0} \quad [1.17]$$

$$\{A_k\} = \{A_k\}_0 + v_k n_1^0 (\alpha - \alpha_0) + \int_{t_0}^t q_k \cdot dt \quad [1.18]$$

This definition of the fractional extent does not impose any upper bound.

### 1.5.2. Rate of a reaction

In order to maintain the intensive nature of the speed of a reaction, we will define a new form of speed that is the speed of the fractional extent or *rate* as the derivative of the fractional extent with respect to time:

$$r = \frac{d\alpha}{dt} = \frac{v_a}{\{A_1\}_0} \quad \text{or} \quad \frac{v_a}{n_1^0} \quad [1.19]$$

NOTE 1.5.– Most books do not give a specific name to this quantity, which is a reaction frequency. They just call it “speed”. Other books use the term “rate” for the absolute speed, which increases confusion.

### 1.5.3. Expression of the volumetric speed (areal) from variations in the amount of a component

We consider a reactor where a single reaction is carried out. Through equations [1.3] and [1.19], for any type of reaction in a closed environment we can write:

$$\frac{d\{A_k\}}{dt} = v_k v_a = v_k \{A_1\}_0 r \quad [1.20]$$

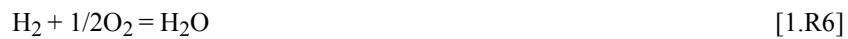
If our reaction is a single-zone reaction, taking into account [1.12] yields:

$$\frac{d\{A_k\}}{dt} = v_k v \cdot V \quad \text{or} \quad v = \frac{1}{v_k V} \frac{d\{A_k\}}{dt} \quad [1.21]$$

If several independent reactions are now carried out in our reactor that involve component  $A_k$  as the reactant or the product, with the algebraic stoichiometric coefficient  $v_{kp}$  in the  $\rho$ -th reaction, the balance of this component – considering only the reactions – will be:

$$\frac{d\{A_k\}}{dt} = \sum_{\rho} v_{kp} (v_a)_{\rho} = \{A_l\}_0 \sum_{\rho} v_{kp} r_{\rho} \quad [1.22]$$

Before applying this equation, it is important that the reactions considered are truly independent. In order to illustrate this, let us consider a reactor containing the following gas constituents: oxygen, nitric oxide and water. From these compounds we can write the following three reactions:



We note that reaction [1.R6] can be obtained by the following linear combination of the above reactions:

$$[1.\text{R}6] = [1.\text{R}1] + 2 \times [1.\text{R}5]$$

This reaction is not independent of the other two and therefore we will only keep reactions [1.R1] and [1.R5].

The application of equation [1.22] to nitric oxide is written as:

$$\frac{d\{\text{NO}\}}{dt} = \{\text{NO}\}_0 (-2r_1 - r_2)$$

Equation [1.22] can be written as [1.23] by introducing the volume  $V$  of the zone:

$$\frac{d\{A_k\}}{dt} = \{A_l\}_0 \sum_{\rho} v_{kp} v_{\rho} V \rho \quad [1.23]$$

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We see that the mixture behaves as if it is the seat of a single reaction whose specific speed is the combination of the independent reactions' specific speeds:

$$v = \sum_{\rho} v_{k\rho} v_{\rho} \quad [1.24]$$

A current of matter  $q_k$  of component  $k$  is exchanged with the exterior (incoming and/or outgoing) in an open system and equation [1.20] is replaced by:

$$\frac{d\{A_k\}}{dt} = v_k v_a + q_k = v_k \{A_l\}_0 r + q_k \quad [1.25]$$

Equation [1.21] is replaced in single-zone system by:

$$\frac{d\{A_k\}}{dt} = v_k v V + q_k = v_k \{A_l\}_0 r + q_k \quad [1.26]$$

Relation [1.22] is replaced by:

$$\frac{d\{A_k\}}{dt} = \sum_{\rho} v_{k\rho} (v_a)_{\rho} + q_k = n_0 \sum_{\rho} v_{k\rho} r_{\rho} + q_k \quad [1.27]$$

and [1.23] becomes:

$$\frac{d\{A_k\}}{dt} = V \sum_{\rho} v_{k\rho} v_{\rho} + q_k \quad [1.28]$$

## 1.6. Reaction speeds and concentrations

During the study of numerous reactions occurring in solution, the measurement of concentrations is frequently used.

### 1.6.1. Concentration of a component in a zone

Concentration in a reaction zone is defined as the amount of substance contained in the unit volume of this area. In the case of homogeneous and uniform reactions, a component will only have one concentration:

$$[A_k] = \frac{\{A_k\}}{V} \quad [1.29]$$

In the case of 2D zones, the concept of superficial concentration is sometimes used, which is the amount of substance contained on a unit area of a surface.

### 1.6.2. Relationship between concentration and fractional extent in a closed environment

If the zone is closed with respect to component  $A_k$ , the only cause of variation in concentration over time is the reaction and, therefore, by using equations [1.15] and [1.29] and by assigning the index zero to the magnitude values at the start of a reaction, we get:

$$[A_k] = [A_k]_0 + v_k [A_l]_0 (\alpha - \alpha_0) \frac{V_0}{V} \quad [1.30]$$

In the case of gaseous components, assuming an ideal gas, the concentration can be replaced by the partial pressure by using:

$$P_k = [A_k] RT \quad [1.31]$$

If several reactions involving the same constituent  $k$ , whose stoichiometric coefficient in the  $\rho$ -th reaction is  $v_{k\rho}$  occur in the same zone, then equation [1.30] becomes:

$$[A_k] = [A_k]_0 + \frac{[A_l]_0 V_0}{V} \sum_{\rho} v_{k\rho} (\alpha_{\rho} - \alpha_{\rho_0}) \quad [1.32]$$

### 1.7. Expression of volumetric speed according to variations in concentration in a closed system

From the concentration expression [1.29], through derivation we obtain:

$$\frac{d[A_k]}{dt} = \frac{1}{V} \frac{d\{A_k\}}{dt} - \frac{[A_k]}{V} \frac{dV}{dt} \quad [1.33]$$

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and by using [1.12] and [1.32] for a reaction with a single zone, we get:

$$v = \frac{1}{v_k} \frac{d[A_k]}{dt} + \frac{[A_k]}{V} \frac{dV}{dt} \quad [1.34]$$

This relationship is extremely useful for the computation of the volumetric speed of a reaction from concentration measurements in a closed system.

It should be noted that if the reaction zone maintains a constant volume during the progress of the reaction, expression [1.34] is simplified to:

$$v = \frac{1}{v_k} \frac{d[A_k]}{dt} \quad [1.35]$$

This will be the case for all homogeneous reactions in gaseous phase in a closed environment with constant volume and in numerous homogeneous reactions in liquid or solid phase (solutions) for which variations in volume will be negligible.

### 1.8. Stoichiometric mixtures and progress

We say that two reactants,  $m$  and  $k$ , are in stoichiometric proportion if they have the same stoichiometric abundance (see section 1.3.1), which means their amounts are such that:

$$\frac{\{A_k\}}{\{A_m\}} = \left| \frac{v_k}{v_m} \right| \quad [1.36]$$

In closed system, if these conditions are met at a moment of reaction they are met at all times<sup>2</sup>, especially at the initial moment.

The same ratio as [1.36] is obtained for the concentrations by dividing the amounts of substance by the same volume:

$$\frac{[A_k]}{[A_m]} = \left| \frac{v_k}{v_m} \right| \quad [1.37]$$

---

<sup>2</sup> See Note 1.5 in section 1.5.2.

By defining a ratio,  $\mu_k$ , we still have the right to write the initial amount of a product as:

$$\{A_k\}_0 = \mu_k \{A_l\}_0 \quad [1.38]$$

In the case of two products  $m$  and  $k$  of the reaction that are in stoichiometric proportion, their amounts satisfy equation [1.36]. As they were already in these proportions at the initial moment we obtain:

$$\frac{\mu_k}{\mu_m} = \left| \frac{v_k}{v_m} \right| \quad [1.39]$$

If all the products of a reaction are in stoichiometric proportions, then the ratio  $\mu/v$  is invariant and, according to [1.15], its value is the fractional extent at the initial state:

$$\frac{\mu_k}{v_k} = \text{constant} = \alpha_0$$

## 1.9. Factors influencing reaction speeds

Many variables can influence the speed of a reaction. Their number cannot be known *a priori*, so they need to be determined by experience. The two main variables are:

- temperature;
- concentrations (or partial pressures of gas) of reactants, products or catalysts.

### 1.9.1. Influence of temperature

The influence of temperature on the speed of reactions was found very early on in chemistry. In general the speed of a reaction increases with temperature, but exceptions to this rule are known (for instance reaction [1.R5] between nitric oxide and oxygen in order to obtain nitrogen dioxide has a speed that decreases as the temperature increases).

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The laws are often complex but a representation of experimental points giving the logarithm of speed versus the inverse of temperature (known as Arrhenius coordinates) quite often lead to a straight line (see Figure 1.2). This suggests that Arrhenius' law, which can take one of the three forms – [1.40], [1.41] or [1.42] – is followed. This appearance is often misleading, however, and it frequently comes from the strong influence of temperature in a restricted range of the temperature and from the linearizing properties of Arrhenius coordinates:

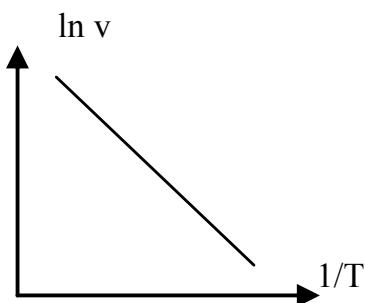
$$v = A \exp -\frac{\Xi}{R T} \quad [1.40]$$

$$\frac{d \ln v}{d \ln(1/T)} = -\frac{\Xi}{R} \quad [1.41]$$

$$\frac{d \ln v}{d \ln(1/T)} = -\frac{\Xi}{R T^2} \quad [1.42]$$

The consequence is that experimenters often confine themselves to this raw result. The computed parameter  $\Xi$  is often called the activation energy of the reaction. This definition is also used for a particular class of reactions, which will be called elementary reactions (see Chapter 2), with a precise physical meaning that is not found for the other types of equations. In the general case and in the absence of any additional information, we prefer to call this parameter the “temperature coefficient”, which is thus defined from the experiment by:

$$\Xi = -\frac{1}{R} \frac{\partial \ln v}{\partial (1/T)} \quad [1.43]$$



**Figure 1.2.** Variation of the speed of a reaction in Arrhenius coordinates

NOTE 1.6.– In a reactor, this is mainly true in industrial reactors, the temperature is not always the same at all points and thus the speeds differ both in time and space.

### **1.9.2. Influence of the concentrations (or partial pressures of gases)**

The relationships between reaction speed and concentrations of reactants, products or catalysts are extremely complex and varied. We will see that the diversity of these relations is a real treasure and makes speed-concentration relationships at constant temperature the main tool of justification for a mechanism.

It should be noted that equations of the following form are sometimes encountered:

$$v = k [A_1]^{\delta_1} [A_2]^{\delta_2} \dots [A_i]^{\delta_i} \quad [1.44]$$

This function only involves the concentrations of the reactants. In this case we say that the reaction admits an order that is the sum of the exponents,  $\delta_i$ , that are themselves partial orders. The “constant”  $k$  would only depend on the temperature.

In the case of closed reactors, we must keep in mind that the concentrations vary solely because of the reaction and therefore evolve with its progress so that the influence of the concentration implicitly contains two distinct variables: the concentration and the extent.

It should be noted that the concentrations can be kept constant throughout the reaction by working in an open reactor with a regulated supply but also by working during sufficiently short times with high concentrations so that the variations in concentrations become fairly insignificant. In these cases, the concentration is detached from the extent.

### **1.9.3. Other variables**

The previous variables are dominant and are called thermal variables. Other variables exist, however, that it is sometimes appropriate to examine. This is, for instance, the wavelength and the light intensity in “photochemical” reactions, which are influenced by light, or the electric potential in “electrochemical” reactions, which involve electrons as a reactant or a product of the reaction. Extensive variables should be added to these intensive variables, such as the amounts of substance, the shapes and dimensions of reaction zones and reactors.



## Chapter 2

# Reaction Mechanisms and Elementary Steps

Apart from being of practical interest, which is linked to the notion of yield, chemical kinetics provides information on how the reaction takes place, which is called its mechanism. Starting from a basic premise of the decomposition of real reactions into elementary steps, we are led to examine the different types of elementary steps that will form the basic tools that will help us to understand the progress of the reaction being studied.

### 2.1. Basic premise of kinetics

It can easily be thought that, in order to react with each other, molecules have to be very close to each other at a given time. This means they must be positioned so that they exert mutual influences that can provoke changes.

Let us consider the reaction forming water:



This reaction involves three molecules as reactants. It is clear that if this reaction occurred in a single step, it would imply that the three molecules (reagents) meet (or are very close to each other) at the same time to give rise to a reaction that is followed by the simultaneous transfer of two electrons. This situation is thought to be unlikely. Indeed the probability of collision of three gas molecules can be calculated through the kinetic theory of gases and is very low, certainly well below the number of molecules that react per second, which can be obtained from the reaction speed that readily becomes explosive. We therefore prefer a path that is a

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bit more complicated, but would make a minimum transformation at each step. Each of these steps will be called an elementary step.

NOTE 2.1.— The above reaction could have been written by dividing the stoichiometric coefficients by two, which would have led to the necessity for only two molecules to collide – a phenomenon that is much more common and sufficient with regard to the order of magnitude of reaction speeds. Such a collision will have produced half a nitrogen molecule, however, which is unacceptable given that there is no such thing as half a water molecule.

Such observations can be made for a large number of reactions, which leads us to admit the following premise that can be considered to be the fundamental principle of kinetics.

PRINCIPLE.— Any real reaction is a more or less complex combination of elementary steps.

### 2.2. Reaction mechanism

#### 2.2.1. *Definition*

A mechanism is a set of elementary reactions that adequately reflect the progress of a reaction.

Therefore, a mechanism is an assumption that must be consistent with all available experimental observations.

The existence of “intermediate” elementary reactions implies the existence of new species that will be termed “intermediate species”. Such intermediate species are not present in the balanced writing of the reaction, which implies that their amount is zero both at the initial and the final state. Thus, these intermediate species will be produced by some elementary steps and consumed by others.

So if we reconsider reaction [2.R1], the mechanism that consists of the six steps [2.R1a], [2.R1b], [2.R1c], [2.R1d], [2.R1e] and [2.R1f] was proposed. It follows that this mechanism suggests the intermediate formation of OH radicals and atoms of hydrogen and oxygen:





NOTE 2.2.– It should be noted that in an elementary reaction, the equals sign (=) between the reactants and the products is replaced by a double arrow ( $\rightleftharpoons$ ), which means that we are dealing with two opposite elementary reactions. A single arrow ( $\rightarrow$ ) is often used in order to indicate the preferred direction of progress of the reaction. So, a chemical equation with arrows, for an elementary step, is a “molecular” equation (then the molecules can be cut). This is not a “molar” equation like the classical chemical reactions.

### 2.2.2. Examples of mechanisms

There are several types of mechanisms: unique sequence mechanisms, chain mechanisms and catalytic mechanisms. While some are specific to a single reaction, others are applicable to a family of reactions. We will give examples of these various types and some will serve as the guiding concept in order to present the different modes of treatment. We will give more information on mechanisms and details about the kinds of elementary reactions in Chapter 9.

#### 2.2.2.1. Hydrogen bromide synthesis

The overall reaction is simply written as:



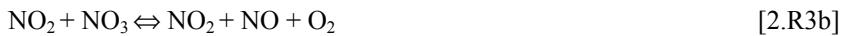
In a simplified form, the mechanism of this reaction can be formulated through the four steps [2.R2a], [2.R2n], [2.R2c] and [2.R2d]



It should be noted that the last step is the opposite reaction of the first step.

### 2.2.2.2. Dinitrogen pentoxide ( $N_2O_5$ ) decomposition

The thermal decomposition of dinitrogen pentoxide in nitrogen dioxide and oxygen (reaction [2.R3]) is a unique sequence reaction with a mechanism that consists of the three steps [2.R3a], [2.R3b] and [2.R3c]:



The aforementioned examples are mechanisms that are specific to a reaction. However, there are templates of mechanisms that are common to a significant number of similar reactions.

### 2.2.2.3. Nucleophilic substitution reactions in organic chemistry

These reactions can be divided into two categories, each leading to a mechanism: the SN1 mechanism (so called because it leads to a speed of first order) with two steps in the mechanism, such as reaction [2.R4] and steps [2.R4a] and [2.R4b]:



and the SN2 mechanism (so-called because it leads to a speed of second order) in a single step, as in reaction [2.R5]:



We can also mention electrophilic substitution reactions, which are divided into two classes: SE1 in two steps and SE2 in a single step.

### 2.3. Reaction intermediates

Once the principle that breaks down a reaction into elementary steps is accepted, it is clear that apart from the reactants – such as catalysts and inhibitors – and the products eventually formed, new species are involved in these elementary steps, as shown by the examples we have given. These species are probably particularly reactive because we can only rarely detect and identify them.

The intermediates involved in the progress of reactions can be activated atoms or molecules, which are those that have acquired an additional energy making them highly reactive, but mostly entities featuring free valences in the form of unpaired electrons, radicals or electric charge, or ions. Finally, in kinetics involving solids, we find adsorbed molecules or atoms, since adsorption is a kind of activation. We can also find point defects in crystals, which are highly mobile species as often shown by electrical conductivity, and therefore likely to move to ensure the transport of matter and charges.

#### 2.3.1. *Excited atoms (or molecules)*

If we consider a set of atoms or molecules of the same nature, it is known that they store energy that is distributed into various forms:

- translation;
- rotation;
- vibration;
- electronic.

At rest and at a certain temperature, these forms present an energy that has a Gaussian shape with a mean value and a standard deviation that increases with temperature. It is possible by various methods to provide energy well above the average to a relatively significant number of these atoms or molecules. The essential activation methods are:

– *thermal activation*: a rise in temperature increases the mean energy but also, as we have said, the deviation around this mean so that a certain number of these atoms (or molecules) – the most energetic – can acquire an energy that is much higher than the average;

– *electromagnetic activation*: the energy is transmitted to the atoms or molecules by a beam of particles (photons, electrons, ions, etc.). In photochemistry, for instance, the excitation is provided by light radiation (visible or ultraviolet), the molecules are cut through an electron beam in a mass spectograph, etc. Such

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reactions are characterized by their quantum yield, which is the ratio of the number of transformed molecules to the number of photons absorbed. This activation leads to photochemistry;

– *electrical activation*: energy is provided by the electric current. These reactions are characterized by Faraday's law, which enables us to determine the number of electrolyzed molecules for a given amount of electricity. This activation leads to electrochemistry;

– *activation through ultrasound*: in liquid or solid phase, the ultrasounds are likely to activate molecules. This activation leads to sonometry;

– *activation through adsorption*: the adsorption of molecules coming from a gas or liquid at the surface of a solid provokes activations that result in changes in the molecule. An example is the dissociative adsorption of hydrogen, which cuts the molecule into two adsorbed atoms. This activation leads to heterogeneous catalysis.

### 2.3.2. Free radicals

Free radicals are unstable molecules; the instability is due to the presence of unpaired or extremely available electrons. For instance, the pyrolysis of tetraethyl lead releases ethyl radicals:



The tert-butyl peroxide is a compound formed from a relatively weak central bond O–O:  $(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$ . It is thus a product that, even at ordinary temperature, tends to break down slowly. It therefore generates free radicals:  $(\text{CH}_3)_3\text{CO}\cdot$ , that are likely to initiate reactions.

The presence of unpaired electrons should be symbolized by a point that follows the radical's formula. The simplest form of the radical is an atom, such as the chlorine atom represented by the symbol  $\text{Cl}\cdot$ .

In some cases, the study of molecular spectrums enables us to demonstrate the presence of radicals. Mass spectrometry also constitutes a valuable guide for the identification of radicals or atoms.

### 2.3.3. Ions

The anions and cations involve two types of reactions. The first is electrochemistry, with the ions in solid or liquid solutions, and gas chemistry, in

which many reactions involve ions such as the carbocations in organic chemistry. We have already seen the example of the tertbutyl cation,  $\text{t-Bu}^+$ , occurring in reaction [2.R4]. Here again spectrography and mass spectrometry are valuable methods for identifying gas-phase ions. In solution, notably in polar solvents such as water, ions are usually solvated, which means they are surrounded by a crown of solvent molecules. The number of solvent molecules surrounding the ion is called the *solvation index*.

#### 2.3.4. Adsorbed species

All heterogeneous catalysis relies on the existence of reactions between adsorbed molecules or atoms (the Langmuir–Hinshelwood mechanism) or between adsorbed molecules or atoms and free molecules (the Rideal mechanism).

#### 2.3.5. Point defects

Heterogeneous reactions involving the stoichiometric participation of solids introduces point defects that are imperfections in the periodic arrangement of the atoms or ions of a crystal (see Annex 1). The main point defects are:

- the vacancies: absence of an ion or atom at a point lattice in the crystal;
- the interstitials: these are atoms or ions inserted between the point lattices of the crystal.

#### 2.3.6. The effect of intermediates on extent and speeds

Let us return to the definitions of the extent and speed of a reaction (see section 1.3). We have implicitly admitted that there a “stoichiometry” relationship exists between the extent (and speeds) of a reaction, which is defined for each of the principal components of the reaction as:

$$\frac{\mathbf{d}\{A_1\}}{v_1} = \frac{\mathbf{d}\{A_2\}}{v_2} = \frac{\mathbf{d}\{A_3\}}{v_3} = \dots = \mathbf{d}\xi \quad [2.1]$$

If different steps exist, and therefore there are intermediate species in the progress of this reaction, nothing says that the various ratios of relation [2.1] are equal to each other. In fact, some periods might exist during which the amount of an intermediate can increase and other periods might exist when it will decrease. Therefore the speeds of the different elementary steps (for which relation [2.1] is

fully met, as there is no intermediate in these steps) will not necessarily be equal. This means that the ratios of relation [2.1] will not be equal.

Let us reconsider the example of reaction [2.R3]. Let us suppose that during a certain period, step [2.R3a] is faster than step [2.R3b]. It is clear that during this period we will produce more nitric dioxide molecules than oxygen molecules, but nothing implies that the ratio one to four is observed.

It follows that the rate should be defined as an extent  $\xi_k$  of each principal component of the reaction. Thus the speed (hence the rate) of the reaction with respect to each component will not generally be equal.

It is only during periods in which *all* the amounts of the intermediate species remain constant that there will be a single extent and a single speed for the reaction regardless of the constituent chosen to define them. In such cases, we will say that we are in steady state conditions for the intermediates.

## 2.4. Reaction sequences and Semenov representation

### 2.4.1. Semenov diagram

In order to sketch a mechanism, we use the *Semenov representation* (see Figure 2.1), where each intermediate compound ( $M_1$  or  $M_2$ ) is represented by a point that will constitute a node of the network. Two nodes, the second resulting from the first through an elementary step, are connected by a vector that indicates the direction of the reaction (step 1). In addition, some steps of the mechanism produce or consume intermediates by involving only the principal components of the reaction (step 2 in Figure 2.1). These steps are represented by an oriented arc ending at or starting from a node.



**Figure 2.1.** Semenov representation of elementary steps

NOTE 2.3.— The previous steps are likely to involve some principal components in one of each member. These components are represented by dots in chemical equations.

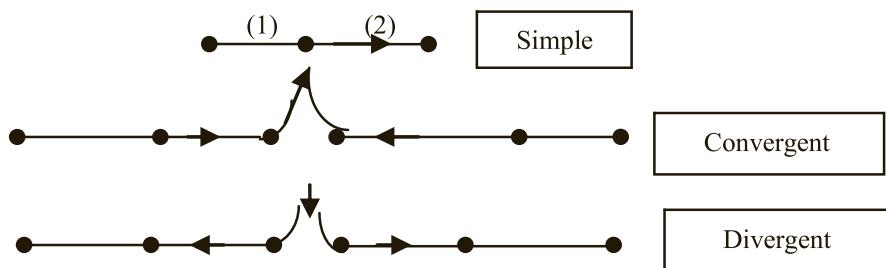
#### 2.4.2. Linear sequences and multipoint sequences

A set of steps that are linked by a mechanism constitutes a sequence characterized by its entry point(s), its exit point(s) and its traversal direction(s). Depending on the reaction intermediates, two types of sequence are distinguished: linear sequences and multipoint sequences. From the perspective of the Semenov diagram's shape, two types of sequence are distinguished: open sequences and closed sequences.

##### 2.4.2.1. Linear sequences

A sequence is linear if each intermediate is produced by a single step and is also consumed by a single step. Depending on the Semenov representation (see Figure 2.2), there are:

- simple linear sequences: The mechanism SN1 of reaction [2.R4] is an example of a simple linear system;
- sequences with convergent paths that present an output disruption. The two simple linear sub-sequences that it is composed of converge at the output;
- sequences with divergent paths, which present an input disruption. The two simple linear sub-sequences that compose it diverge at the output.

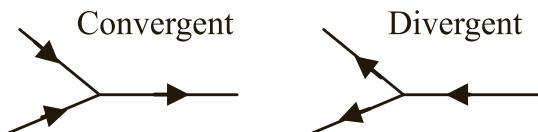


**Figure 2.2.** Different types of linear sequences

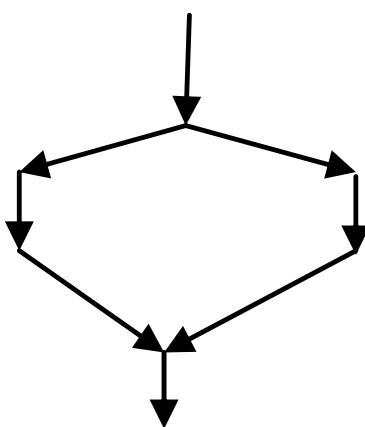
##### 2.4.2.2. Multipoint sequences

A multipoint sequence comprises an intermediate that is produced or consumed by at least two steps (see Figure 2.3):

- if the steps go toward the multipoints then the sequence is convergent;
- if not, the sequence is divergent.

**Figure 2.3.** Multipoint sequences**2.4.2.3. Cyclic sequences**

The Semenov diagram shows a cycle that has either parallel branches (see Figure 2.4) or is traversed in a single direction.

**Figure 2.4.** Closed system with a parallel loop**2.5. Chain reactions****2.5.1. Definition**

A chain reaction is a reaction in which a small number of elementary steps are repeated a large number of times following each other through a small number of intermediate species that are constantly formed and destroyed. Such an example is given by the mechanism of the synthesis of hydrogen bromide, expressed in section 2.2. A repetitive sequence is called a repeat unit in the chain (like the two steps [2.R2a] and [2.R2b] in hydrogen bromide synthesis).

By extension, a simple linear reaction consisting of a large number of steps very close to each other is also called a chain reaction. Thus, polymerization and polycondensation reactions (see section 2.6.5) are also considered to be chain

reactions. Each step is very similar to the previous step because each time just a small entity is added in the molecular chain.

### **2.5.2. The different categories of chain reactions**

In homogeneous kinetics, chain reactions can be grouped into three broad groups:

- reactions involving halogens or their derivatives;
- oxidation and combustion reactions (hydrogen, hydrocarbons);
- reactions involving the formation of macromolecules (polymerization and polycondensation).

The first two groups are real chain reactions with repetition of intermediates, while in the third group the intermediates are slightly different as the chain grows.

### **2.5.3. The steps in a chain reaction**

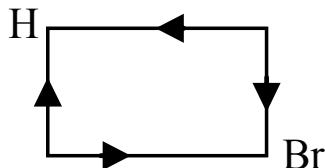
In a chain reaction we are led to distinguish four types of sequences:

- the initiation steps that create the first intermediate, such as [2.R2a] of hydrogen bromide synthesis (section 2.2.2.1);
- the propagation steps. These are the steps that are reproduced a large number of times and are the main consumers of reagent, such as [2.R2b] and [2.R2c] of the hydrogen bromide synthesis;
- the breaking steps. These steps destroy intermediates, which leads to the termination of the chain, as in [2.R2d] of hydrogen bromide synthesis;
- the branching steps. These are steps that produce two intermediates that each give rise to a chain. Step [2.R1d] of water synthesis is an example.

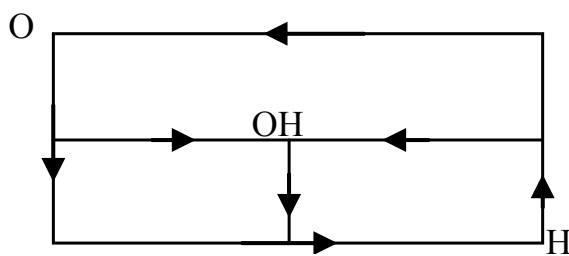
The first three phases are the minimum necessary.

### **2.5.4. Sequence of chain reactions**

Chain reactions are reactions that have a closed sequence in which the loop is traversed completely in one direction, such as the hydrogen bromide synthesis in which the sequence constituting the repeat unit (reaction sequence that is repeated indefinitely) is linear (see Figure 2.5).

**Figure 2.5.** Cycle of the repeat unit of HBr synthesis

In branched chain reactions, such as water synthesis, the repeat unit includes multipoint sequences (see Figure 2.7), which leads to multiple loops nested within each other.

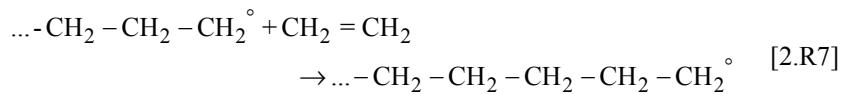
**Figure 2.6.** Semenov cycle of the branched chain reaction of water synthesis

### 2.5.5. Reactions of macromolecule formation

Macromolecules are formed by two types of chain reactions: polymerizations and polycondensations.

#### 2.5.5.1. Polymerizations

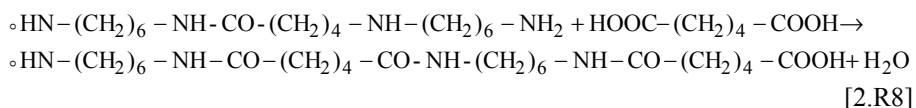
Polymerization involves a series of reactions, each adding a simple molecule to an already polymerized molecule. An example is the polymerization of ethylene, where the propagation step is a series of additions of ethylene molecules:



Such a reaction may involve either a single simple molecule, as in the previous example, or alternatively several different simple molecules; the latter situation is called copolymerization.

### 2.5.5.2. Polycondensations

Polycondensation occurs like polymerization with a series of reactions where each adds a pattern to the chain. Instead of a simple addition, however, there is an elimination of a small molecule at each step (water, ammonia, etc.). An example is the production of nylon through polycondensation between adipic acid and hexamethylenediamine with the elimination of water:



In both types of reactions (polymerization and polycondensation):

- if the monomer molecules have two anchor-points, linear molecules will be obtained, which are commonly used in the manufacture of threads;
- if the monomer molecules have three anchor-points, 2D planar molecules will be obtained, which are commonly used in the manufacture of varnishes and paints;
- if the monomer molecules have more than three anchor-points, spatial molecules are obtained, which are commonly used in the manufacture of synthetic resins for molding.

## 2.6. Catalytic reactions

Catalysis is the acceleration of a reaction through the inclusion of an additional constituent: the catalyst.

To catalyze a reaction is to change its mechanism in order to reduce its energy requirements. In the simplest case of a regime with one step that determines the speed, catalyzation involves replacing this potentially slow step by an other step that has a lower activation energy.

At the end of the reaction, the catalyst is chemically reconstituted and is identical to what it was at the beginning of the reaction. This property implies that catalysis does not change the thermodynamic state functions – such as enthalpy, entropy and Gibbs free energy – of the reaction.

NOTE 2.4.– At the end of the reaction, in the case of heterogeneous catalysis, despite the fact that the catalyst is fully regenerated in quantity, its surface can be contaminated by strongly adsorbed species. This makes the surface more difficult to

access by the reactants. This situation is called catalyst poisoning. Likewise, after use a catalyst may have significant textural differences compared to its initial state.

Although the catalyst is not consumed by the reaction, its amount greatly affects the speed of the catalyzed reaction.

There are two areas of catalysis depending on whether the catalyst belongs to the same phase as the principal constituents or a separate phase (usually a solid). The first case constitutes homogeneous catalysis, mainly in liquid phase. The second is heterogeneous catalysis for reactions between catalyzed gases by a solid.

### 2.6.1. *Homogeneous catalysis*

In homogeneous catalysis, all the reactants and the catalyst belong to the same phase. The most common are catalysts in liquid medium.

#### 2.6.1.1. *Herzfeld mechanism in homogeneous catalysis*

A very general mechanism of homogeneous catalysis has been proposed by Herzfeld.

Let us consider a reaction of the form:



Catalyzed by a substance *C*, Hertzfeld proposed the following mechanism:



It can be seen that the sum of the three steps [2.R9a], [2.R9b] and [2.R9c] gives back the overall reaction.

NOTE 2.5.— It should be noted in this mechanism that a quadratic step [2.R9c] intervenes. This is a step where two intermediates react with one another.

### 2.6.1.2. Enzyme catalysis

Enzymes are substances present in living organisms. They catalyze most biochemical reactions. These catalysts have three specific properties:

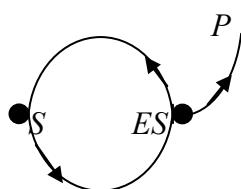
- an enzyme is very specific to a very particular reaction and this specificity can even be stereochemical;
- enzymes are hydrosoluble substances;
- enzymes are catalysts that have an optimum temperature of action. The existence of an optimum temperature is due to the fact that enzymes are not stable with temperature and thus this instability counteracts the kinetic effect of temperature.

A two-step mechanism of enzymatic action was proposed by Michaelis and Menten:

- during the first step, a complex is formed between the enzyme  $E$  and the substrate (reactant)  $S$ :



- this complex is broken down during the second step, which produces the product  $P$  and regenerates the enzyme:



**Figure 2.7. Loop of the Michaelis mechanism**

### 2.6.2. Heterogeneous catalysis

This is a reaction between reactants leading to products that usually belong to the same phase (liquid or gas) and utilize the surface of a solid phase in their mechanism.

### 2.6.2.1. *Heterogeneous catalysis variables*

The speed of a heterogeneous catalysis reaction generally depends on three categories of variables:

- the concentrations or partial pressures of reactants and/or products formed;
- the temperature;
- the variables related to the catalyst, its nature and the actual area in contact with the gas.

### 2.6.2.2. *The mechanism of catalysis and the catalytic act*

Heterogeneous catalysis causes a reaction to take place at the surface of a solid through to the adsorption phenomenon.

The full mechanism of heterogeneous catalysis involves five steps:

- diffusions of reactants in the products toward the surface of the catalyst. The reactants are consumed at the catalyst's surface, resulting in a partial pressure gradient between the gas phase (away from the catalyst) and the catalyst's surface. This gradient is the cause of movement of the gas molecules towards the catalyst, which is called a diffusion;
- adsorption of the reactants on the catalyst surface;
- the catalytic act, which is the chemical reaction itself that also occurs at the catalyst's surface;
- desorption of the gases produced at the catalyst's surface;
- interdiffusions of gases produced at the catalyst's surface toward the volume of gas and away from the solid. In the same way as for the reagents, but in reverse, the reaction creates a partial pressure gradient of the products that are produced at the catalyst's surface, which leads to diffusion of these products from the surface.

The catalytic act, which is the purely chemical part of heterogeneous catalysis, can occur according to two mechanisms:

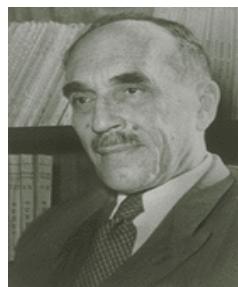
- the Langmuir–Hinshelwood mechanism in which the catalytic act is a reaction between two adsorbed molecules;
- the Rideal–Elsey mechanism in which the catalytic act is a reaction between an adsorbed molecule and a molecule in the gaseous phase.

### 2.7. Important figures in reaction mechanisms

The men whose work has led to our current understanding of reaction mechanisms and who have been awarded the Nobel prize for chemistry are shown in Figure 2.8.



**Sir Cyril Norman  
Hinshelwood**  
(1897-1967)  
Nobel prize for chemistry  
in 1956



**Nikolai Semenov**  
(1896-1986)  
Nobel prize for chemistry  
in 1956



**Irving Langmuir**  
(1881-1957)  
Nobel prize for  
chemistry in 1932

**Figure 2.8. Important chemists**



## Chapter 3

# Kinetic Properties of Elementary Reactions

The science of kinetics is useful for determining mechanisms. The latter justifies the importance given to the kinetic properties of elementary reactions. Indeed, the basic verification of a mechanism will be its resolution, which consists of deducing the kinetic properties of the overall reaction from the kinetic properties of elementary steps, in order to compare them with those provided by the experiment.

### 3.1. Space function of an elementary reaction

Each elementary step occurs in a single zone. In fact, if it involves two zones, then one part of the reaction will occur in one zone and the second part in the other. In this case, the reaction would no longer be elementary since it would occur in two steps and at least one intermediate species would be formed between both steps.

In an elementary reaction, which occurs in a single zone, the *space function of this elementary step* is the ratio of the volume (or area) of the reaction zone to the reference amount chosen to define the fractional extent:

$$E = \frac{V}{n_0} \quad \text{or} \quad \frac{V}{\{A_1\}_0} \quad \text{or} \quad \frac{S}{n_0} \quad \text{or} \quad \frac{S}{\{A_1\}_0} \quad [3.1]$$

The space function is expressed in m<sup>3</sup> per mole or m<sup>2</sup> per mole. The notion of space function is not defined for a non-elementary reaction.

### 3.2. Reactivity and rate of an elementary step

From relations [1.11] and [1.19] we deduce the following relation for a reaction involving a single zone:

$$r = \frac{v \cdot V}{\{A_1\}_0} \quad [3.2]$$

The *reactivity*  $\phi$  (or *chemical flux*<sup>1</sup> according to Lafitte and Rouquerol) of an *elementary step* is its specific speed. Therefore by using equation [3.1], we obtain the following fundamental relationship:

$$r = \phi \cdot E \quad [3.3]$$

The rate of an elementary reaction (with a single zone) is the product of its reactivity by its space function<sup>2</sup>. This relation is always true, whether we are dealing with a volume zone or a surface zone.

The reactivity is expressed in moles per second per m<sup>3</sup> (m<sup>2</sup>).

In the general case, both properties  $\phi$  and  $E$  are functions of different parameters affecting the speed (temperature, concentrations, partial pressures, pressure, the zone's sizes, amounts of substances, etc.) and fractional extent, and thus time.

NOTE 3.1.– The need to have a different name for the specific speed of an elementary step emerges because this reactivity has a property that the specific speed of a reaction usually does not have. For instance, if the reaction volume of an elementary step is doubled, then its rate is also doubled; this is not always the case for a non-elementary reaction. In order to illustrate this, let us reconsider the example of our catalytic reaction in Figure 1.1b and double the reactor's volume. The reaction speed has no reason to be multiplied by two. So then let us double the area of the catalyst. If gas diffusion towards the catalyst occurs, multiplying the area of the catalyst by two will not double its speed, thereby the overall speed is not doubled. Later we shall see other properties that distinguish the reactivity of an elementary step from a simple specific speed of any kind of reaction.

<sup>1</sup> We do not retain this term because, as discussed in section 3.7.4, it can be confused with the flux used in diffusion.

<sup>2</sup> The analogy between this relationship and Ohm's law, which gives the electrical resistance of a wire as the product of its resistivity by a geometric function  $l/s : R = \rho l/s$ , should be noticed. The vocabulary used for the "reactivity" stems from the term "resistivity" in this analogy.

### 3.3. Kinetic constants of an elementary step

#### 3.3.1. Expression of reactivity as a function of concentrations

An elementary reaction is a reaction that takes place in a single step in which the reactants react directly with each other. It does not involve any intermediate species.

An elementary reaction between two species,  $A_1$  and  $A_2$ , will be written as follows:



REMINDER.– The arrow (different from the = sign encountered in the writing of a reaction) means that we are dealing with an elementary reaction.

We have no right to modify the stoichiometric numbers (for example, divided each of them by  $\beta_1$ ) as can usually be done in the writing of a reaction because the writing of an elementary step reflects the mechanistic reality. This is the concomitant attack of  $\beta_1$  molecules of  $A_1$  by  $\beta_2$  molecules of  $A_2$ .

The reactivity of an elementary thermal reaction at a given temperature, such as [3.R1], obeys van 't Hoff's law and is written:

$$\phi = k[A_1]^{\beta_1} [A_2]^{\beta_2} \quad [3.4]$$

The quantity  $k$ , which does not depend on the concentrations of reactants or products, is called the rate coefficient (or rate constant). This is less stringent because this “constant” varies with temperature.  $\beta_1$  and  $\beta_2$  are the *partial orders* with respect to  $A_1$  and  $A_2$  respectively. The sum  $\beta = \beta_1 + \beta_2$  is called the *total order* of the reaction.

It should be noted that the unit of the rate coefficient depends on the total order of the reaction.

This expression involves only the concentrations of reactants.

Expression [3.4] does not include condensed reactants that would be pure in their phase (essentially pure solids) because their concentration is constant and equal to the ratio of their molar mass to their molar volume.

This expression rarely includes the components that would be present in very large amounts, as the variation in their concentration would be insignificant. This

concentration is in fact included in coefficient  $k$ , which becomes a “pseudo-coefficient” rate:

- if  $\beta = 1$  then the reaction is known as monomolecular (for example  $A_2$  does not exist);
- if  $\beta = 2$ , then the reaction is known as bimolecular;
- if  $\beta = 3$ , then the reaction is known as trimolecular.

NOTE 3.2.– When a reactant is in gaseous form, its concentration will be replaced by its partial pressure. For ideal gases, it is expressed as follows:

$$P_i = [A_i]RT \quad [3.5]$$

Therefore, the rate coefficient defined from the partial pressures contains a term that is inversely proportional to the temperature, whose influence is also negligible.

NOTE 3.3.– The fundamental difference here appears between the reactivity of an elementary step and the specific speed of a non-elementary reaction for which there is no reason *a priori* that it obeys relation [3.4]. We will actually find numerous cases where this relation is not applicable.

### 3.3.2. Rate factor of an elementary reaction

In an elementary reaction belonging to a given mechanism and involving reaction intermediates, the *rate factor* is the product of the rate coefficient plus the concentrations of the principal components (reactants or products) involved in this elementary step raised to the power of partial orders.

In order to illustrate this definition, let us reconsider step [2.R1b] of the water synthesis reaction. The reactivity of this step is:

$$\phi = k_2[OH][H_2] = f_2[OH] \text{ with } f_2 = k_2[H_2]$$

where  $f_2$  is the rate factor of this step that involves the reactant  $H_2$ .

The unit of a rate factor depends on the elementary reaction, like a rate coefficient.

NOTE 3.4.– The rate factors of a reaction carried out at constant concentrations are independent of time.

### 3.4. Opposite elementary reactions

If an elementary reaction is possible in one direction then it is also theoretically possible in the opposite direction. The reverse reaction is often negligible, but in many cases this is not true and we have to take into account the rates of both opposing reactions.

#### 3.4.1. Reactivity of two opposite elementary reactions

If the opposite reaction to [3.R1] occurs, it will be written as:



where the reactivity of the reaction from left to right is:

$$\phi' = k' [A_1]^{\beta_1} [A_2]^{\beta_2} \quad [3.6]$$

and the reactivity of the reaction from right to left:

$$\phi'' = k'' [A'_1]^{\beta'_1} [A'_2]^{\beta'_2} \quad [3.7]$$

The volumetric speed, which is the difference in the reactivities of both opposite reactions, is also called reactivity. Since it is obvious that the reactions take place in the same area, the global reactivity is:

$$\phi = \phi' - \phi'' = k' [A_1]^{\beta_1} [A_2]^{\beta_2} - k'' [A'_1]^{\beta'_1} [A'_2]^{\beta'_2} \quad [3.8]$$

which can be written as:

$$\phi = k' [A_1]^{\beta_1} [A_2]^{\beta_2} \left[ 1 - \frac{k'' [A'_1]^{\beta'_1} [A'_2]^{\beta'_2}}{k' [A_1]^{\beta_1} [A_2]^{\beta_2}} \right] \quad [3.9]$$

We will make the following assumption, which is generally implicitly accepted.

**ASSUMPTION.–** The rate coefficient of an elementary step is the same at equilibrium as in a non-equilibrium situation at the same temperature.

At thermodynamic equilibrium, the overall rate is zero. From this comes the relation between the values of the concentrations taken at equilibrium:

$$\left( \frac{[A'_1]^{\beta'_1} [A'_2]^{\beta'_2}}{[A_1]^{\beta_1} [A_2]^{\beta_2}} \right)_{\text{equil}} = \frac{k'}{k''} = K \quad [3.10]$$

where  $K$  is the equilibrium constant at the temperature considered. Thus the reactivity becomes:

$$\phi = k' [A_1]^{\beta_1} [A_2]^{\beta_2} \left[ 1 - \frac{[A'_1]^{\beta'_1} [A'_2]^{\beta'_2}}{K [A_1]^{\beta_1} [A_2]^{\beta_2}} \right] \quad [3.11]$$

### 3.4.2. Distance from equilibrium conditions

According to thermodynamics, the Gibbs free energy variation combined with the reaction is:

$$\Delta G = -RT \ln K + RT \ln \frac{[A'_1]^{\beta'_1} [A'_2]^{\beta'_2}}{[A_1]^{\beta_1} [A_2]^{\beta_2}} \quad [3.12]$$

The reactivity becomes:

$$\phi = k' [A_1]^{\beta_1} [A_2]^{\beta_2} \left\{ 1 - \exp \frac{\Delta G}{RT} \right\} \quad [3.13]$$

The quantity  $\epsilon$ , defined by [3.14] represents the distance between the equilibrium conditions and the experimental conditions chosen to carry out reaction [3.R2]:

$$\epsilon = 1 - \exp \frac{\Delta G}{RT} \quad [3.14]$$

NOTE 3.5.– Expression [3.13], which involves the affinity  $\aleph$  of the reaction (as defined by De Donder) instead of Gibbs free energy, is often written as:

$$\phi = k' [A_1]^{\beta_1} [A_2]^{\beta_2} \left\{ 1 - \exp \frac{-\aleph}{RT} \right\} \quad [3.15]$$

NOTE 3.6.– When the experimental conditions are a long way from equilibrium (for example in the case of the continuing absence of products being formed) the

exponential term is negligible compared to one and the reactivity takes the form in [3.4].

### 3.4.3. Principle of partial equilibria

During the study of the setting of reaction speeds with several steps, we will use the following principle.

PRINCIPLE.– When a system is in equilibrium all the elementary steps are at equilibrium.

As a direct consequence of this principle, when a system is a long way from equilibrium at least one of its steps is far from equilibrium.

## 3.5. Influence of temperature on the reactivities of elementary steps

The rate coefficient  $k$  of an elementary reaction obeys Arrhenius' law, which is written as:

$$k = A \exp - \frac{E_a}{R T} \quad [3.16]$$

where  $E_a$  is called the activation energy and is a positive quantity.  $A$  is called the pre-exponential term (the term frequency factor, which is often encountered, should be banned because the coefficient rate is expressed in  $s^{-1}$  only in first order reactions). In all strictness, it appears that  $A$  is not completely independent of temperature (this is obvious if we replace the concentrations with the partial pressures) but this variation is negligible compared to the exponential variation. Moreover, measurements are often performed in narrow temperature ranges in order to avoid reactions that are either too slow or too fast.

Arrhenius' law is often encountered in its differential form:

$$\frac{d \ln k}{d(1/T)} = - \frac{E_a}{R} \quad [3.17]$$

Given its definition (see section 3.3.2), with constant concentrations it is obvious that a rate obeys Arrhenius' law with temperature.

### 3.5.1. Influence of temperature near the equilibrium

Let us reconsider equation [3.13]. At constant concentrations, only the rate coefficient  $k'$  and Gibbs free energy vary with temperature by following Arrhenius' law for the former. The reactivity can therefore be written as:

$$\frac{\phi}{1 - \exp - \frac{\Delta G}{RT}} = A[A_1]^{\beta_1}[A_2]^{\beta_2} \exp - \frac{E_a}{RT} \quad [3.18]$$

Thus, near the equilibrium, it is no longer the reactivity but the ratio  $\frac{\phi}{1 - \exp - \frac{\Delta G}{RT}}$  that follows Arrhenius' law.

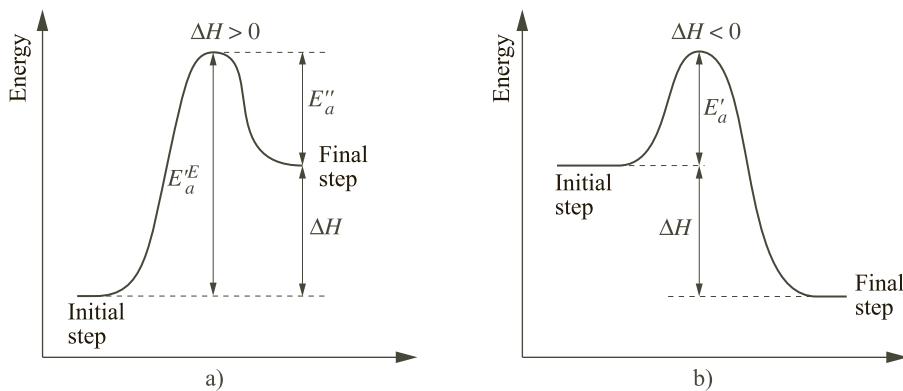
### 3.5.2. Activation energies of opposite elementary reactions and reaction enthalpy

The application of Arrhenius' law to the rate coefficients,  $k'$  and  $k''$ , of two opposite elementary reactions leads to the definition of two activation energies,  $E_a$  and  $E'_a$ . We will see in this chapter (see section 3.6) and Chapter 10 (section 10.2.7) on the modeling of elementary steps that the physical meaning of activation energy is the energy that the reaction system must exceed in order to react. This energy appears in Figure 3.1a, by plotting the energy of the system made up of the whole of the atoms involved in the elementary reaction as a function of the reaction path which represents in fact the various relative positions of these atoms during the reaction. The system starts from an initial state in which the reactants of the step are infinitely distant from each other (without interaction) and reaches a final state in which the products formed are infinitely distant from each other (without interaction). Each intermediate abscissa is a relative position of the atoms included in all the reactants (and the products). We see that a change in the spatial distribution of atoms is followed by an energetic modification. The activation energy is thus the height of the barrier appearing in the energy diagram.

The difference in energy between the initial and final states is the reaction enthalpy. If the reaction is endothermic (see Figure 3.1a), the final level is higher than the initial level ( $\Delta H > 0$ ). For an exothermic reaction (see Figure 3.1b), the final level is lower than the initial level ( $\Delta H < 0$ ).

From the diagram, we can deduce that the difference between the activation energies of the direct reaction and the reverse reaction is equal to the enthalpy of the reaction:

$$E'_a - E''_a = \Delta H \quad [3.19]$$



**Figure 3.1.** Activation energies of elementary reactions:  
a) endothermic; and b) exothermic reactions

The immediate consequences of Figures 3.1a and 3.1b are:

- an endothermic reaction has an activation energy that is at least equal to the enthalpy of the reaction;
- an exothermic reaction can have a null activation energy;
- a negative activation energy is inconceivable because it would mean that the state corresponding to this energy would be more stable than the initial state, which would therefore not exist.

NOTE 3.7.– Everything we have just discussed concerning opposite reactions and the energy diagram in Figure 3.1 applies to elementary reactions alone. Any use, especially the interpretation of a so-called activation energy for non-elementary steps, is the result of a fast extrapolation without any foundation.

### 3.6. Modeling of a gas phase elementary step

After decomposition into elementary steps reaction, it is necessary to understand how this elementary step occurs. We will examine this issue in the case of a gas

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phase reaction that allows a more simple approach to the medium. More developments will be studied in Chapters 10 and 11.

### 3.6.1. Collision theory

The relationship between the molecularity of a reaction and the number of molecules that must collide simultaneously during the elementary act is the basic idea of the modeling of elementary steps. Bimolecular reactions are by far the most frequent. Sometimes the collision happens between identical species  $A_1$  and  $A_2$ , that is to say two molecules of the same compound. Trimolecular reactions are extremely rare because they involve the simultaneous collision of three molecules, which is an exceptional phenomenon in a gaseous or liquid mixture with or without solid particles. Reactions of an order equal or greater than four are excluded because the probability of four or more molecules colliding in a single impact is null.

The first model is therefore devoted to bimolecular reactions and describes the reaction as being due to the mechanical impact between two molecules.

#### 3.6.1.1. Bimolecular reactions

Trautz and Mac Lewis developed collision theory in 1917 independently of one another and simultaneously.

In order that  $A$  molecules react with  $B$  molecules, the authors suggested it was essential that a molecule of  $A$  collides with a molecule of  $B$ . If this hypothesis is correct, then the speed of reaction will be proportional to the frequency of impacts.

In the case of gases, the kinetic theory of gases enables us to calculate the number of impacts per second (equation [3.20]) in a medium containing  $n_A$  molecules of  $A$  and  $n_B$  molecules of  $B$  per  $\text{cm}^3$ . Since the values of diameters  $\sigma_A$  and  $\sigma_B$  of the assumed spherical molecules and the molecular masses  $M_A$  and  $M_B$  are:

$$Z_0 = n_A n_B \pi (\sigma_A + \sigma_B)^2 \sqrt{\frac{8RT}{\pi} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)} \quad [3.20]$$

the volumetric speed will be obtained by:

$$v = -\frac{d[A]}{dt} = \frac{Z_0}{1000 N_a} \text{ mole.l}^{-1}\text{s}^{-1} \quad [3.21]$$

By performing the numerical calculations, we realize that the reactions should almost all be almost instantaneous. Moreover, expression [3.21] shows that these speeds should vary as the square root of temperature.

The authors therefore suggested that the impacts might not all be effective and only those involving enough energy are effective. However, Boltzmann has enabled us to establish that, among all the impacts, the number that involve energy greater than value,  $E$ , is obtained by:

$$Z = Z_0 \exp\left(-\frac{E}{RT}\right) \quad [3.22]$$

hence the new expression of the speed:

$$v = -\frac{d[A]}{dt} = \frac{Z_0}{1000N_a} \exp\left(-\frac{E}{RT}\right) = k_0[A][B] \exp\left(-\frac{E}{RT}\right) \quad [3.23]$$

The energy,  $E$ , is not calculable but will be determined experimentally, because we calculate:

$$k = \frac{Z_0}{1,000N_a[A][B]} \exp\left(-\frac{E}{RT}\right) = k_0 \exp\left(-\frac{E}{RT}\right) \quad [3.24]$$

It is now appropriate to ensure that the values of  $k_0$  that we have calculated are consistent with the experimental values. Table 3.1 provides some examples of values for the ratio  $f$  of the experimental value to the calculated value.

Reaction	$f = \frac{k_0(\text{experimental})}{k_0(\text{computed})}$
$2 \text{IH} \rightarrow \text{I}_2 + \text{H}_2$	1.2
$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$	$7.5 \times 10^{-2}$
$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{CO}_2\text{Na} + \text{C}_2\text{H}_5\text{OH}$	$2 \times 10^{-5}$
$\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$	$5 \times 10^{-2}$

**Table 3.1.** Steric factor of a few elementary reactions

It will be observed that the more the initial molecules deviate geometrically from the sphere and the more complicated they are, the more the ratio  $f$  deviates from one. This is the reason that coefficient  $f$  is designated a steric factor. In fact the  $\text{IH}$  molecule is roughly a sphere with only a small excrescence due to the hydrogen atom. In contrast, the ethyl acetate molecule is a practically linear chain.

The speed given by collision theory should therefore be corrected by a steric factor. In other words, in order to be effective the impact should not only be enough energetic but it must also occur in specific parts of the molecules.

Finally, the big drawback is that this collision theory does not enable us to calculate this steric factor or the energy,  $E$ . Thus, we are unable to definitively calculate the elementary speed of the reactions *a priori*.

### 3.6.2. Theory of activated complex

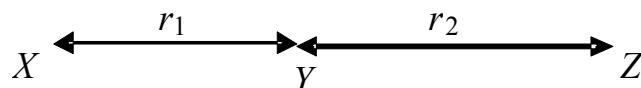
Following collision theory, a model of the bimolecular reaction, called the theory of activated complexes or the theory of absolute speeds, was established in 1938 by Eyring and Polanyi respectively.

This theory is based on the following reflection. Collision theory describes a physical impact using classical mechanics. At the scale of the impact between two molecules, classical mechanics fails and so this is replaced by quantum mechanics. In the latter, the molecules are no longer rigid, which leads to the replacement of the “mechanical impact” by an “energetic impact”, which is an interaction between the atoms of two molecules.

To introduce the elements of this theory, we will reason on the reaction between an atom  $X$  and a diatomic molecule  $YZ$ , such as:

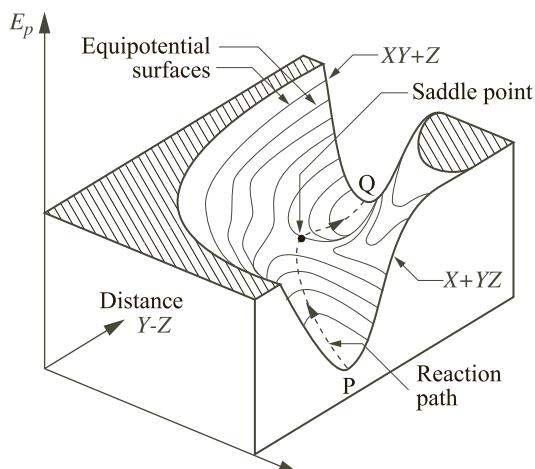


The theory calculates the potential energy of all three atoms by considering all possible configurations. We show that the minimum energy configurations are the three collinear atoms. We therefore retain this disposition and each configuration is then defined by the distances  $r_1$ , between atoms of  $X$  and  $Y$ , and  $r_2$  between atoms  $Y$  and  $Z$  (see Figure 3.2).



**Figure 3.2. Minimum energy configuration**

This can be plotted in the space potential energy surfaces as a function of both configuration variables by using the calculated energies (see Figure 3.3).



**Figure 3.3.** Equipotential surfaces and reaction path

We observe that these surfaces clearly show two valleys separated by pass, called the saddle point, and assume that the potential energy will always be minimal. We deduce that during the reaction, the system follows these two valleys. Thus, starting from point *P* (far *X*) we follow the first valley, then we pass through the saddle point – which is characterized by its two distances – and we follow the second valley to reach point *Q*, where atom *Z* is separated from molecule *XY*.

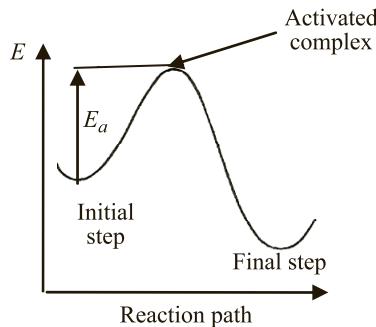
The top of the saddle point is called the activated complex, which will be denoted  $(XYZ)^{\ddagger}$  (hence one of the names of the theory).

The path followed by the system is called the reaction path and is plotted on the abscissa in Figure 3.4. The potential energy is plotted on the ordinate.

We can then identify the energy of the saddle point that is represented by the height of the top of the barrier. The calculation of activation energy is thus possible using this theory.

The theory also enables us to establish an expression of speed from the crossing speed at the top of the saddle point. Relation [3.31] is obtained where  $k_B$  is Boltzmann's constant ( $1.38 \times 10^{-23} \text{ J.K}^{-1}$ ) and  $h$  is Planck's constant ( $6.62 \times 10^{-34} \text{ J.s}$ ):

$$v = \frac{k_B T}{h} F \cdot [A][B] \exp\left(-\frac{E}{RT}\right) \quad [3.25]$$



**Figure 3.4.** Reaction path and activation energy

There is a factor  $F$  in this expression that is related to the various forms of molecule energy (translation, rotation, vibration). This can be calculated through statistical thermodynamics. Thus it is *a priori* possible to calculate the speed, hence the second name of this theory. We will see how to calculate this speed in Chapters 10 and 11.

The results are now in satisfactory agreement with the speeds measured.

### 3.6.2.1. Monomolecular reactions

Monomolecular reactions are mainly related to decomposition reactions such as:



If this scheme was valid, there would theoretically be no need for collision between molecules because each molecule would spontaneously break down, which is not the case. Lindemann was the first to consider a bimolecular scheme, by introducing an initial activation step of the molecule that consists of its collision with another molecule:



Then the activated molecule can choose between two behaviors:

- simple deactivation by collision with another molecule:



– the possibility of decomposing:



The speed is therefore proportional to the concentration of the activated molecules:

$$v = k_3[R^*] \quad [3.26]$$

With some approximations (see Chapter 10), Lindeman expressed the concentration of the activated molecules as:

$$[R^*] = \frac{k_1[R]^2}{k_2[R] + k_3} \quad [3.27]$$

and by using [3.26], the speed becomes:

$$v = \frac{k_1 k_3 [R]^2}{k_2 [R] + k_3} \quad [3.28]$$

where  $k_1$ ,  $k_2$  and  $k_3$  are the rate coefficients of steps [3.R4a], [3.R4n] and [3.R4c], respectively.

From relation [3.28], if we stay under high pressure from  $R$  the concentration of  $R$  becomes significant and we will obtain:

$$k_2[R] \gg k_3 \quad [3.29]$$

In other words, deactivation [3.R4b] is much more likely to occur than decomposition [3.R4c], and then:

$$v = \frac{k_1 k_3 [R]}{k_2} \quad [3.30]$$

The reaction becomes of first order.

In the opposite case, decomposition is most likely under low pressures, and a second order expression should be obtained:

$$v = k_1[R]^2 \quad [3.31]$$

Indeed, for a monomolecular reaction, when we plot the speed with pressure after an experiment we find a second order reaction under low pressures.

### 3.7. A particular elementary step: diffusion

An extremely important phenomenon that occurs in kinetics is the transport of species from one point to another in the reactor. This is called *diffusion*. It is mainly seen during the study of heterogeneous reactions with several zones.

#### 3.7.1. The diffusion phenomenon

Diffusion is a natural phenomenon of species motion that is due to the existence of a concentration gradient of the species. The motion occurs to counteract this gradient, i.e. to balance the concentrations and lead towards equilibrium. The motion occurs therefore in the direction of decreasing concentrations.

Diffusion can be represented by a chemical equation like a chemical reaction with unit stoichiometric coefficients, provided that the components located at the starting point of diffusion are considered distinct from those at the end of the diffusion path.

#### 3.7.2. Diffusion flux and Fick's first law

Diffusion is characterized by its *flux*, which gives the amount of a component that passes through a unit area that is perpendicular to the diffusive direction per time unit. It can be seen that diffusion has the same units as a surface-specific speed.

Fick postulated that for a component, *A*, this flux varies with the concentration gradient along a direction Ox according to a law, known as Fick's first law, with the following proportionality:

$$J = -D \frac{\partial [A]}{\partial x} \quad [3.32]$$

In the case of diffusion in all directions in space, this law can be generalized as:

$$J = -D \overrightarrow{\text{grad}[A]} \quad [3.33]$$

In these expressions, *D* is the *diffusion coefficient* and is independent of concentrations.

The diffusion coefficient is expressed in  $\text{m}^2\text{s}^{-1}$ .

### 3.7.2.1. Mass balance of the diffusing species and Fick's second law

The concentration of the diffusing component is obtained at time  $t$  and a point in space, by the solution of the second order differential equation with partial derivatives (the symbol  $\Delta[A]$  denotes the Laplacian of the concentration), see section 6.3.4:

$$\frac{\partial[A]}{\partial t} = D\Delta[A] \quad [3.34]$$

For diffusion in a single direction  $Ox$ , the Laplacian expression leads to the following relation:

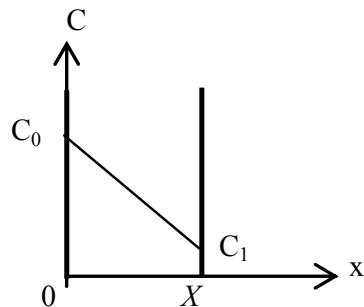
$$\frac{\partial[A]}{\partial t} = D \frac{\partial^2 [A]}{\partial x^2} \quad [3.35]$$

### 3.7.3. Diffusion flux in a steady state system

A particularly simple solution to Fick's second law is the set of steady state solutions that assume the concentration is independent of time at each point.

Let us then consider a plate of thickness  $X$ , whose other dimensions are very large compared to  $X$  in order to avoid any edge effect.

A species diffuses through this plate under the action of a concentration gradient imposed by the values of concentrations at both ends that are held constant (see Figure 3.5).



**Figure 3.5.** Diffusion through a plate of thickness  $x$

According to [3.35], we write the steady state in Fick's law as:

$$\frac{d^2[A]}{dx^2} = 0 \quad [3.36]$$

with the conditions:

$$\text{for } t > 0 \begin{cases} \text{if } x = 0, [A] = [A]_0 \\ \text{if } x = X, [A] = [A]_l \end{cases}$$

hence the solution:

$$[A] = \frac{[A]_l - [A]_0}{X} x + [A]_0 \quad [3.37]$$

Thus the concentration gradient is constant and therefore also the flux. From [3.32], the flux's value can be obtained:

$$|J| = D \frac{|[A]_0 - [A]_l|}{X} \quad [3.38]$$

### 3.7.4. Reactivity and diffusion space function

Here we should ask ourselves the following important question: is diffusion an elementary process?

If we examine the solution of the flux in equation [3.38], we find a specific law of speed that is proportional to the difference between concentrations at the start and arrival of diffusion. This is consistent with an expected first order law of the chemical equation that we have written as:



Furthermore, constant  $D$  obeys Arrhenius' law like the rate coefficient of an elementary reaction.

The expression of the flux, however, reveals another term that called the diffusion factor,  $G$ :

$$G = \frac{l_0}{X} \quad [3.39]$$

This term does not appear in the specific speed equation of an elementary reaction. The answer to our question is therefore that diffusion is not an elementary step.

More formally, we will introduce a reactivity and a space function that will give an elementary step character to the diffusion.

For steady state (or close to steady state) diffusion, we can provide an expression for the absolute speed, which is the flow rate:

$$\frac{d\xi}{dt} = |J| S \quad [3.40]$$

This flow, which acts as an areal speed, not only depends on intensive variables but also contains factor  $G$ , which is a geometric term. In order to separate both contributions, the flux can be written as:

$$|J| = \phi |G| \quad [3.41]$$

The function  $\phi$  is the diffusion reactivity. It has the same dimensions as surface reaction reactivity and is obtained through:

$$\phi = \frac{D |[A]_i - [A]_e|}{l_0} \quad [3.42]$$

We arbitrarily choose  $l_0 = 1$  meter. Hence according to [3.40]:

$$\frac{d\xi}{dt} = \phi G S \quad [3.43]$$

The following function  $E$  ( $l_0 = 1$  m) can therefore be called the diffusion space function:

$$E = \frac{GS}{[A]_0} = \frac{S}{X[A]_0} \quad [3.44]$$

NOTE 3.8.— If diffusion is far from equilibrium (which leads to a very high concentration gradient for diffusion), the concentration at the end of the diffusion path is insignificant compared to that at the starting point. The reactivity can then be written as:

$$\phi = D[A]_i \quad [3.45]$$

Reactivity  $\phi$  therefore only depends on intensive properties (temperature via  $D$  and concentrations at the ends of the diffusion zone).

It is expressed in  $\text{m}^2$  per mole, like the reactivity of a surface elementary reaction.

From this and by using relation [3.3], it can be seen that the rate will always have the following form – whether we are measuring an elementary chemical reaction or diffusion (close to steady state):

$$r = \frac{d\alpha}{dt} = \phi E \quad [3.46]$$

### 3.7.5. Diffusion in solids

Diffusion in solids is performed through the jump from a point defect (see Annex 1) of one site to an equivalent site. Thus, we distinguish interstitial diffusion and vacancy diffusion. This jump is activated and the start and host sites are energetically equivalent, as shown in Figure 3.6, which gives the energy of the system during a jump. The enthalpy of diffusion is therefore null, and the diffusion coefficient obeys Arrhenius' law with diffusion activation energy according to:

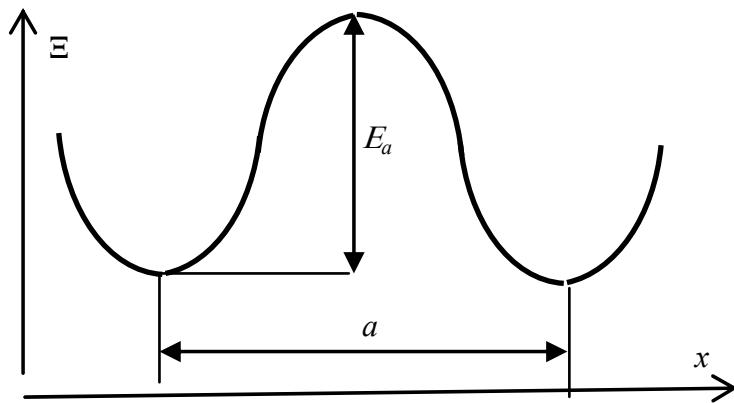
$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \quad [3.47]$$

The magnitude of the diffusion coefficient is  $10^{-12} \text{ m}^2\text{s}^{-1}$  and the magnitude of the diffusion activation energy is  $\sim 100 \text{ KJ}$  per mole.

If  $a$  is the distance between two host sites of the diffusing particles and  $k_B$  and  $h$  are Boltzmann's constant and Planck's constant, respectively, it is shown that the pre-exponential term of the diffusion coefficient obeys the relation:

$$D = \frac{a^2 k_B T}{2h} \exp\left(-\frac{E_D}{RT}\right) \quad [3.48]$$

The laws established in solid medium also are valid in liquid medium for dilute solutions and the magnitude of diffusion coefficients in liquids is  $10^{-9} \text{ m}^2\text{s}^{-1}$ .



**Figure 3.6.** Diffusion jump in a solid

### 3.7.6. Interdiffusion of gases

The interdiffusion coefficient of two gases 1 and 2, one inside the other, is obtained at temperature  $T$  and under total pressure  $P$  through the kinetic theory of gases by the following expression:

$$D = \frac{2P}{3(\sigma_1 + \sigma_2)} \left( \frac{2T}{\pi} \right)^{3/2} \sqrt{k_B \frac{M_1 + M_2}{M_1 M_2}} = \frac{\lambda_0 \bar{c}}{3P} \quad [3.49]$$

In this expression:

- $\sigma_1$  and  $\sigma_2$  are the radii of gas molecules 1 and 2;
- $M_1$  and  $M_2$  are their molar masses;
- $k_B$  is Boltzmann's constant;
- $\lambda_0$  is the mean free path under the unit pressure; and
- $\bar{c}$  is the average speed of molecule movement.

It should be noted that diffusion in gases is not activated (there is no Arrhenius law) and it varies like  $T^{3/2}$  and is inversely proportional to pressure.

The magnitude of the interdiffusion coefficients of gases is  $10^{-4} \text{ m}^2 \text{s}^{-1}$ .

### 3.7.7. Diffusion of a gas in a cylindrical pore

We consider cylindrical pores with average radius,  $\bar{r}$ . Depending on the gas pressure domain and the pore's radius, there are two types of regimes.

If the pressure is such that the pore radii are comparable or larger than the mean free path of molecules, we say that we have a *molecular regime*. The diffusion coefficient can then be calculated through Gilliland's equation by using the gas molecular mass  $M$  and its molar volume  $V_m$ :

$$D = 4.3 \times 10^{-7} \frac{MT^{3/2}}{PV_m^{2/3}} \quad [3.50]$$

If the pressure is such that the pore radii are small compared to the mean free path of molecules (pore diameter  $< 500 \mu\text{m}$  under atmospheric pressure), we say that we have a *Knudsen regime*. The diffusion coefficient can then be calculated by:

$$D = \frac{2\bar{r}^3}{3} \sqrt{\frac{8k_B T}{\pi m}} = 9 \times 10^{-7} \bar{r} \sqrt{\frac{T}{M}} \text{ m}^2\text{s}^{-1} \quad [3.51]$$

## 3.8. Gases adsorption onto solids

Each time a gas is close to a solid, it binds to the surface of this solid: this is the adsorption phenomenon. More precisely, there are two types of adsorption:

– *Physical adsorption* (or *physisorption*), which is especially visible at low temperatures. Here the bond between the gas molecule and the solid surface has energy of the same magnitude as the Van der Waals energy between molecules. This physical adsorption is mainly used to determine the specific area of solids (solid area per gram of solid) and the porosity of the solid (shape and pores' dimensions). Physisorption is not a temperature-activated phenomenon.

– *Chemical adsorption* (or *chemisorption*), which is especially sensitive to high temperatures, in which the binding energies between the molecule (or atoms) and the surface are of the same order of magnitude as the energy of chemical bonds. Chemisorption is an important phenomenon in all reactions bringing together a gas and a solid (heterogeneous catalysts, heterogeneous reactions, etc.). Chemisorption is a temperature-activated phenomenon.

### 3.8.1. Chemisorption equilibrium: Langmuir model

The Langmuir model is the basic model for chemisorption equilibria. It relies on a number of assumptions:

- a single monolayer of gas is formed on the surface of the solid, hence we have a saturation effect;
- there is a chemical reaction between the gas and the sites located on the solid's surface. These sites are usually denoted by  $s$  but are identified in the case where the solid is well known;
- in order to account for the properties of the adsorption equilibrium, which shows that the amount adsorbed depends on both gas pressure and temperature, we introduce the existence of a surface solution composed of unfilled sites  $s$  and sets  $G - s$  that identify the adsorbed molecule.

In these circumstances, we write the adsorption reaction as:



Given the assumption that species  $s$  and  $G - s$  are two components of the same "phase", the application of the law of mass action to balance the previous reaction is written as follows:

$$\frac{x}{P(1-x)} = K \quad [3.52]$$

where  $x$  denotes the molar fraction of the  $G - s$  occupied sites.

Let  $S_0$  be the total number of sites per unit area before adsorption and  $S$  the number of sites unfilled at a given time. The amount of  $G - s$  will then be  $S_0 - S$  and the fractional coverage will be defined by:

$$\theta = \frac{S_0 - S}{S_0} \quad [3.53]$$

The molar fractions of the two components of the solution will be:

$$1 - x = \frac{S}{S_0} = 1 - \theta \text{ and } x = \theta \quad [3.54]$$

At the adsorption equilibrium, the fractional coverage is  $\theta_\infty$  and equilibrium equation [3.52] becomes:

$$\frac{\theta_\infty}{P(1-\theta_\infty)} = K \text{ or } \theta_\infty = \frac{KP}{1+KP} \quad [3.55]$$

This equation is called the Langmuir isotherm.

Since  $K$  is an equilibrium constant, it obeys van 't Hoff's law with temperature:

$$K = K^0 \exp\left(-\frac{\Delta_a(H^0)}{R T}\right) \quad [3.56]$$

where  $\Delta_a(H^0)$  is the adsorption enthalpy which is negative since the adsorption is an exothermic phenomenon.

Given the variations of the equilibrium constant with temperature [3.61], the Langmuir equation is then written as:

$$\theta_\infty = \frac{K^0 P \exp\left(-\frac{\Delta_a(H^0)}{R T}\right)}{1 + K^0 P \exp\left(-\frac{\Delta_a(H^0)}{R T}\right)} \quad [3.57]$$

### 3.8.2. Dissociative adsorption and the Langmuir model

It is difficult to imagine how some molecules of stable and saturated gases ( $H_2$ ,  $O_2$ , etc.) could form a chemical bond with a surface atom of the solid. To explain this association, we were led to admit that adsorption is most often accompanied with dissociation of the gas molecule. This has been confirmed through experiments by comparing the adsorption of hydrogen, nitrogen, carbon monoxide and ethane on

nickel. We notice that the maximum amounts adsorbed are present in the following ratios:

$$\frac{\{H_2\}}{\{CO\}} = \frac{1}{2} ; \frac{\{N_2\}}{\{CO\}} = \frac{1}{2} \text{ and } \frac{\{C_2H_4\}}{\{CO\}} = \frac{1}{4}$$

We deduce that if we assume that the carbon monoxide (which has the possibility of binding) binds to the nickel without decomposing, the dihydrogen and dinitrogen molecules will be dissociated into two atoms and the ethane molecules into four clusters.

This dissociation has been verified by quantum computations of minimum energy path, such as during the adsorption of dihydrogen.

Therefore, let  $G_i$  be a gas of atomicity  $i$  that dissociates during adsorption according to:

$$G_i = iG \quad [3.R6]$$

The equilibrium binding will be written as:

$$\frac{1}{i}G_i + s = G - s \quad [3.R7]$$

The same reasoning as that of section 3.8.1 leads to:

$$\frac{\theta_\infty}{P^{1/i}(1 - \theta_\infty)} = K \quad [3.58]$$

This is the new Langmuir equation with gas dissociation during the adsorption.

It is possible that the different fragments of gas  $AB$  do not bind to the same sites. So, for instance, for a gas that dissociates into two entities,  $A$  and  $B$ , the equilibrium is written as follows:

$$AB + s_A + s_B = A - s_A + B - s_B \quad [3.R8]$$

From the equilibrium we obtain:

$$\frac{\theta_A \theta_B}{P(1 - \theta_A)(1 - \theta_B)} = K \quad [3.59]$$

but the fractional coverages of both entities are identical, hence:

$$\frac{\theta_A^2}{P(1 - \theta_A)^2} = K \quad [3.60]$$

We obtain a new Langmuir isotherm for the dissociative adsorption of a molecule into two portions.

### 3.8.3. Chemisorption of gas mixtures in the Langmuir model

Let us consider the adsorption of a mixture of two gases, *A* and *B*, that takes place on the same surface. Two cases can occur:

- there are specific sites devoted to *A* and specific sites devoted to *B*, in which case both adsorption reactions are independent and the isotherm equations are given by relations [3.55] or [3.58]; or

- the adsorption sites of the solid are competitive with respect to *A* and *B*. In this case, let  $\theta_A$  and  $\theta_B$  be the surface fractions at equilibrium covered by *A* and *B*, respectively, and  $P_A$  and  $P_B$  be the partial pressures of both gases, respectively. The adsorption equilibria will be:



and:



The molar fractions of the species will be:

$$x_{A-s} = \theta_A, x_{B-s} = \theta_B \text{ and } x_s = 1 - \theta_A - \theta_B \quad [3.61]$$

Then by applying the law of mass action to both equilibria, the isotherms become:

$$\frac{\theta_A}{P_A(1 - \theta_A - \theta_B)} = K_A \text{ and } \frac{\theta_B}{P_B(1 - \theta_A - \theta_B)} = K_B \quad [3.62]$$

The fractional coverages can then be obtained:

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B} \text{ and } \theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B} \quad [3.63]$$

It is observed that the ratio of fractional coverage is proportional to the ratio of partial pressures:

$$\frac{\theta_A}{\theta_B} = \frac{K_A}{K_B} \cdot \frac{P_A}{P_B} \quad [3.64]$$

These results are easily generalized to the adsorption of more complex mixtures and it is shown that for gas *A*, belonging to a mixture, we have the following expression:

$$\theta_A = \frac{K_A P_A}{1 + \sum_j K_j P_j} \quad [3.65]$$

The sum is extended to all the gases present in the mixture whose adsorption takes place on the same sites as gas *A*.

NOTE 3.9.— If the gases are dissociated and the sites are competitive, by following the same approach with dissociating molecules of the preceding section, the partial pressures should be raised to the power of  $1/i_j$ ,  $i_j$  denoting the atomicity of the gas *j*.

### 3.8.4. Chemisorption kinetic in the Langmuir model

Chemisorption, which is a temperature-activated phenomenon, does not occur instantaneously and features some speed, like a chemical reaction.

We will stick to the assumptions that led to the Langmuir isotherms and consider the adsorption as an elementary step. We will consider the dissociative adsorption and distinguish two cases depending on whether the adsorption of both fragments of the molecule takes place on similar or different sites.

#### 3.8.4.1. Fixation of both fragments on similar sites

The adsorption reaction can be written as:



The speed per unit area will be expressed as:

$$v = \kappa' P (1 - \theta)^2 \exp\left(-\frac{E_a}{RT}\right) - \kappa'' P \theta^2 \exp\left(-\frac{E_d}{RT}\right) \quad [3.66]$$

or:

$$v = \kappa' P (1 - \theta)^2 \left(1 - \frac{\theta^2}{KP(1-\theta)^2}\right) \quad [3.67]$$

and:

$$\frac{d\theta}{dt} = 2v \quad [3.68]$$

NOTE 3.10.– We have no right to choose fractional stoichiometric coefficients because the fixation reaction is considered equivalent to an elementary step.

#### 3.8.4.2. Fixation of both fragments on different sites

In this case the equivalent reaction will be written as:



If  $\theta$  and  $\theta'$  denote the fractional coverage of both types of sites, respectively, the expression of speed becomes:

$$v = \kappa' P(1 - \theta)(1 - \theta') - \kappa'' \theta \theta' \quad [3.69]$$

but if we assume the same number of sites for both types on the bare surface:

$$\theta = \theta' \quad [3.70]$$

we obtain the same expression of speed as [3.69], but this time:

$$\frac{d\theta}{dt} = \frac{d\theta'}{dt} = v \quad [3.71]$$

### 3.9. Important figures in the kinetic properties of elementary reactions

The men whose work has led to our current understanding of the kinetic properties of elementary reactions and who have been awarded the Nobel prize for chemistry are shown in Figure 3.7.



**Jacobus van 't Hoff**  
(1852-1911)  
Nobel prize for chemistry in  
1909



**Svante August Arrhenius**  
(1859-1927)  
Nobel prize for chemistry  
in 1903



**Henry Eyring**  
(1901-1981)



**Michael Polanyi**  
(1899-1976)

**Figure 3.7. Important chemists**



## Chapter 4

# Kinetic Data Acquisition

In this chapter we will see some experimental techniques that are useful for monitoring the evolution of a system that is undergoing a reaction. The aim is to acquire a file of triplets representing the extent, speed and time of a reaction. Continuous measurements are used as much as possible to avoid having to update a variable several times. These data should be acquired for different values of the variables, which are the concentrations of different species, the temperature, and eventually the light intensity for photochemical reactions and the electric voltage for electrochemical reactions.

To these macroscopic basic measures we add the acquisition methods of other data that are related to modeling and we are able to provide additional information that helps to establish a mechanism.

### 4.1. Experimental kinetic data of a reaction

The experiment aims to derive a number of kinetic properties, such as the extent, fractional extent and speed (speed, specific speed or rate), which are not directly measurable. The results are grouped into two families:

- integral curves, which represent the extent or fractional extent in function of time or concentrations of components versus time in a closed environment;
- derivative curves, which represent a speed (absolute, volumetric or rate) as a function of time, fractional extent or concentrations of different species.

## 4.2. Generalities on measuring methods

A chemical transformation depends on temperature, concentrations and time. The measurements are therefore generally carried out at a constant temperature and at different times. There is no method by which to directly measure the kinetic properties of a reaction. The measurement methods are most often performed by the measurement of quantities that are related to the extent or fractional extent versus time, and we thus obtain the integral curves. The derivation of these data with respect to time leads to the rate of transformation at any time and then to the different derivative curves.

Kinetics measurements are generally carried out in difficult conditions because the experimenter has to meet extremely strict conditions:

- first, reactions take place over a large variety of time scales, ranging from substantially geological durations to durations of less than a nanosecond. We need some methods to perform measurements in the nano scale as well as some methods to perform measurements in the thousands-of-years scale;
- second, many reactions involve complex mixtures of species that might have very different concentrations and we want to be able to measure the individual concentrations and the variations of all these species;
- third, we want to carry out all these measurements without interfering with the reaction, hence the advantage of non-destructive physical measurements;
- fourth, we would ideally like to automate and computerize the measurement and new data acquisition techniques to enable modern treatment of the data.

We will distinguish two categories of methods: chemical methods and physical methods.

## 4.3. Chemical methods

Chemical methods are applicable to homogeneous reactions in gas or liquid phase. They consist of measuring a concentration at every known time interval. In general, these methods are discontinuous. The reaction mixture is placed in sealed vials that are kept at desired temperature by immersion in a thermostated bath. The vials are collected at known intervals. The reaction is stopped either through quench – by rapidly placing the vial in a cold bath – or through a chemical method – by emptying the vial into a suitable reagent, which leads to a fast reaction with one of the reactants. The difficulty is to be able to stop the reaction in order to analyze the vial. This approach applies to reactions that are not too fast because the time spent setting the temperature should be negligible, which is easier for gases.

For example, Bodenstein studied hydrogen iodide decomposition according to:



by placing several sealed vials that contained acid and are analyzed at different time intervals in the same chamber and by breaking them in a solution that contains excess sodium hydroxide with respect to the initial amount of acid. The iodine was then analysed through iodometry; while the sodium hydroxide remained through acidimetry; and the hydrogen volume was formed. These three results enable overlapping (see section 7.1.5.1). The fractional extent is obtained by using the following equations:

$$\alpha = \frac{[\text{I}_2]}{[\text{IH}]_0} \quad \alpha = \frac{\{\text{H}_2\}}{\{\text{IH}\}_0} \quad \alpha = \frac{[\text{IH}]_0 - [\text{IH}]}{2[\text{IH}]_0} \quad [4.1]$$

#### 4.4. Physical methods

Here, analyses are replaced by the continuous acquisition of a property provided by the method. We then need to know how to relate this quantity to the fractional extent or the rate of the reaction. There are two categories of methods:

- those that require the separation of a component; and
- those that apply directly to the reaction mixture.

##### 4.4.1. Methods without separation of components

###### 4.4.1.1. Manometric method

This method is used in the gas phase when there is a change in the number of moles of gas due to the reaction. The total pressure is measured in a closed gas chamber.

Let us reconsider the reaction described by chemical equation [1.R3].

We start from a stoichiometric mixture of reactants, which means we have  $\{\text{A}_1\}_0$  moles of component  $\text{A}_1$  and  $\frac{\beta_i \{\text{A}_1\}_0}{\beta_1}$  moles of each of the other reagents  $i$ , which leads to pressure  $P_0$ . It can be proven that if  $P$  is the pressure at time  $t$  and  $P_\infty$  the pressure reached when the reaction is complete, we have:

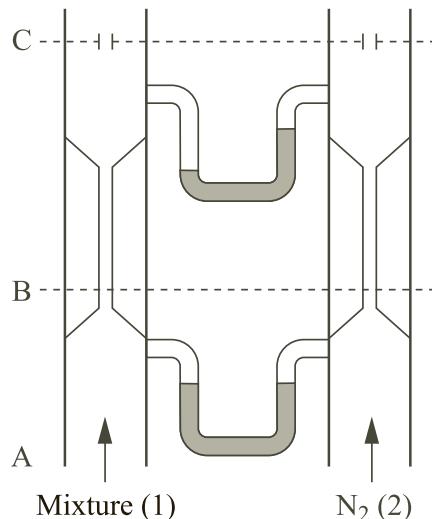
$$\alpha = \frac{P - P_0}{P_\infty - P_0} \quad [4.2]$$

This method applies to gas-phase reactions or to heterogeneous reactions that lead to a change in gas amount, such as the decomposition of a carbonate.

#### 4.4.1.2. Variations in density and viscosity

This method simultaneously uses the properties of viscosity and density. In two identical cells (see Figure 4.1), we introduce the reaction mixture in one side and a pure gas, such as nitrogen in the other. Let us assume that, under the same pressure, the mixture's viscosity is lower than nitrogen's viscosity and that its density is the highest. Thus the mixture flows faster in its capillary tube (lower viscosity) than nitrogen. As the mixture has the highest density, it crosses the hole more slowly when it reaches C, so there is an accumulation of the mixture in part BC and the pressure here is higher than in the cell (2).

This pressure will vary with the composition of the mixture, which means it varies with the fractional extent of the reaction. This method only applies to gases and requires prior calibration.

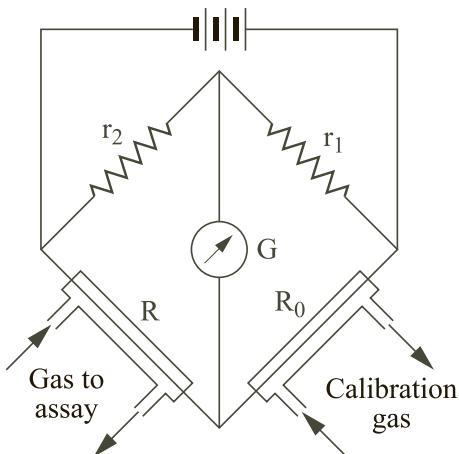


**Figure 4.1.** Device to follow the reaction with viscosity and density measurements

#### 4.4.1.3. Thermal conductivity variations

Thermal conductivity depends on the gas studied. Furthermore, in the case of a mixture, it characterizes the concentrations when blending is known. A device called a katharometer is used and consists of two identical cells. The reaction mixture passes through one cell and the reactants pass through the other (at constant speeds, see Figure 4.2).

Let us recall that the heat conduction between two points is expressed in joules per second per meter and per degree, and that it is proportional to the temperature difference between two points.



**Figure 4.2. Katharometer**

If an electric current passes through the resistors of each cell, the internal temperature of each cell will rise until it reaches the limit value corresponding to thermal equilibrium (the energy absorbed by the gas is equal to that released through the resistance).

There is a set composition of the reaction mixture flowing through the right cell for each limit temperature, and therefore a corresponding resistor value. Hence, if a gas with a constant volume passes through the left-hand cell there will be some deviation in the galvanometer.

The method is restricted to homogeneous reactions in gas phase and requires a prior calibration.

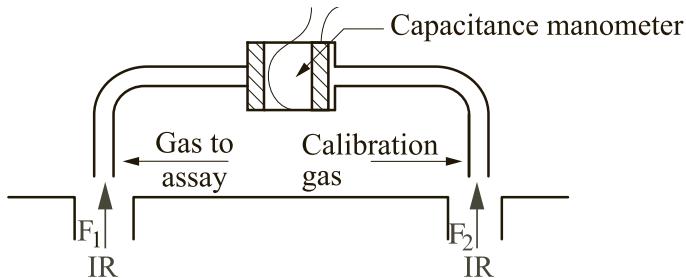
#### 4.4.1.4. Spectrographic methods

Let  $I_0$  and  $I$  be the intensities of incident beams that pass through the gas mixture or absorbing liquid within the wavelength range of the incident light. For a component  $A$  in the mixture at concentration  $[A]$ , the Beer–Lambert law is written as follows:

$$\ln \frac{I}{I_0} = KI[A] \quad [4.3]$$

In the case where the spectra of different substances that are present in the mixture overlap, it will be necessary to use a monochromatic light corresponding to an absorption peak for the species to be assayed.

The colorimetry in the visible range and the photometry in the infrared and ultraviolet ranges constitute the techniques that are used. If there is no interference between components and the mixture absorbs in the infrared range, the total infrared analyzer will be used (see Figure 4.3).



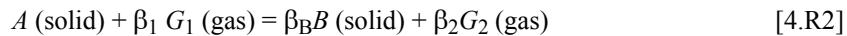
**Figure 4.3. Cell for total infrared measurement**

The rise in temperature of a gas in an enclosure subjected to an infra-red radiation is all stronger as the gas absorbs more the radiation, the rise in pressure will thus be greater. The variation in pressure causes the deformation of a capacitor plate, which modifies its capacity according to the composition of the mixture.

#### 4.4.1.5. The measurement of masses in condensed phases

The mass of a solid sample heated to a chosen temperature in a specific gaseous atmosphere is continuously measured via an electronic gravimetric device. This method is suitable for all heterogeneous reactions involving a solid and producing a variation in the number of gaseous moles.

Let us assume that the reaction is written as follows:



It is easy to show that the fractional extent of the reaction is obtained through:

$$\alpha = M_A \frac{m - m_0}{m_0 (\beta_1 M_1 - \beta_2 M_2)} \quad [4.4]$$

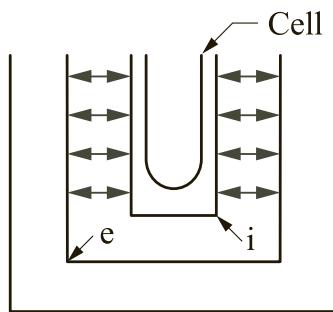
In this expression  $M_1$ ,  $M_2$  and  $M_A$  are the molar masses of both gases and solid  $A$ , respectively.

#### 4.4.1.6. Measurement of a heat flux

A Calvet-type microcalorimeter (see Figure 4.4) enables us to measure the heat flux that is released or absorbed by the sample that is in the cell. It can be easily proven that the reaction speed is related to the heat flux using the following equation:

$$\frac{dQ}{dt} = \Delta H \frac{d\xi}{dt} \quad [4.5]$$

In this equation,  $\Delta H$  is the enthalpy associated with the reaction. This technique can be used for liquid-phase reactions and heterogeneous reactions involving solids or a liquid in addition to gas.



**Figure 4.4.** A Calvet-type microcalorimeter

#### 4.4.1.7. Dilatometric method

This method is mostly used in a liquid medium through a rod dilatometer thermostated to 1/1,000°C. It relies on the differences in molar volume of different components (the solution is assumed to be ideal). During the reaction, the difference in the volume of a liquid between times  $\theta$  and  $t$  is related to the various amounts of species in the medium. If  $v_k^0$  denotes the molar volume of component  $k$ , this relationship is expressed as follows:

$$V - V_0 = \sum_k v_k^0 \{A_k\} - \sum_k v_k^0 \{A_k\}_0 \quad [4.6]$$

hence the relationship between the variation in volume and the reaction speed:

$$\frac{dV}{dt} = \frac{d\xi}{dt} \sum_k v_k^0 v_k \quad [4.7]$$

The volumetric speed is obtained through:

$$v = \frac{1}{V \sum_k v_k^0 v_k} \frac{dV}{dt} \quad [4.8]$$

#### 4.4.1.8. Polarimetry

This method can be used for homogeneous reactions in liquid medium provided that at least one of the principal components of the reaction is optically active. Accordingly, the reaction is performed in a thermostated polarimeter.

Biot's law determines the angle  $\theta$  of rotation of the polarization plane of light after the liquid containing the optically active component, which has the concentration  $[A_i]$ , travels a given length  $l$ . This law is almost additive for a mixture of optically active substances:

$$\theta = l \sum_j k_j [A_j] \quad [4.9]$$

where  $k_j$  is the specific optical rotation of the component  $A_j$  and is a feature of the substance. Each of the concentrations involved is related to the initial conditions and the fractional extent through equation [1.30], which can be calculated if the volume of the reaction zone is known.

#### 4.4.1.9. Refractometry

Macroscopic property  $P_m$  is called molecular polarization, which is constant for a pure compound. It is related to the refractive index  $n_R$ , the molar mass  $M$  and the density  $\rho$  of this compound through the equation:

$$\frac{n_R^2 - 1}{n_R^2 + 2} \frac{M}{\rho} = P_m \quad [4.10]$$

For a mixture of density  $d$ , which is composed of substances of  $M_1, M_2$ , etc. molar masses, we assume, with a good approximation, that the molecular polarizations are additive. So, if  $x_1, x_2$  etc. are the mole fractions in the mixture:

$$\frac{n_R^2 - 1}{n_R^2 + 2} \frac{x_1 M_1 + x_2 M_2 + \dots}{d} = \text{Const} \quad [4.11]$$

a molar fraction is defined as:

$$x_k = \frac{\{A_k\}}{\sum_k \{A_k\}} = \frac{[A_k]}{\sum_k [A_k]} \quad [4.12]$$

If a reaction is taking place within the mixture, the molar fractions will vary and therefore the refractive index will vary. It is possible to obtain the fractional extent because all of the molar fractions are related to the concentrations by means of the above equation and thus to fractional extent.

In order to obtain the refractive index, a beam is pointed onto the mixture under grazing incidence, the maximum refraction angle  $\theta$  is measured and the index is deduced as follows:

$$n_R = 1 / \sin \theta \quad [4.13]$$

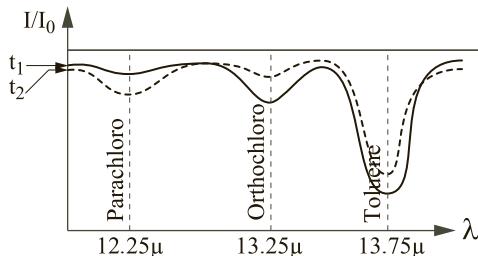
The method is used for homogeneous reactions in liquid medium.

A variant of this method involves measuring the permittivity  $\epsilon$  of the mixture, which is linked to the refractive index through the following equation:

$$\epsilon = n_R^2 \quad [4.14]$$

#### 4.4.1.10. Absorption spectroscopy

The liquid reaction medium is placed in the path of a beam of suitable radiation. The transmittance obtained enables us to directly obtain the concentration of the component that is absorbed by this wavelength, through the application of Beer-Lambert's law. This method is particularly suitable for reactions in liquid medium. The wavelength chosen for a component does not interfere with the absorption of other components.



**Figure 4.5. Absorption spectrum during toluene chlorination**

Figure 4.5 shows the spectrum obtained at two different times during the catalytic chlorination of toluene. The three chosen wavelengths enable us to assay each of the compounds formed and the initial toluene, which is thus subjected to two parallel reactions in homogeneous phase.

#### 4.4.1.11. Electrical conductivity

In a sufficiently dilute solution of strong electrolytes, we assume that the equivalent conductivities  $\Lambda$  (ratio of the conductivity to the concentration) remain approximately constant. The participation of each electrolyte in the total conductivity is proportional to its concentration.

In order to use this method, at least one of the principal components must be an electrolyte. If it is a strong electrolyte, calculation of the extent of the reaction is greatly simplified. If the solutions are not diluted enough or if weak electrolytes are involved, a prior calibration of the solutions should be performed using mixtures of electrolytes that are present.

#### 4.4.1.12. Potentiometry

The potential of an electrode immersed in a solution of its ions (electrode of the first type) is linked to the concentration of the corresponding ions through Nernst law:

$$\Pi = \Pi^0 + \frac{RT}{nF} \ln [M^{+n}] \quad [4.15]$$

For instance, we can monitor the evolution of a reaction involving acids or bases by using a pH indicator electrode.

The potential measurement is made by assigning the measuring electrode to a reference electrode and evaluating the e.m.f. of the resulting battery.

This method is especially useful in dilute liquid solutions, which is the domain of validity Nernst Law in concentrations.

#### 4.4.1.13. Polarography

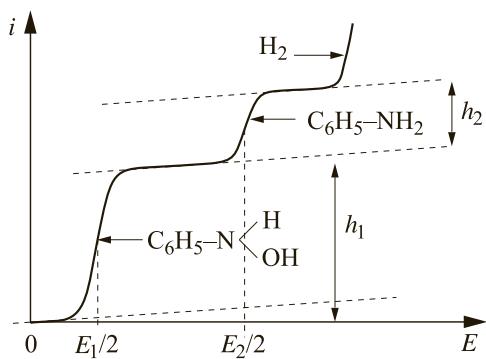
A polarograph automatically records the intensity of the electrolytic current as a function of the potential difference that has been determined.

Each substance likely to be reduced by electrolysis or to deposit a metal leads to a wave that has a half-wave potential, which characterizes the electrolysis considered independent of concentrations.

The solution is subjected to several assays (the electrolyzed amount is negligible) and the evolution can be monitored over time. This is done by setting a voltage  $E$  so that the level of the wave is reached and measuring the amplitude of the current of level ( $h$ ) as a function of time.

The electrolytic potential should be within the 0.4 V (for a mercury electrode) to -1.8 V range. In order to separate two components (see Figure 4.6), their half-wave potentials should be distant from 0.1 V.

This method is especially useful with species that are present at low concentrations.



**Figure 4.6. Example of polarogram separating two species**

#### 4.4.2. Physical methods with separation of components

In these methods one or more components of the reaction are separately assayed.

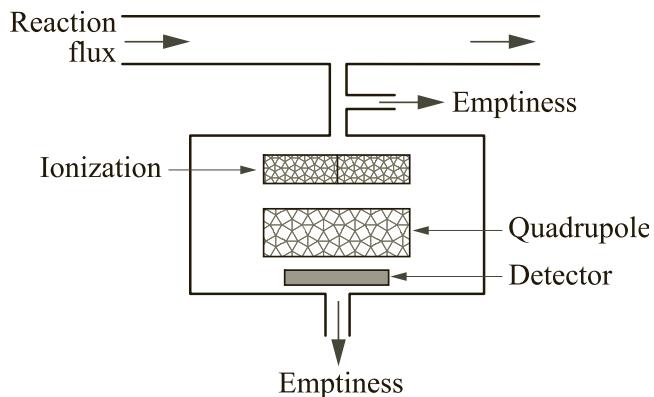
##### 4.4.2.1. Chromatographic method

The reaction mixture studied passes through a column containing substance of a suitable steady state phase. The phenomena of adsorption, desorption or dissolution at the column exit delay the various components of the mixture, which are thus separated. It is then, therefore, possible to assay these components.

This method is used for gases (gas-phase chromatography), liquids (liquid-phase chromatography) and eventually for ions (ion chromatography).

##### 4.4.2.2. Mass spectroscopy

The mass spectrometer is a detection and assay device for chemical entities in gas phase. The reactor, which is supplied with reagents, operates in continuous flow. A tiny hole ( $\approx 0.4 \text{ mm}^2$ ) is pricked in the reactor, which enables leakage of the reaction mixture. A second hole of the same size is located opposite the former: the leakage becomes a molecular beam that passes through the elements of a quadrupole system (Figure 4.7). The latter serves as mass selector. Finally the ion detector enables us to measure the ions created from the molecules of the components of the reaction by the ionization source. The entities are often numerous and the selection is difficult, however, hence the use of the mass spectrometer after a gas-phase chromatograph that has already been performed to separate the components.



**Figure 4.7.** Circuit diagram of a device of measuring reaction kinetics through mass spectrometry

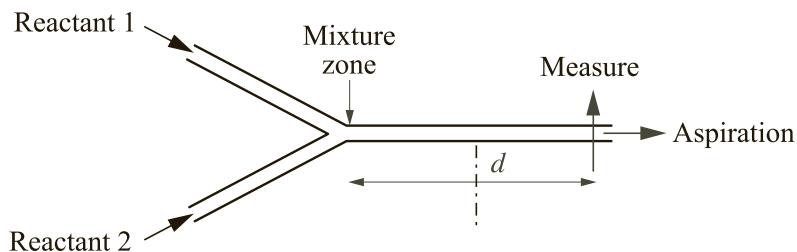
#### 4.4.3. Study of fast reactions

We must consider how the mixture of reactants and the start of the reaction will be performed regardless of the method chosen to obtain a specific property. This raises a real problem, mainly for fast reactions. In fact, it is well understood that a blending time of 1 second is not acceptable if the reaction lasts 100 ms. The method must be fast in terms of the reaction timescale, which is difficult in conventional reactors. Thus novel methods suited to fast reactions have been developed and we will now consider three of them.

##### 4.4.3.1. Continuous flow method

The introduction of continuous flow techniques enables us to measure the speeds of reactions that last 1 second or less. The idea is to place the reactants in a micro-mixer that features a graduated capillary tube. The flow rate is kept constant by an aspirating pump.

When the steady state mode is established, a reactant or a product is assayed, generally through spectroscopy at various distances from the mixer along the capillary. Under constant flow rate, each distance corresponds to a reaction time and the experimenter can measure these. This method also enables us to measure extremely fast reactions.



**Figure 4.8.** Principle of the measurement system in continuous flow

The analysis of the mixture can be completed in 1 ms, as with a flow rate of 10 m/s, a length of 1 cm corresponds to 1 ms of reaction.

This method can be used in gas or liquid phase.

##### 4.4.3.2. Flash photolysis

The idea of this method is to utilize a flash of intense and fast light, usually from a laser, in order to generate reactive species, especially atoms and free radicals. The

reaction of these species with other reactants present in the system is usually monitored through spectrometry. The problem of reactants blending is resolved by the fact that radicals are generated *in situ*.

#### 4.4.3.3. Relaxation methods

Relaxation methods are a convenient way of addressing the problem of blending time. We start from a system already in thermodynamic equilibrium and we disturb this equilibrium through a small and very fast variation in one of the equilibrium variables (temperature, pressure and eventually electric field for the ionic reactions). Then we measure the variations of one species concentration, usually through rapid spectroscopy, during the system's return to equilibrium. For instance, a system can be heated very rapidly (<30 ns) by using a laser pulse.

The relaxation time represents the time it takes the disturbance's amplitude to decrease by a factor of 1/e.

Let us consider the example of the following reaction:



and assume that the speed from left to right is:

$$-\frac{d[A]}{dt} = k'[A][B] \quad [4.16]$$

and from right to left is:

$$\frac{d[A]}{dt} = k''[C][D] \quad [4.17]$$

Let  $a$ ,  $b$ ,  $c$  and  $d$  be the concentrations of the four species in equilibrium. After the disturbance, at a time  $t$ , let us assume that the concentration of  $a$  is:  $a - x$ .

The speed at that time will be written as follows:

$$-\frac{dx}{dt} = k'(a-x)(b-x) - k''(c+x)(d+x) \quad [4.18]$$

By ignoring the term in  $x^2$  (small disturbance) and noting that according to the law of mass action we have the following relation:

$$k'ab - k''cd \quad [4.19]$$

we get:

$$-\frac{dx}{dt} = x[k'(a+b) + k''(c+d)] \quad [4.20]$$

With an initial disturbance  $x_0$  and through integration we obtain:

$$x = x_0 \exp\left\{-[k'(a+b) + k''(c+d)]t\right\} = x_0 \exp\left(-\frac{t}{\tau}\right) \quad [4.21]$$

thus, we deduce that the relaxation time will be:

$$\frac{1}{\tau} = k'(a+b) + k''(c+d) \quad [4.22]$$

where  $\tau$  is determined for different sets of concentrations  $a, b, c$  and  $d$ , and the graph of  $1/\tau$  is plotted as a function of  $(a+b)$ . We thus obtain a straight line of slope  $k'$ , whose intercept enables us to calculate  $k''$ .

For more complex reactions, the reasoning is obviously more complicated, but computer analysis of data helps provide information as well as in the case of several successive reactions.

Other methods, that are more specific to a given reaction, can also be used as long they provide the expected information on the evolution of the reaction.

#### 4.5. Researching the influence of various variables

The form of speed law can be very diverse according to the various variables: concentrations, temperature and extent. A number of complementary experiments will bring us information on these forms of law. These complementary experiments are carried out in accordance with certain methodologies.

Having identified the reactions that occur with their stoichiometric coefficients, it is now important to see whether we can obtain the kinetic properties, which are the extent (or fractional extent) and speed (or reactivity) from experimental quantities (measured speed and extent). For this research it is essential to perform the pseudo-steady state test (see section 7.1.5). In fact, this test only enables us to characterize the reaction by a single definition of speed regardless of the component analyzed or the property selected to monitor the evolution of the system. If this test is not satisfied, we should be aware that each property corresponds to a specific extent that is proper to it or to a combination of several extents.

#### **4.5.1. Ostwald's isolation method**

This method is intended, in closed systems, to “isolate” the variations in the amount of one component of the reaction. So, the reaction is monitored within a mixture in which all the components, except one, are in very large excess compared to the component being studied. Thus, the amounts (and eventually the concentrations) of all these excess components will be considered to be virtually constant during the measurement time and therefore their influence will be constant. Only the amount of the isolated component will be a function of the fractional extent.

We should not forget to consider the products formed from among the components.

This method can be varied so that all of the components in the reaction are available in constant amounts. This is equivalent to performing the reaction in an extremely narrow range of fractional extent.

#### **4.5.2. Variables separation**

In order to carry out modeling, it is useful to know whether the speed variables, *a priori* temperature, concentration or partial pressure and the fractional extent are separate variables in the expression of speed. In other words, whether the speed can be written as a product of several functions, each function having a single variable, which means that the speed would be written:

$$r = f([A_1], \dots, [A_i], T, \alpha) = g_1([A_1]) \dots g_i([A_i]).h(T).m(\alpha) \quad [4.23]$$

This method relies on the theorem of separate variables, which is stated as follows.

If two curves representing a function  $y$  of one variable  $x$ , obtained for two values of parameter  $a$ , are deduced from one another through an orthogonal affinity of axis Ox, of direction Oy and of ratio  $k$ , then in the function's expression, variable  $x$  is separated. This means that we can write the following logical expression: if  $k$  is independent of  $x$  and:

$$\frac{y_1}{y_2} = \frac{f(a_1, x)}{f(a_2, x)} = k \quad [4.24]$$

then:

$$y = f(a, x) = g(a).h(x) \quad [4.25]$$

and vice versa. We will describe and use this method in Chapter 9 section 9.6.1.3.

The influence of concentrations and temperature are also important parts of the experimental work. We will see later (sections 8.7.1 and 9.7.2) how to manage such studies.



## Chapter 5

# Experimental Laws and Calculation of Kinetic Laws of Homogeneous Systems

Reaction models that specify the elementary steps and their location should enable us to obtain the experimental kinetic laws, such as fractional extent as a function of time; and speed as a function of the physical variables such as pressure, temperature and introduced concentrations of reactants and products. In the first step we consider the cases of homogeneous reactions where all the components belong to the same phase. It is known that such reactions occur in a single reaction zone, which is within the volume of the mixture. All the intermediate steps will then take place in the single reaction zone and will therefore have the same space function, which is the volume reduced to a mole of a reactant:

$$E = V/n_0 \quad [5.1]$$

### 5.1. Experimental laws in homogeneous kinetics

The experimental speed is usually obtained for closed systems as a function of the concentrations and temperature. Curiously, however, speeds as a function of time or fractional extent are never obtained. At most, the intervention of time appears in some reactions through a notion of current order that differs from an initial order. Moreover, it is not specified whether the speeds are compared at constant time or fractional extent.

For closed systems, the integral laws appear mostly as a concentration depending on time and the initial concentrations.

The influence of temperature mostly appears as Arrhenius' law upon a "constant" of speed or sometimes directly upon the speed (certainly at given concentrations).

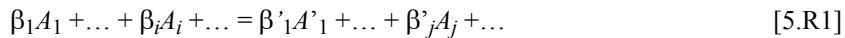
### 5.1.1. Influence of concentrations

For speed-concentration relationships, four cases can be distinguished, that will be discussed in sections 5.1.1.1 to 5.1.1.4.

#### 5.1.1.1. The reaction admits an order with partial orders equal to a series of stoichiometric coefficients

If a reaction admits an order, with partial orders equal to a series of stoichiometric coefficients, it is said that such a reaction obeys van 't Hoff's principle. At first this author believed there to be a universal law similar to that of mass action for chemical equilibria.

For a reaction written as follows:



the volumetric speed is obtained from van 't Hoff's law as follows:

$$-\frac{d[A_i]}{dt} = k[A_1]^{\beta_1} \dots [A_i]^{\beta_i} \quad [5.2]$$

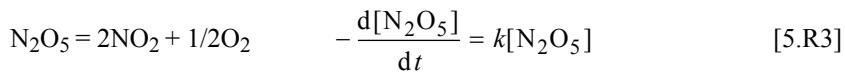
for example, substitution reactions of second order (SN2 reactions), such as:

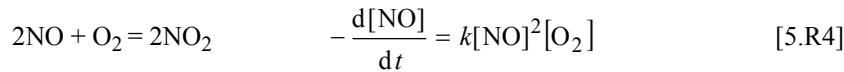


whose speed is:

$$-\frac{d[\text{Ph - CHCl}]}{dt} = k[\text{Ph - CH}_2\text{Cl}][\text{HCH}_2\text{OH}] \quad [5.3]$$

or the reactions:





It should be noted that everything goes as if the reaction was elementary, which is usually the case for reaction [5.R2] but not for the other examples.

#### 5.1.1.2. *The reaction admits an order, but the partial orders do not correspond to any series of stoichiometric coefficients*

The reduction reaction of hydrogen peroxide by bromides:



turns and leads to the following speed law:

$$\frac{d[\text{Br}_2]}{dt} = k[\text{H}_2\text{O}_2]^3[\text{HBr}] \quad [5.4]$$

which is of the third order with respect to hydrogen peroxide and first order with respect to hydrogen bromide. Thus the law admits partial orders but they do not correspond to any series of stoichiometric coefficients.

#### 5.1.1.3. *The reaction follows different laws at the initial and current time*

Formaldehyde decomposition according to:



has a speed equation that is written at the initial time (in the absence of products formed) as:

$$\frac{d[\text{CO}]}{dt} = k[\text{CH}_3\text{CHO}]^{3/2} \quad [5.5]$$

and at current time (in the presence products formed) as:

$$\frac{d[\text{CO}]}{dt} = \frac{k[\text{CH}_3\text{CHO}]^2}{\sqrt{[\text{CH}_3\text{CHO}]_0}} \quad [5.6]$$

We see that the law differs depending on the time of measurement. It admits an order (that does not correspond to a series of integer stoichiometric coefficients) at the initial time, but not during the measurement.

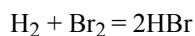
Note that [5.6] can be written:

$$\frac{d[CO]}{dt} = k[CH_3CHO]^{3/2}(1 - \alpha)^{1/2}$$

which has the same form as [5.8] with  $\alpha=0$ .

#### 5.1.1.4. The reaction admits no order

The following hydrogen bromide synthesis reaction:



admits no order. The concentrations law is written as follows:

$$v = \frac{[H_2][Br_2]^{1/2}}{1 + k_2 \frac{[HBr]}{[Br_2]}} \quad [5.8]$$

where  $k_1$  and  $k_2$  are two constants depending on temperature.

The decomposition reaction of  $N_2O$  into nitrogen and oxygen gives a speed expression that admits no order because it is written as follows:

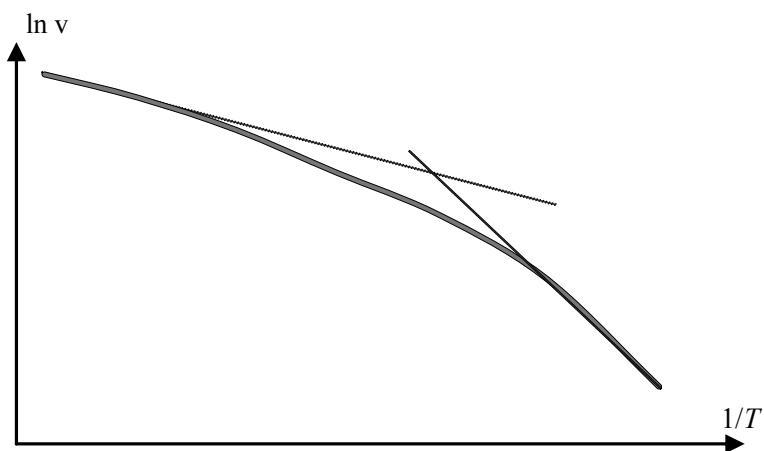
$$\frac{d[O_2]}{dt} = \frac{k_1[N_2O](k_2[N_2O] + k^3)}{k_2 + k_3} \quad [5.9]$$

#### 5.1.2. Influence of temperature

The reaction speeds frequently obey Arrhenius' law, which does not mean that the temperature coefficient defined in section 4.5.4.1 is an activation energy. In addition to this, we note that several nitric monoxide reactions have a negative temperature coefficient. Should we therefore conclude that the latter leads to a negative activation energy?

In other cases it is necessary to introduce two temperature coefficients depending on the field in order to account for the influence of temperature. This is the case, for example, in the reduction of nitrogen dioxide by carbon monoxide. Figure 5.1 shows the shape of the curve in "Arrhenius" coordinates.

NOTE 5.1.– Some authors interpret the change in slope of the preceding curve as a change in mechanism, thus assigning a mechanism to an activation energy and vice versa. We will show later that this is completely wrong. Changes in mechanism are rare and the change in slope is easily explained by changes in first species mode (section 7.4.5), which means it is related to the fact that the calculation of speed utilizes approximation methods. In fact, the definition of two slopes from this type of curve is usually also an approximation (see Figure 5.1).



**Figure 5.1.** Arrhenius “two-slope” curve

NOTE 5.2.– It should be noted that for all reactions that admit an order, concentrations variables that are separate from each other and from temperature in the volumetric expression of speed, which means that the speed obeys an expression written as follows:

$$v = f(T) \cdot g_1([A_1]) \cdot g_2([A_2]) \dots \quad [5.10]$$

## 5.2. Relationship between the speed of a reaction and the speeds of its elementary steps

If we consider a component of reaction  $A$ , its balance can be written as [1.22] by taking into account [3.3] and extending the sum to all the steps of the mechanism that involve component  $A$ , either as a reactant or as a product, with the stoichiometric coefficient  $v_{A,p}$ :

$$\frac{d[A]}{dt} = v_a v_A = \sum_{\rho} v_{A,\rho} \Phi_{\rho} E_{\rho} n_0 \quad [5.11]$$

In the case of a homogeneous reaction, since all the steps take place in the same zone – they have the same space function – a simple relationship between the volumetric speed and the reactivities of elementary steps is obtained by taking into account [1.12]:

$$\frac{1}{Vv_A} \frac{d[A]}{dt} = v = \frac{1}{v_A} \sum_{\rho} v_{A,\rho} \Phi_{\rho} \quad [5.12]$$

If the volume is constant throughout the reaction, we deduce that:

$$\frac{d[A]}{dt} = \sum_{\rho} v_{A,\rho} \Phi_{\rho} \quad [5.13]$$

It should be noted that if we change the component by substituting  $A$  with  $B$ , the equivalent of the previous relationship would not necessarily involve the same steps in the sum, nor the same coefficients. This would mean that there are several volumetric speeds depending on the component chosen to define it, which contradicts relation [1.3]. We will return to this problem in Chapters 6 and 7.

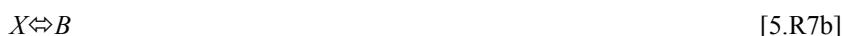
### 5.3. Mathematical formulation of speed from a mechanism and experimental conditions

#### 5.3.1. Example of resolution of a mechanism in a closed system

We will consider the following reaction, which will be called our reference reaction because it will help us to illustrate several of our statements:



Its mechanism involves an intermediate component  $X$ , two successive steps and their opposites, both steps taking place in the same volume zone (homogeneous reaction):



Let us assume that this reaction is performed in a closed system with respect to all of the components. We will reason about the speed per volume unit and by applying [5.13] to the concentrations of the three components  $A$ ,  $X$  and  $B$ , we can write:

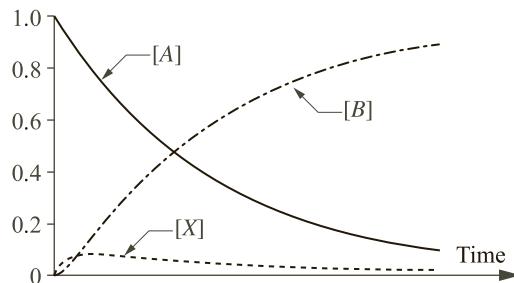
$$\frac{d[A][A]_0}{dt} = k'_1 \frac{[A]}{[A]_0} - k''_1 \frac{[X]}{[A]_0} \quad [5.14]$$

$$\frac{d[X][A]_0}{dt} = k'_1 \frac{[A]}{[A]_0} - (k''_1 + k'_2) \frac{[X]}{[A]_0} + k''_2 \frac{[B]}{[A]_0} \quad [5.15]$$

$$\frac{d[B][A]_0}{dt} = k'_2 \frac{[X]}{[A]_0} - k''_2 \frac{[B]}{[A]_0} \quad [5.16]$$

We also have the total concentration balance, which enables us to write:

$$\frac{[A] + [X] + [B]}{[A]_0} = 1 \quad [5.17]$$



**Figure 5.2.** Evolution of concentrations of the various components of the reaction system composed of steps [5.R7a] and [5.R7b] over time

Our three unknowns are the three relative concentrations. Thus we only need three of the four equations in order to solve the system, or at best two differential equations chosen from [5.14], [5.15] and [5.16] and the algebraic equation [5.17]. Figure 5.2 shows the variations of the three relative concentrations versus time for a series of values of the rate factors  $k'_1$  and  $k''_1$  for the opposite reactions of step [5.R7a], and  $k'_2$  and  $k''_2$  for both opposite steps of reaction [5.R7b]. The system cannot be resolved algebraically, hence the use of numerical methods. We have used

the Runge–Kutta method with four factors in order to obtain the curves in Figure 5.2. It can be seen that the concentration of *A* decreases with time while that of *B* increases. The concentration of intermediate *X*, which starts from zero and reaches zero at the end of the reaction, passes through a maximum value.

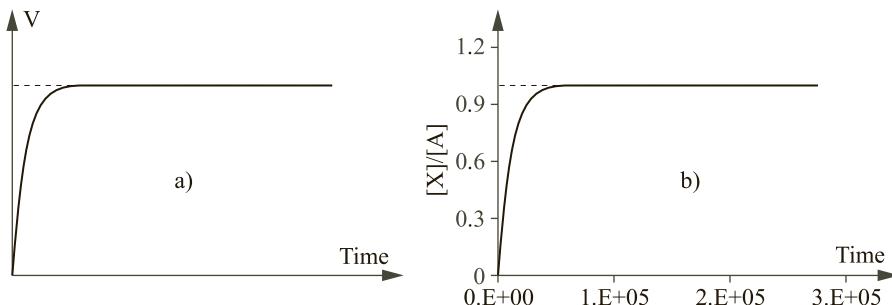
### 5.3.2. Example of resolution of a mechanism in an open system with constant concentrations

Equation [5.13] is kept and the constant concentrations of reactants and products are added to it:

$$[A] = [A]_0 \quad \text{and} \quad [B] = [B]_0 \quad [5.18]$$

This gives us three equations for three unknowns. A speed equation is then chosen. Let us assume that it is the production of *B* from one mole of *A*:

$$v_B = k'_2 \frac{[X]}{[A]_0} - k''_2 \frac{[B]}{[A]_0} \quad [5.19]$$



**Figure 5.3.** a) Variations of the speed with time; and b) variations of the concentration of intermediate *X* with time for reaction [5.R7] in a system with constant concentrations

Figure 5.3a shows the variations of speed with time. We see that after a transition period, the speed becomes independent of time. Figure 5.3b shows that after the transition mode, the concentration of intermediate *X* remains constant.

Several conclusions can be drawn from this study of reaction [5.R7]:

- the mathematical system we want to solve rapidly becomes complex and, in most cases, only a numerical computation will enable us to obtain the solution.

However, we still have to obtain the numerical values of the rate coefficients, which is rarely the case;

– this solution depends on the operating conditions and the quantity chosen to express the speed.

We will now examine the mathematical formulation of some types of reactions.

#### 5.4. Mathematical formulation of a homogeneous reaction with open sequence

We will reconsider the example of the decomposition reaction of dinitrogen pentoxide with its mechanism composed of steps, which are recalled below. The opposite steps of [5.R3b] and [5.R3c] are not taken into account:



The two opposite rate coefficients of reaction [5.R8a] are  $k'_1$  and  $k''_1$ , and those of reactions [5.R8b] and [5.R8c] are  $k_2$  and  $k_3$ .

##### 5.4.1. Mathematical formulation in a closed system

Initially the reactor contains only nitrogen pentoxide, and the volume is constant throughout the reaction. We have five unknowns – concentrations  $[\text{N}_2\text{O}_5]$ ,  $[\text{NO}_3]$ ,  $[\text{NO}]$ ,  $[\text{N}_2\text{O}_4]$ , and  $[\text{O}_2]$  – and the five following equations:

– the balance of the intermediate NO species:

$$\begin{aligned} \frac{1}{V} \frac{d\{\text{NO}\}}{dt} &= \frac{d[\text{NO}]}{dt} = (\phi_2 - \phi_3) \\ &= k_2 [\text{NO}_2][\text{NO}_3] - k_3 [\text{NO}][\text{N}_2\text{O}_5] \end{aligned} \quad [5.20]$$

– the balance of the intermediate  $\text{NO}_3$  species:

$$\begin{aligned} \frac{d[\text{NO}_3]}{dt} &= (\phi_1 - \phi_2) = k'_1 [\text{N}_2\text{O}_5] - k''_1 [\text{NO}_2][\text{NO}_3] \\ &\quad - k_2 [\text{NO}_2][\text{NO}_3] \end{aligned} \quad [5.21]$$

– oxygen conservation:



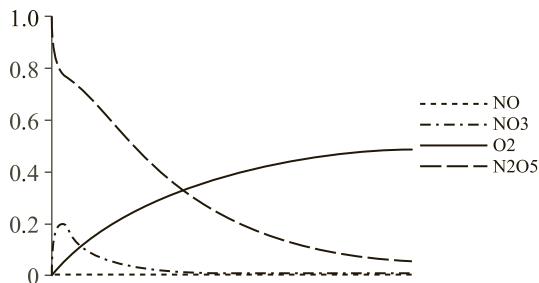
– nitrogen conservation:



Let us choose to measure the speed of the reaction through the speed of oxygen production:

$$v_O = \frac{d[O_2]}{dt} = \phi_2 = k_2[NO_2][NO_3] \quad [5.24]$$

The resolution of the system consisting of equations [5.20], [5.21], [5.22], [5.23] and [5.24] would enable us to obtain the chosen speed as a function of the variables of the problem: the initial concentration of pentoxide and time at a given temperature. This involves knowing the values of the rate coefficients of the four elementary steps concerned. Figure 5.4 shows the concentration curves obtained from such a resolution for a set of values of these coefficients.



**Figure 5.4.** Concentration versus time during the decomposition of dinitrogen pentoxide in a closed system

It can be seen that the concentrations of the intermediate species remain small compared those of the initial and final products.

#### 5.4.2. Mathematical formulation of a system with constant concentrations

We start from an initial state containing nitrogen pentoxide, carbon dioxide and dioxygen in known concentrations. Thus, the intermediate concentrations and an

expression of speed remain unknown. We keep equations [5.20] and [5.21] to which we add the following initial conditions:

$$[N_2O_5] = [N_2O_5]_0 ; [NO_2] = [NO_2]_0 ; [O_2] = [O_2]_0 \quad [5.25]$$

By assuming that the speed is measured by the heat flux involved, if  $\Delta H_i$  denotes the enthalpy associated with step  $i$ , we will obtain:

$$\begin{aligned} \frac{dQ}{dt} &= k'_1 [N_2O_5]\Delta H_1 + k''_1 [NO_2][NO_3]\Delta H'_1 \\ &+ k_2 [NO_2][NO_3]\Delta H'_2 + k_3 [NO][NO_3]\Delta H_3 \end{aligned} \quad [5.26]$$

The resolution of the system consisting of equations [5.20], [5.21], [5.25] and [5.26] enables us to obtain the heat flux as a function of time and the initial concentrations of the principal components of the reaction, which are held constant.

## 5.5. Mathematical formulation of chain reactions

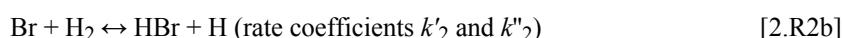
We will examine the mathematical formulation of chain reactions in terms of two examples: the first in a simple chain reaction; and the second in a reaction producing macromolecules.

### 5.5.1. Mathematical formulation of a simple homogeneous chain reaction

We will reason on hydrogen bromide synthesis (originally shown in [2.R2]):



We have seen that the proposed mechanism of this reaction can be formulated, in a simplified form, through the four steps that are recalled below:



We will only consider the case of a closed system with constant volume and will start with a known concentration of dihydrogen and dibromine. Let us write the balance of the intermediates, which are the atoms of hydrogen, bromine and the hydrogen bromide formed:

$$\frac{1}{V} \frac{d\{H\}}{dt} = \frac{d[H]}{dt} = \phi'_1 - \phi''_1 - \phi_2 \\ = k'_2 [Br] [H_2] - k''_2 [H] [HBr] - k_3 [H] [Br_2] \quad [5.27]$$

$$\frac{d[Br]}{dt} = 2\phi_3 - \phi'_1 - 2\phi_4 = 2k'_1 [Br_2] - k'_2 [H_2] [Br] \\ + k_3 [H] [Br_2] - 2k'_1 [Br]^2 \quad [5.28]$$

$$\frac{d[HBr]}{dt} = \phi'_1 - \phi''_1 - \phi_2 \\ = k'_2 [H_2] [Br] - k''_2 [H] [HBr] + k_3 [H] [Br_2] \quad [5.29]$$

We write the conservation of bromine and hydrogen as:

$$[Br_2]_0 = [Br_2] + \frac{1}{2}[Br] + \frac{1}{2}[HBr] \quad [5.30]$$

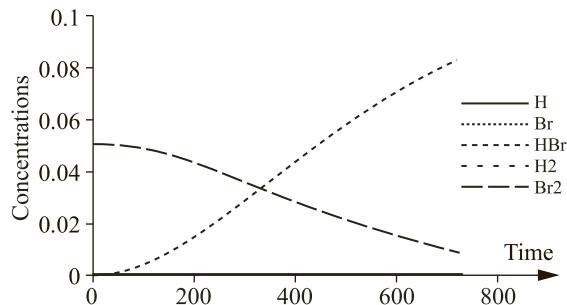
$$[H_2]_0 = [H_2] + \frac{1}{2}[H] + \frac{1}{2}[HBr] \quad [5.31]$$

We will express speed through the production of hydrogen bromide:

$$v_{HBr} = \frac{1}{2} \frac{d[HBr]}{dt} \quad [5.32]$$

The resolution of the system consisting of four equations chosen from among [5.27], [5.28], [5.29], [5.30], [5.31] and [5.32] enables us to express the concentrations of the different species and speed as a function of time at a given temperature. It can be seen from the example of such a calculation, shown in Figure 5.5, that the concentrations of intermediate species are extremely low compared to those of the principal components.

NOTE 5.3.— The thermal initiation step could be replaced by the same step performed photochemically, i.e. with a speed proportional to light intensity at the appropriate wavelength.



**Figure 5.5.** Variation of species concentrations during the chain reaction of hydrogen bromide synthesis

### 5.5.2. Mathematical formulation of a reaction forming a macromolecule through polymerization

Here we will only consider the case of a closed system with a constant volume.

#### 5.5.2.1. Speed of polymerization

We will illustrate polymerization through the example of a polymerization that, from a monomer ( $M$ ), leads to the polymer  $P_{\bar{N}}$ , where  $\bar{N}$  is the average number of monomer molecules contained in a polymer molecule (such as an alkene). The reaction takes place in homogeneous phase and the volume remains virtually constant during the reaction.

We assume that chain initiation is performed by an unstable substance  $S$ , which breaks down into two activated radicals according to the following reaction:



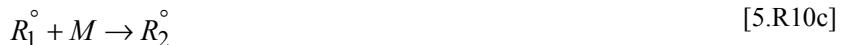
The second step of the initiation is the reaction of one activated radical with a monomer molecule in order to produce a new activated radical that contains a monomer molecule according to the following reaction:



If  $k_i$  denotes the speed of the first step of the initiation and  $v_i$  the speed (per unit volume) of radical formation  $R_1^\circ$  (in the second step), the balance with radical  $R_c^\circ$  is written as follows:

$$\frac{d\{R_c^\circ\}}{dt} = 2k_i [S] - v_i \quad [5.33]$$

Radicals  $R_1^\circ$  that were formed through the initiation phase are the propagation centers of the chain. They affect the monomer  $M$  according to the reaction:



and, recursively, each radical reacts with a monomer molecule in order to lengthen the polymer radical:



It is assumed that these reactions could continue indefinitely ( $j$  could increase indefinitely).

The breaking reaction occurs when two radicals of arbitrary length combine to produce a polymer molecule according to:



We want to assess the extinction speed of the monomer. This involves positing two hypotheses:

- It is assumed that the rate coefficients of reactions of a monomer binding to a radical have the same value  $k_p$ . This hypothesis is justified by the fact that in all these reactions the same double bond (the monomer bond) is cut.

- The constant  $k_t$  of breaking reactions is independent of the length of the radicals ( $j$  and  $m$ ) involved.

The monomer balance is written as follows:

$$-\frac{1}{V} \frac{d\{M\}}{dt} = \frac{d[M]}{dt} = v_i - \sum_j \varphi_j = v_i + k_P [M] \sum_j [R_j^\circ] \quad [5.34]$$

In order to determine the concentrations of the various radicals, we should write the balance for each of them:

$$\begin{aligned} \frac{1}{V} \frac{d[R_1^\circ]}{dt} &= \frac{d[R_1^\circ]}{dt} = v_i - (\varphi_P)_1 - \sum_j (\varphi_t)_j \\ &= v_i - k_P [M] [R_1^\circ] - k_t [R_1^\circ] \sum_j [R_j^\circ] \end{aligned} \quad [5.35]$$

$$\begin{aligned} \frac{d[R_2^\circ]}{dt} &= (\varphi_P)_1 - (\varphi_P)_2 - \sum_j (\varphi_t)_j \\ &= k_P [M] [R_1^\circ] - [R_2^\circ] - k_t [R_2^\circ] \sum_j [R_j^\circ] \end{aligned} \quad [5.36]$$

$$\begin{aligned} \frac{d[R_j^\circ]}{dt} &= (\varphi_P)_{j-1} - (\varphi_P)_j - \sum_j (\varphi_t)_j \\ &= k_P [M] [R_{j-1}^\circ] - [R_j^\circ] - k_t [R_j^\circ] \sum_j [R_j^\circ] \end{aligned} \quad [5.37]$$

The resolution of the system consisting of equations [5.34] to [5.37] will normally enable us to express the extinction speed of the monomer as a function of time through parameters  $v_i$ ,  $k_P$  and  $k_t$ . Unfortunately, we obtain a mathematic system that is too complicated to be solved and in addition a primordial reason is that the number of equations of the system varies with time (the problem's variable). We shall see in Chapter 7 how to bypass this difficulty.

### 5.5.2.2. Degree of polymerization

Let  $\bar{n}$  denote the average number of monomers per radical formed. This number is defined by:

$$\bar{n} = \frac{\text{number of monomeric units}}{\text{number of formed radicals}} \quad [5.38]$$

We note that for such a reaction, viewed as the result of breaking reactions, a polymerized molecule results from a breaking reaction of, on average, two radicals of the same length,  $\bar{n}$ . Therefore, the chain length is on average the half of the degree of polymerization. Thus the average degree of polymerization will be:

$$\bar{N} = 2\bar{n} \quad [5.39]$$

In order to assess  $\bar{n}$ , let us look at the evolution of a monomer radical  $R_1^\circ$ . It reacts either with a monomer with a reaction probability  $p$ , or with another radical in a breaking reaction with a probability  $1-p$ . Likewise, a radical  $R_2^\circ$  produces  $R_3^\circ$  with a probability  $p$  and produces a polymer molecule with a probability  $1-p$ .

If the probability of encountering a radical  $R_1^\circ$  is 1, the probability of encountering  $R_2^\circ$  is  $p$ , and  $R_3^\circ$  is  $p^2$ , then the probability of encountering  $R_j^\circ$  is  $p^{j-1}$ . The overall number of radicals will then be ( $p < 1$ ):

$$1 + p + p^2 + \dots + p^{j-1} = \frac{1}{1-p} \quad [5.40]$$

The number of monomeric units present in these radicals will be:

$$1 + 2p + 3p^2 + \dots + jp^{j-1} = \frac{1}{(1-p)^2} \quad [5.41]$$

We deduce that the average number of monomers is:

$$\bar{n} = \frac{1}{1-p} \quad [5.42]$$

hence the average degree of polymerization is:

$$\bar{N} = \frac{2}{1-p} \quad [5.43]$$

It is necessary to evaluate the chain propagation probability  $p$ .

During the time interval  $dt$ :

– the number of radicals  $R_1^\circ$  transformed into  $R_2^\circ$  is:

$$k_P[M] \left[ R_1^\circ \right]$$

– the total number of radicals  $R_1^\circ$  that disappear (including the chains that use this radical breaking) is:

$$k_P[M] + k_t \left( \sum_j \left[ R_j^\circ \right] \right)$$

hence, the value of the probability is obtained by the ratio of the number of favorable cases to the number of possible cases:

$$\begin{aligned} p &= \frac{k_P[M] \left[ R_1^\circ \right]}{k_P[M] \left[ R_1^\circ \right] + k_t \left[ R_1^\circ \right] \left( \sum_j \left[ R_j^\circ \right] \right)} \\ &= \frac{k_P[M]}{k_P[M] + k_t \left( \sum_j \left[ R_j^\circ \right] \right)} < 1 \end{aligned} \quad [5.44]$$

This number will be easy to calculate if we have solved the system of equations [5.34] to [5.44], which means that we know the concentrations of all the radicals as a function of the variables and parameters. We will solve this problem later (see Chapter 7, section 7.4.4).

In summary, the mathematical formulation of a mechanism will provide us with the means to find the quantitative laws of evolution (extent-time, speed-time and speed-extent) as well as the influence of concentrations on speeds. The influence of temperature will only show up by making Arrhenius' law explicit on the different rate coefficients.



## Chapter 6

# Experimental Data and Calculation of Kinetic Laws of Heterogeneous Reactions

Although heterogeneous reactions have the same basic equations as homogeneous reactions, they feature very different properties – mainly related to their multizone nature – and lead to very different kinetic laws and mathematical formulations of speed. Moreover, two new processes are involved:

- adsorption related to the existence of gas–solid interfaces; and
- diffusion related to the need to transport species from one zone to another.

### 6.1. Heterogeneous reactions

#### 6.1.1. Distinctive nature of heterogeneous systems

Each heterogeneous reaction exhibits several reaction zones and part of the reaction – a number of elementary steps – takes place within each of these. The sizes of these zones might vary simply because of the reaction.

An important consequence of the existence of several reaction zones is the presence of a process transporting species from one zone to another. Thus, the diffusion phenomenon is always present in the mechanism of a heterogeneous reaction.

A second consequence of the multizone nature of heterogeneous reactions is that the elementary chemical steps will most often take place in 2D zones and will therefore be characterized by surface reactivities and surface space functions.

### 6.1.2. Rate of a heterogeneous reaction

The speed of a heterogeneous reaction (or its rate) is usually an extremely complex function that depends on physico-chemical and textural variables (shapes and phase dimensions). Generally, the volumetric or areal speed cannot be defined. Despite thus, a certain number of heterogeneous reactions follow the “ $\phi E$  law”, which means that the rate can be written as a product of two functions as in the case of the elementary steps:

$$r = \phi \cdot E$$

One of these,  $\phi$ , is expressed in mol/m<sup>2</sup>/s and only depends on intensive quantities: pressure, temperature, concentrations, light intensity, electric or magnetic fields, etc. It acts as an areal speed.

The other,  $E$ , is expressed in m<sup>2</sup>/mol and only depends on the morphological characteristics of the system.

In this book, unless explicitly stated otherwise, we will only consider the case of reactions that obey  $\phi E$  law.

### 6.1.3. Different kinetic classes of heterogeneous reactions

Three families of heterogeneous reactions can be distinguished:

- reactions that occur without the creation of a new condensed phase and without a change in phase dimensions;
- reactions that occur without the creation of a new condensed phase with changes in dimensions of a solid phase; and
- reactions that occur with the creation of a new condensed phase.

#### 6.1.3.1. Reactions that occur without creation of a new condensed phase and without change in phase dimensions

In this family we have:

- catalytic reactions in which a condensed phase (usually a solid) affects the speed of a reaction that involves only a single phase without consuming the solid phase;
- gas dissolutions in which one or more gases dissolve in a liquid or solid phase.

**6.1.3.2. Reactions that occur without creation of a new condensed phase with changes in dimensions of a solid phase**

This family includes:

- stoichiometric reactions of gasification during which only gases are obtained through the transformation of a solid, for example during coal gasification or  $\text{UF}_6$  production through  $\text{UF}_4$  fluoridation;
- vaporization and sublimation transformations; and
- dissolutions of a solid into a liquid or another solid.

**6.1.3.3. Reactions that occur with the creation of a new condensed phase**

In this family there are:

– *Stoichiometric heterogeneous reactions*: these are the chemical reactions that produce a new solid  $B$  usually from a solid  $A$ , either through heating or through the action of another reactant (gas, liquid or solid). In addition to the new solid, these reactions eventually produce gases. They can be represented by the following reaction:



We classify them into three subfamilies:

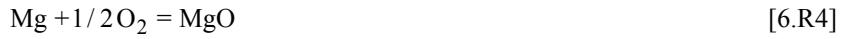
- decompositions of solids, such as the decomposition reaction of calcium carbonate, used in the industrial preparation of lime:



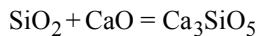
- gas-solid reactions, such as the reduction reaction of uranium oxide used in the nuclear industry:



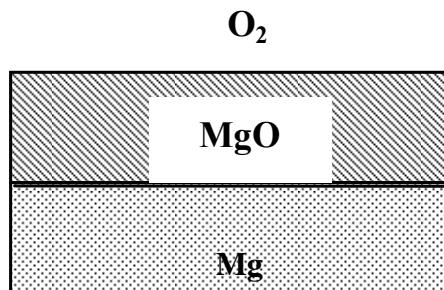
- in this category, we can also find all the oxidation reactions of metals through high temperature gases, such as magnesium oxidation:



– *Reactions between solids that produce a new solid:* such as the reaction between oxides of silicon and calcium used in the industrial manufacture of cements:



[6.R5]



**Figure 6.1.** The relative layout of phases during magnesium oxidation

A reaction, such as [6.R4] for example, does not occur as simply as described by the writing of the chemical reaction. In fact, the most elementary phenomena combine together. For instance, it can be seen in Figure 6.1 that, in order to continue, the reaction requires permanent “contact” between the reactants, which are yet separated by the solid formed.

The following will not be covered in this book:

- solid–liquid reactions that usually occur as the succession of two processes of dissolution and precipitation;
- the condensation of gases or crystallization of liquids;
- the precipitation of solids from liquids or solid solutions.

## 6.2. Experimental kinetic data of heterogeneous reactions

The experimental kinetic data of heterogeneous reactions exhibit three aspects:

- In this type of reaction, the reaction extent (or its speed) is usually measured as a function of time. The system is closed with respect to the initial solid, if it is

involved in the reaction, which is the basic constituent used to define the fractional extent.

– Influences of concentrations, which are usually partial pressures of gases, and the effect of temperature on speed are also studied, such as in homogeneous kinetics.

– Finally, the influences of the solid phase, especially of its surface, or of grain sizes in the case of powders, are also important factors.

NOTE 6.1.– In heterogeneous reactions that involve pure solids in their phase, it is not necessary to study the influence of solid concentration because this is a constant (ratio of molar mass to molar volume) that cannot be changed from one experiment to another. This does not mean that the amount of the solid phase has no influence on the speed and does not need to be studied, but rather that this quantity should not be confused with a concentration.

### **6.2.1. Catalytic reactions**

It is very important to know the influence of time during a heterogeneous catalytic reaction. This type of reaction is often assayed in an open circuit with respect to gas, under gas flux. Either time has no influence on speed or there is a decrease in the speed of reaction. The physico-chemical conditions remain constant during the experiment and we talk about the catalyst aging, which is due to several causes (see section 7.4.5).

When it is possible to compare the kinetics of a reaction both with and without a catalyst – which means that each reaction takes place at a suitable speed that can be measured under the same conditions of temperature and partial pressures by giving the same final products – different speed-concentration relationships and different temperature coefficients are obtained in both measuring conditions, proving the influence of the presence of the catalyst.

#### *6.2.1.1. Influence of partial pressures of gases*

In the presence of a catalyst, different types of speed-partial pressure relationships are obtained. In order to examine them, we consider two types of reactions to one or more reagents.

##### *6.2.1.1.1. Case of reactions with a single reactant*

This reaction is represented through:



Expressions that are apparently very different are identified. We get a speed without influence of partial pressures, such as:

$$-\frac{dP_A}{dt} = \text{Const} \quad [6.1]$$

A speed proportional to the pressure of the reactant gas (first order):

$$-\frac{dP_A}{dt} = kP_A \quad [6.2]$$

or of first order with respect to the reactant and minus first order with respect to a gas product:

$$-\frac{dP_A}{dt} = \frac{kP_A}{P_j} \quad [6.3]$$

Homographic laws with the pressure of the reactant are also encountered:

$$-\frac{dP_A}{dt} = \frac{k_1 P_A}{1 + k_2 P_A} \quad [6.4]$$

that are of the first order with respect to the reactant and decrease with the pressure of a gas product:

$$-\frac{dP_A}{dt} = \frac{k_1 P_A}{(1 + k_2 P_j)^2} \quad [6.5]$$

It will be seen that these relationships are specific forms of a more general expression if we neglect some terms:

$$-\frac{dP_A}{dt} = \frac{k_1 P_A}{(1 + k_2 P_j)} \quad [6.6]$$

## 6.2.1.1.2. Case of reactions with two reactants

Here, the reactions will be written as follows:



Orders	Laws of the family [6.7]	Laws of the family [6.8]
Order 1 – 1	$kP_A P_B$	$kP_A P_B$
No order	$\frac{k_1 P_A}{(1 + k_2 P_A)^2}$	$\frac{k_1 P_A}{1 + k_2 P_A}$
Order 1 and -1 or 0 and 1	$k \frac{P_A}{P_B}$	$kP_B$
Complex	$\frac{k_1 P_A P_B}{(P_A + k_2 P_B)^2}$	
Influences of products	$\frac{kP_A P_B}{(P_i)^2}$	$\frac{kP_A P_B}{P_j}$

**Table 6.1.** Examples of the speed laws of a catalytic reaction with two gaseous reactants

The results of such reactions are very diverse. These relationships appear to belong to two families of functions. One of them, subject to various approximations, is derived from:

$$-\frac{dP_A}{dt} = \frac{k_1 P_A P_B}{\left(1 + \sum_i k_i P_i\right)^2} \quad [6.7]$$

The others can be obtained through the function given by:

$$-\frac{dP_A}{dt} = \frac{kRTS}{Vs} \frac{K_A P_A P_B}{1 + \sum_i K_i P_i} \quad [6.8]$$

Table 6.1 gathers examples of laws obtained with two gas reactants.

#### 6.2.1.2. *The catalyst surface*

Generally, absolute speeds are proportional to the catalyst area. This surface is the real area, including pore walls (and not the outer area of the solid). It is called the specific area (measured in m<sup>2</sup>/gram of the catalyst).

This proportionality of speed with catalyst initial area often disappears with time, either because the specific area decreases (coalescence of the catalyst) or a portion of the area no longer seems active for the reaction (catalyst poisoning).

#### 6.2.2. *Stoichiometric heterogeneous gas–solid reactions*

In heterogeneous kinetics with the creation of a new condensed phase, it is common to present experimental results under various equivalent forms. Thus there will be: data of the fractional extent (restricted to a solid reactant) as a function of time and data of the rate (or speed) versus the fractional extent as a function of intensive variables such as partial pressures of gases and temperature, versus the powder grain sizes forming one of the solid reactants. We will now quickly provide an outline of the results commonly obtained.

##### 6.2.2.1. *$\phi E$ law for heterogeneous reactions*

We have seen that for the heterogeneous reactions we use the  $\phi E$  law. For the moment we will only consider the stoichiometric reactions for which the space

function depends on the fractional extent of the reaction alone and is independent of any other variable. This assumption will be abandoned in Chapter 14. We will thus have:

$$\frac{d\alpha}{dt} = \phi(T, P_i).E(\alpha) \quad [6.9]$$

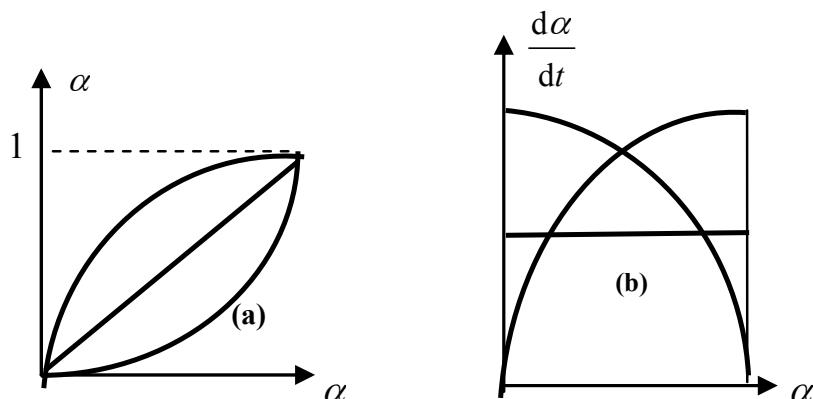
#### 6.2.2.2. Fractional extent – time and speed – fractional extent curves

Within the framework of the reactions studied here, speed is a monotonic function of fractional extent (or time), see Figure 6.2b. It is continuously increasing, continuously decreasing or constant. The corresponding kinetic curves, see Figure 6.2a, therefore curve upwards, downwards or are in straight lines.

For these curves with monotone speed, different laws have been proposed. Among the best known are linear law with constant speed [6.10] and the parabolic law [6.11] for plane solid samples:

$$\alpha = kt \text{ or } \frac{d\alpha}{dt} = k \quad [6.10]$$

$$\alpha^2 = kt \text{ or } \frac{d\alpha}{dt} = \frac{k}{2\alpha} \quad [6.11]$$



**Figure 6.2.** General paces of kinetic and speed curves for stoichiometric heterogeneous reactions

The law known as the “shrinking core” for powders that consist of spherical grains of equal size is written as follows:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^{2/3} \quad [6.12]$$

A number of laws, like the shrinking core, appear in the following more general form:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad [6.13]$$

In these different expressions,  $k$  is a quantity that depends on the temperature (usually under the Arrhenius form) and partial pressures of gases.  $n$  takes different values: 1, 1/2, 2/3, etc. In fact, by referring to relation [6.9] we see that we follow the variations of the space function  $E$  and that:

$$k = \phi \quad [6.14a]$$

NOTE 6.2.— Exponent  $n$  of equation [6.13] should never be confused with a reaction order, which is defined by speed-concentration relationships and not speed-fractional extent. It is the same for coefficient  $k$ , which can be called a kinetic coefficient. It should not be confused with a speed coefficient. Hence there are some cases where Arrhenius’ law is not followed.

#### 6.2.2.3. Variations of speed with intensive variables

By considering relation [6.9], the intensive variables are those of the function  $\phi$ . For thermal decomposition, a decreasing influence of pressure on speed is often highlighted. It is rightly attributed to what might be called the thermodynamic-type influence: the speed decreases with the pressure of the gas product until it reaches a null value for the equilibrium pressure.

Some influences, of catalytic type, are occasionally attributed to steam, even though this is not a main component of the reaction. For reactions between a gas and a solid, it has been reported that the influences of partial pressure are extremely varied, ranging from no influence to homographic influences of the pressure or its square root with expressions such as:

$$\frac{d\alpha}{dt} = \frac{kP}{1 + k'P} \quad [6.14b]$$

$$\frac{d\alpha}{dt} = \frac{k\sqrt{P}}{1 + k'\sqrt{P}} \quad [6.15]$$

Some reactions have been reported that have an order with respect to the gas, but these orders are often very fractional (1/4, 1/6, etc.). We can, however, say that the notion of order has been completely dropped in heterogeneous kinetics due to the low number of cases encountered.

To sum up, studies of the influence of partial pressures of gases are crucial for understanding the mechanisms of a reaction, such as the influence of the concentrations of reactants and products in homogeneous kinetics.

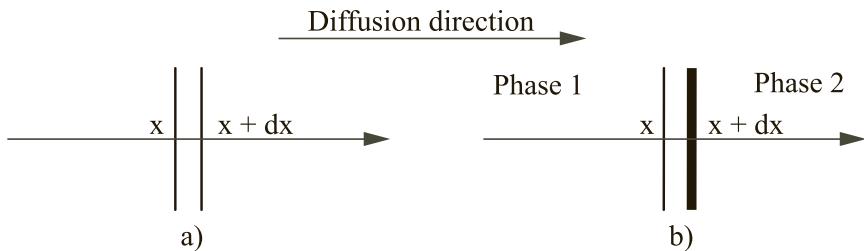
With regards to the influence of temperature, Arrhenius' law generally provides a correct result, at least within a sufficiently small interval of temperature, and allows us to assign a temperature coefficient for wider intervals a change in the law of variation of the reactivity  $\phi$  with pressure is often reported, along with a change in the temperature coefficient from one range of temperature to another.

#### 6.2.2.4. Influence of the shape and sizes of the solid reactant

For powder samples, the shape and size of the grains are of very high importance in kinetic or speed laws. If the assumption of proportionality of the space function to the surface of an interface at any moment is accepted, the shape of the solid samples often determines the form of variation of speed with fractional extent, as shown by the comparison of the two relations [6.10] and [6.12]. Coefficient  $n$ , which appears in the general form in [6.13], is partly due to the shape of the solid sample.

### 6.3. Involvement of diffusion in matter balances

In homogeneous reactions, the laws were obtained by establishing a global balance of species, which only involves reactions. Following the localization of phenomena, the study of heterogeneous systems requires the establishment of local balances resulting from reactions and diffusions. We therefore wish to locally establish the balance of a component subjected to several reactions and diffusion.



**Figure 6.3.** Volume of an element with diffusion: a) at the center; b) near an interface

This is performed by considering a portion (slice) of the volume located in the phase in which the component belongs. Within this slice, chemical reactions and diffusion in a normal direction occur. We should distinguish two cases depending on whether the slice is at the center of a volume zone (Figure 6.3a) or near an interface, i.e. in a 2D zone (Figure 6.3b).

### 6.3.1. Balance in a slice of a volume zone

A slice of thickness  $dx$  and surface  $S$  is located at the center of the phase in which component  $X$  belongs (Figure 6.3a).

The balance of  $X$  consists of two types of terms:

- The source terms that are provided during the time  $dt$  by the speeds of chemical reactions that involve  $X$  in the slice. In each reaction  $\rho$  in which  $X$  is involved, its algebraic stoichiometric coefficient is  $v_\rho$  (which might be null if  $X$  is not involved in the corresponding reaction).
- The exchange terms that are due to diffusion across the surfaces that limit the volume element. The flux diffusion is  $J_x$  at entry at the point of abscissa  $x$  and  $J_{x+dx}$  at the exit at the  $x+dx$  point of the abscissa.

The balance, which reflects the variation of the amount of  $X$  that is contained in the slice during time  $dt$ , can thus be written as follows:

$$\frac{\partial \{X\}}{\partial t} = \sum_{\rho} v_{\rho} (v_a)_{\rho} + (J_x - J_{x+dx}) S \quad [6.16]$$

The sum of the second member is extended to all the independent reactions that take place in the slice.

The mean value theorem enables us to write:

$$J_{x+\delta x} = J_x + \left( \frac{\partial J_x}{\partial x} \right)_x dx \quad [6.17]$$

and the balance relation becomes:

$$\frac{\partial \{X\}}{\partial t} = \sum_{\rho} v_{\rho} (v_a)_{\rho} - \left( \frac{\partial J_x}{\partial x} \right)_x S \cdot dx$$

and by using Fick's first law [3.32], we introduce the second derivative of the concentration:

$$\frac{\partial \{X\}}{\partial t} = \sum_{\rho} v_{\rho} (v_a)_{\rho} + \left( \frac{\partial^2 [X]}{\partial x^2} \right)_x S \cdot dx \quad [6.18]$$

This balance can also be expressed from the concentration of  $X$ . Here, we obtain:

$$\frac{\partial [X]}{\partial t} = \frac{1}{V} \cdot \frac{\partial \{X\}}{\partial t} - \frac{\{X\}}{V^2} \frac{dV}{dt} = \frac{1}{V} \cdot \frac{\partial \{X\}}{\partial t} - \frac{[X]}{V} \frac{dV}{dt} \quad [6.19]$$

hence:

$$\frac{\partial [X]}{\partial t} = \sum_{\rho} v_{\rho} \frac{(v_a)_{\rho}}{S \cdot dx} - \left( \frac{\partial J_x}{\partial x} \right)_x - \frac{[X]}{V} \frac{dV}{dt} \quad [6.20]$$

and by using Fick's first law and the volumetric speeds, we obtain:

$$\frac{\partial [X]}{\partial t} = \sum_{\rho} v_{\rho} (v)_{\rho} + D \left( \frac{\partial^2 [X]}{\partial x^2} \right)_x - \frac{[X]}{V} \frac{dV}{dt} \quad [6.21]$$

The term  $dV/dt$  reflects the variation in size of the zone during the progress of all the reactions.

### 6.3.2. Balance in a 2D zone

A slice of thickness  $dx$  is located following the indication of Figure 6.3b near an interface inside phase 1 in which component  $X$  exists.

We reason in the same way as previously, except that in the exchange term there is no diffusion flux across the direction normal to the surface at  $x + dx$ . If a chemical species passes through the interface, it is no longer the same component that is on the other side: the interface's traversal is actually a reaction of disappearance of the component from the inside the slice, which is a source term. Therefore, instead of [6.18], we will obtain:

$$\frac{\partial \{X\}}{\partial t} = \sum_{\rho} v_{\rho} (v_a)_{\rho} - J_{xx} S \quad [6.22]$$

By using Fick's first law, we get:

$$\frac{\partial \{X\}}{\partial t} = \sum_{\rho} v_{\rho} (v_a)_{\rho} + D \frac{\partial [X]}{\partial x} S \quad [6.23]$$

In terms of volume concentration, if  $a = \delta x$  denotes a length of the order of magnitude of the mesh parameter, by using [6.19] we will obtain:

$$\frac{\partial [X]}{\partial t} = \sum_{\rho} v_{\rho} \frac{(v_a)_{\rho}}{aS} - \frac{J_x}{a} - \frac{[X]}{S} \frac{dS}{dt} \quad [6.24]$$

By making the flux expression explicit through the Fick's first law [3.32] and by introducing the areal speeds (i.e. per unit of area), we obtain:

$$\frac{\partial [X]}{\partial t} = \sum_{\rho} v_{\rho} \frac{(v)_{\rho}}{a} + \frac{D_x}{a} \frac{\partial [X]}{\partial x} - \frac{[X]}{S} \frac{dS}{dt} \quad [6.25]$$

We can also reason in terms of surface concentration defined by:

$$[X]_s = \frac{\{X\}}{S} = a[X] \quad [6.26]$$

We obtain:

$$\frac{\partial([X]_s)}{\partial t} = \sum_{\rho} v_{\rho} (v_a)_{\rho} - J_x - \frac{[X]_s}{S} \frac{dS}{dt} \quad [6.27]$$

so by bringing up the areal speeds of reactions and by making the flux explicit through Fick's first law [3.32], we get:

$$\frac{\partial([X]_s)}{\partial t} = \sum_{\rho} v_{\rho} [(v)]_{\rho} + \frac{D}{e} \frac{\partial[X]}{\partial x} - \frac{[X]_s}{S} \frac{dS}{dt} \quad [6.28]$$

### 6.3.3. Application of balances to the elementary steps of a sequence of reactions

The previous relations can be applied when all of the reactions involved consist of elementary steps. Here, we just need to make the expression of absolute speeds explicit through volume or surface reactivities and space functions. In this instance, [6.18] and [6.22] become:

– in volume:

$$\frac{\partial\{X\}}{\partial t} = n_0 \sum_{\rho} v_{\rho} \phi_{\rho} E_{\rho} + D \left( \frac{\partial^2 [X]}{\partial x^2} \right)_x S \cdot dx \quad [6.29]$$

– and at an interface:

$$\frac{\partial\{X\}}{\partial t} = n_0 \sum_{\rho} v_{\rho} \phi_{\rho} E_{\rho} + \frac{\partial[X]}{\partial x} S \quad [6.30]$$

By using expressions [3.44] and [3.45], the latter relationship can finally follow a very general form for steady state diffusions:

$$\frac{\partial\{X\}}{\partial t} = n_0 \sum_{\rho} v_{\rho} \phi_{\rho} E_{\rho} \quad [6.31]$$

### 6.3.4. Application to Fick's second law

If we consider the case of the volume zone of constant sizes, but without any chemical reaction, relation [6.21] gives:

$$\frac{\partial[X]}{\partial t} = D \frac{\partial^2[X]}{\partial x^2} \quad [6.32]$$

This relation is Fick's second law of diffusion, which is discussed in section 3.7.2.1.

## 6.4. Example of mathematical formulation of a heterogeneous catalytic reaction

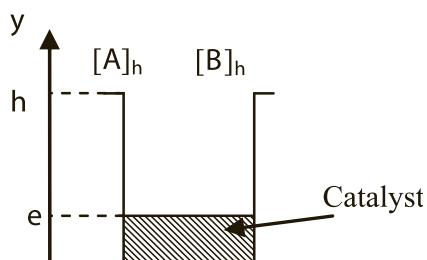
Thus, let us consider the reaction of gas *A* that turns into gas *B* (such as an isomerization) catalyzed by a solid in a closed system at constant temperature:



As the reaction takes place in a closed reactor, the catalyst is contained in the bottom of an air crucible with base *S* and height *h*. The catalyst forms a regular pile of height *e* (see Figure 6.4). The reaction is monitored through measurement of the concentration of product *B* formed in the reactor near the exit of the crucible.  $[B_h]$  will denote this concentration, which in practical terms is the one that prevails throughout the reactor outside the crucible. The system temperature is kept constant.

A heterogeneous catalytic reaction usually includes two reaction zones:

- the diffusion zone between the catalyst and an adequate distance in the reactor where the concentrations are uniform; and
- an adsorption zone and reaction on the catalyst surface.



**Figure 6.4. Catalytic reaction in a reactor**

In these two zones, three groups of steps usually take place: the diffusions of reactants and products of the catalyst towards the exterior or the interior, adsorptions and desorptions of gas (or solutes) at the surface of the catalyst – the catalytic act – which is the chemical reaction itself, at the contact the catalyst.

In our specific case we will consider five elementary steps:

– diffusion of reactant  $A$  from the top of the crucible, where we assume that the partial pressure no longer depends on coordinates of the space in the rest of the reactor up to the surface:



– adsorption of reactant  $A$  on sites  $s$  of the catalyst, which will be written as follows:



– a chemical reaction that transforms  $A$  in the adsorbed phase into  $B$  in the adsorbed phase, which will be written as follows:



– desorption of product  $B$  according to:



– diffusion of  $B$  towards the top of the crucible:



If  $\theta_A$  and  $\theta_B$  denote the surface fractions covered by  $A$  adsorbed and  $B$  adsorbed, respectively, the reactivity of each of the steps except diffusion is:

$$\phi_2 = k'_2[(A)_e](1 - \theta_A - \theta_B) - k''_2 \theta_A \quad [6.33]$$

$$\phi_3 = k'_3 \theta_A - k''_3 \theta_B \quad [6.34]$$

$$\phi_4 = k'_4 \theta_B - k''_4 [(B)_e](1 - \theta_A - \theta_B) \quad [6.35]$$

It should be noted that we assumed that the molecules of *A* and *B* are located at the same surface sites; a contrary assumption could be envisaged and is actually encountered.

The rate coefficients are calculated per area unit and, thus, conventional rate coefficients are multiplied by the “thickness” of surface (*a*), which is invariable.

For diffusions, we dispose of both Fick’s laws for species *A* and *B*:

$$J_A = -D_A \frac{\partial [A]}{\partial y} \quad [6.36]$$

$$\frac{\partial [A]}{\partial t} = D_A \frac{\partial^2 [A]}{\partial y^2} \quad [6.37]$$

$$J_B = -D_B \frac{\partial [B]}{\partial y} \quad [6.38]$$

$$\frac{\partial [B]}{\partial t} = D_B \frac{\partial^2 [B]}{\partial y^2} \quad [6.39]$$

NOTE 6.3.— Volume concentration is related to surface concentration through the “thickness” of the surface (*a*), which is invariable:

$$[X]_s = [X].a \quad [6.40]$$

Let us write the balances of the different species using [6.27] without surface variation. At the catalyst surface:

$$\frac{\partial ([A]_e)_s}{\partial t} = -\phi_2 + \frac{D_x}{a} \left( \frac{\partial ([A]_e)}{\partial y} \right)_e \quad [6.41]$$

We will see that the surface of the two zones does not change with time. We can thus work per surface unit with a null volume and zone surface variation, hence the balances in surface concentrations are:

$$\frac{d\theta_A}{dt} = \phi_2 - \phi_3 \quad [6.42]$$

$$\frac{d\theta_B}{dt} = \varphi_3 - \varphi_4 \quad [6.43]$$

$$\frac{d[(B)_e]_s}{dt} = \varphi_4 - D \frac{\left( \frac{\partial[(B)_e]}{\partial y} \right)_e}{e} \quad [6.44]$$

We can add the closure condition of the system, which reflects the conservation of species:

$$\{A\}_0 = \left| \int_e^h \frac{\partial[A]}{\partial y} dy \right| + \{A-s\} + \{B-s\} + \left| \int_e^h \frac{\partial[B]}{\partial y} dy \right| \quad [6.45]$$

Speed is measured through the production of  $B$  away from the catalyst:

$$v = \frac{d[(B)_h]_s}{dt} = \frac{D}{e} \left| \left( \frac{\partial[(B)_h]}{\partial y} \right)_h \right| \quad [6.46]$$

The resolution of the system of equations [6.33] to [6.46] enables us to express, at a given temperature, the speed as a function of time, initial concentration of the reactant  $A$  and various rate and diffusion coefficients. The complexity of all these equations will lead us to detail different modes that will often enable us to simplify the mathematical aspect of the problem, as discussed in Chapter 7.

## 6.5. Example of the mathematical formulation of an evolution process of a phase

We will give the simplified mechanism of the evolution process of magnesium oxide in the oxidation reaction of a magnesium plate as an example (see Figure 6.6). The thickness of the magnesium plate is negligible compared to size of the top and bottom, so oxidation of the smaller faces becomes insignificant. Magnesium oxide is produced by oxygen gas in isothermal conditions and under a constant pressure  $P$  of pure oxygen. The overall reaction is:



Given relation [6.9], we will divide the modeling process into two parts:

- a physico-chemical modeling of  $\phi$  by using a reaction mechanism as in homogeneous kinetics to model an areal speed;
- modeling of the space function that will take into account the shape of the sample.

We will only consider the example discussed at the first modeling and we will return to the dual modeling in Chapter 8 (section 8.1.5.2.5).

Magnesium oxide is formed at the metal surface in a uniform layer that is infinitely thin from the initial instant and grows perpendicularly to the surface.

Magnesium oxide consists of two types of sites that are not normally empty in the perfect crystal: divalent magnesium ions and oxygen ions. The building unit is composed of:  $\text{Mg}_{\text{Mg}}$  and  $\text{O}_{\text{O}}$ . This oxide admits a sub-stoichiometry in oxygen in the form of oxygen vacancies (see Appendix 1), which are assumed to be neutral: the defect is thus composed of the entity denoted  $V_{\text{O}}$ .

The mechanism can be written in four steps using Kröger's notation (see Appendix 1):

- at the surface of the dioxide formed, we have the dissociative adsorption of oxygen on sites  $s$  according to:



- at the outer interface, oxygen vacancies (which will be formed at the inner interface) react with this oxygen, which is adsorbed according to:



- oxygen vacancies diffuse from the inner interface toward the outer interface:



- oxygen vacancies are formed from the metal at the inner interface, as follows:



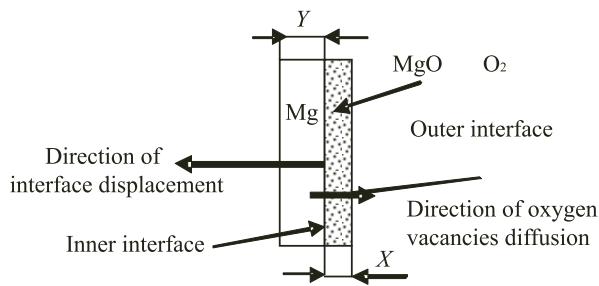
The network of the metal is destroyed at the inner interface and the network construction of the new phase occurs at this same interface. The latter therefore "penetrates" the metal. It is said that the growth is with inner development (it

should be noted that this is not always the case – reactions exist for which the network of the new phase is constructed at the outer interface, which are then said to be outer development).

We verify that, after multiplying equation [6.R4a] by  $\frac{1}{2}$  and summing the four steps, we obtain the overall reaction [6.R4], with the disappearance of intermediate species.

We will only consider systems operating in an open environment under constant pressure with respect to gas with constant concentrations and closed with respect to the solid.

We consider the case in which a plate of initial thickness  $e_0$  and of unit area is attacked (see Figure 6.5).



**Figure 6.5.** Attack on a plate of magnesium

### 6.5.1. Balance of intermediates

These balances are derived from the general form of equation [6.22]. There are as many equations as there are intermediate, thus five in our example.

$\phi_i$  will denote the surface reactivity of reaction  $i$  and  $J$  will denote the flux of oxygen vacancies – it can be taken at the inner ( $i$ ) or outer ( $e$ ) interface. The amounts of the various intermediates are taken at the inner ( $i$ ) or outer ( $e$ ) interface of areas  $S_i$  and  $S_e$ .

We thus have three equations: two at the outer surface [6.47] and [6.48]; and one [6.49] at the inner interface:

$$\frac{d\{O-s\}}{dt} = (2\phi_1 - \phi_2)S_e \quad [6.47]$$

$$\frac{d\{(V_O)_e\}}{dt} = (J_e - \phi_2)S_e \quad [6.48]$$

$$\frac{d\{(V_O)_i\}}{dt} = (\phi_4 - J_i)S_i \quad [6.49]$$

### 6.5.2. Expressions of the reactivities of elementary chemical steps

The reactivities of elementary reactions can be obtained through the application of van 't Hoff's principle, with  $\theta$  being the degree of recovery of oxygen adsorbed and  $P$  being the pressure of this gas. In our case, there are three reactivities and they are written as follows:

$$\phi_1 = k'_1(1 - \theta)^2 P \left\{ 1 - \frac{\theta^2}{K_1(1 - \theta)^2 P} \right\} \quad [6.50]$$

$$\phi_2 = k'_2 \theta [V_O]_e \left\{ 1 - \frac{(1 - \theta)}{K_2 \theta [V_O]_e} \right\} \quad [6.51]$$

$$\phi_4 = k'_4 \left\{ 1 - \frac{[V_O]_i}{K_4} \right\} \quad [6.52]$$

### 6.5.3. Expressions of the concentrations of species at the interfaces

In our example we have two expressions that help us to write that each concentration is the ratio of the amount of substance to the volume:

$$[V_O]_e = \frac{\{V_O\}_e}{a.S_e} \quad [6.53]$$

$$\left[ V_O \right]_i = \frac{\{V_O\}_i}{a.S_i} \quad [6.54]$$

#### 6.5.4. Diffusion equations of the defects

$C$  will denote the concentration in oxygen vacancies at  $x$ , which depends on  $x$ , and the time.  $D$  will denote the diffusion coefficient of oxygen vacancies, which is assumed to be constant. Given the geometry of the system, we use the flux expression according to Fick's first law:

$$J = - D \cdot \frac{\partial C}{\partial x} \quad [6.55]$$

From Fick's second law in the dioxide layer, we obtain:

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2} \quad [6.56]$$

The application of this expression to the concentration at the inner and outer interfaces enables us to calculate the concentrations of species at the interfaces:

$$\left[ V_O \right]_i = C(Y) \quad [6.57a]$$

and:

$$\left[ V_O \right]_e = C(Y+X) \quad [6.57b]$$

From the application of the flux functions to the inner and outer interfaces, we obtain:

$$(J)_i = J_Y \quad [6.58a]$$

$$(J)_e = J_{Y+X} \quad [6.58b]$$

### 6.5.5. Expressions of the variations in sizes of the zones involved in the reaction

The new phase is produced through step [6.R4d] at the inner interface and penetrates into the first phase (see Figure 6.5). With  $V_M$  being the molar volume of the oxide, let us write the volume of the former phase consumed during the time  $dt$ :

$$s dY = -V_M \phi_4 s dt \quad [6.59]$$

Let us write that the ratio between the volume of the oxide formed and the volume of the metal from which it is derived is the expansion coefficient  $z$ :

$$sX = z(s(e_0 - Y)) \quad [6.60]$$

The areas of the inner and outer surfaces each have the value of  $1 \text{ m}^2$  ( $s = 1$ ).

### 6.5.6. Evolution law of the rate chosen to characterize the speed

We have seen that we can define as many fractional extents and rates as the number of components that are present in the overall reaction.

Thus in the chosen example, the step that decays the metal is [6.R4d]. The rate with respect to reactant  $A$  (here magnesium), is therefore:

$$\frac{d\alpha_{\text{Mg}}}{dt} = \phi_4 \frac{S_i}{n_0} = \frac{\phi_4}{n_0} \quad [6.61]$$

With respect to the solid formed (magnesium oxide), the step that produces this solid is still [6.R4d] and therefore we will have the same expression as before:

$$\frac{d\alpha_{\text{MgO}}}{dt} = \phi_4 \frac{S_i}{n_0} = \frac{\phi_4}{n_0} \quad [6.62]$$

The rate with respect to the gas (oxygen) takes a different form, however, because this gas is consumed through step [6.R4a], thus the corresponding rate will be:

$$\frac{d\alpha_{\text{O}}}{dt} = \phi_1 \frac{S_e}{n_0} = \frac{\phi_1}{n_0} \quad [6.63]$$

The resolution of one of the resulting systems of equations – depending on whether we use [6.61] [6.62] or [6.63] – enable us to calculate, through integration, one of the rates and one of the fractional extents as a function of time, oxygen pressure and temperature via the constants specific to a reaction.

NOTE 6.4.– There is no reason for the different rates to be identical and lead to the same expressions and vary in the same manner with the different variables, since we sometimes have distinct equations of definition: [6.61] or [6.62] and [6.63].

To conclude, it can be seen that the quantitative knowledge of the reaction from the mechanism requires the resolution of a system of differential equations that gives the balance of each intermediate and some of the main components. To these we can add algebraic equations that capture either the conservation of matter in a closed system or the fixed concentrations in open system. The resulting system, which is not always linear and whose rate coefficients are unknown, therefore leads to a complex problem. We are thus led to seek approximate analytical solutions by using physical assumptions that simplify the system of equations. The resulting special solution characterizes a *kinetic mode*. For a given reaction there are as many kinetic modes as there are special solutions.



## Chapter 7

# Pseudo- and Quasi-steady State Modes

We have seen that the calculation of reaction rates from mechanisms quickly led to complex systems of differential equations that cannot be solved analytically or numerically because the numerical values of the rate coefficients involved are unknown. Fortunately, in a very large number of cases, reactions occur according to permanent or quasi-permanent modes so it is possible to identify them experimentally. This simplifies the equations, thus enabling us to obtain expressions of speed that can then be compared to the experiment in order to validate the mechanisms.

Concepts of the pseudo-steady and quasi-steady states are apparently very close to one another. However the difference is fundamental. Whereas the pseudo-steady states define kinetic modes of reaction, the quasi-steady states are simple mathematical approximations. Moreover the difference is palpable in the sense that the first concept can be directly checked by the experiment independently of the kinetic law, the second is checked only by the conformity between the kinetic law speed, concentrations calculated and the experimental corresponding law. But many other factors must intervene in addition so that these two laws coincide, in particular a correct choice of the mechanism of the reaction.

### 7.1. Pseudo-steady state mode

#### 7.1.1. *Definition*

A mode is said to be in pseudo-steady state if the amount of each of the intermediates remains small compared to the amounts of the principal components

of the reaction and if this amount hardly varies with time. Therefore, the pseudo-steady state mode will be defined through two conditions:

$$\frac{d\{X_i\}}{dt} \approx 0 \quad \text{and} \quad \{X_i\} \text{ small} \quad \forall i \quad [7.1]$$

We have already seen in Figure 5.2 that these conditions are roughly met for our reference reaction [5.R7] for the chosen values of speed coefficients.

Such a mode would not be a good approximation at the reaction start and end, because neither of the two conditions [7.1] will be met in a closed system. At the reaction start, the intermediaries that are not at the origin appear and therefore their concentration is not constant and negligible compared with that of the products. Likewise these intermediates should vanish at the reaction end. We will see that these conditions are often acceptable, however, with respect to measurement accuracy.

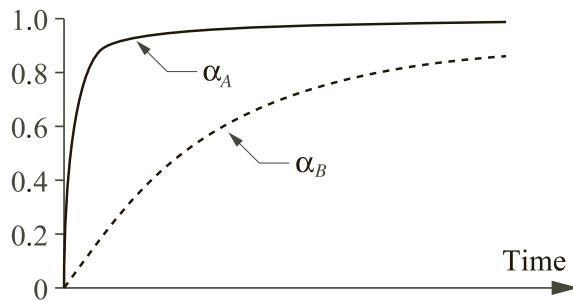
### 7.1.2. *Uniqueness of the reaction speed in pseudo-steady state mode*

When we have written that the extent of the reaction follows relation [1.3], the latter does not depend on the chosen component. This implies that the extent of the reaction does not depend on the component chosen to define it, which means that the stoichiometry relation among the components can be observed at any time. This is strictly true if the reaction occurs in a single step (in the case of elementary steps). If several steps are involved, however, during a given time period there can be accumulation (positive or negative) of one or more intermediates which will lead to the non-compliance of the stoichiometry relation among the main components of the reaction. Therefore, the speed will depend on the component chosen to define it, as we have already noted in the conclusions of section 5.2 (Chapter 5) and shown in Figure 7.1, which for certain values of the rate coefficients for our reference reaction [5.R7], gives different extents depending on whether the fractional extent is defined from the concentrations of reactant *A* or the amount of product *B*.

If the system is in the pseudo-steady state mode, every intermediate will be at a constant amount over time and therefore the stoichiometry relation will be preserved throughout the reaction. Thus, we can state the following theorem:

**THEOREM 7.1.**— The extent and speed of a reaction in pseudo-steady state mode is independent of the component chosen to define them.

Following this theorem, we can talk about the extent and speed of a reaction in pseudo-steady state conditions. In other cases the definition of these quantities must be specified and we usually obtain speeds that depend on the component chosen to define it.



**Figure 7.1.** Differences among extent curves depending on the component it is defined from

### 7.1.3. Linear sequences in pseudo-steady state modes

We will demonstrate two properties of linear sequences in pseudo-steady state modes.

For this we will use a linear sequence containing intermediates  $X_1, X_2 \dots X_i$  produced by steps 1, 2 ...  $i$  succeeding one another to yield a reaction that produces  $B$  from  $A$ .

#### 7.1.3.1. Multiplying coefficients and elimination of intermediates

It is known that a linear combination of all steps should eliminate the intermediate species, since they do not exist at the beginning or end of the reaction. In this linear combination, step  $\rho$  is weighted by a coefficient  $\lambda_\rho$ , which is called the multiplying coefficient of step  $\rho$ .

Since there is an elimination of intermediates, for a component  $X_i$  weighted by the stoichiometric algebraic coefficient  $v_{i,\rho}$  in the  $\rho$ -th step we should therefore have:

$$\sum_{\rho} v_{i,\rho} \lambda_{\rho} = 0 \quad [7.2]$$

In fact there is an infinite series of multiplying coefficients, all proportional to each other. For the main component  $A$  whose algebraic stoichiometric coefficient in the overall reaction is  $v_A$ , the following relation should be respected:

$$\sum_{\rho} v_{A,\rho} \lambda_{\rho} = v_A \quad [7.3]$$

#### 7.1.3.2. Equality of speeds law for linear pseudo-steady state sequences

We will prove the following theorem.

**THEOREM 7.2.**— In the pseudo-steady state mode of a linear sequence, the rates of two arbitrary steps are proportional to each other and the proportionality ratio is the inverse of the ratio of their multiplying coefficients.

Let us prove the *direct theorem* by writing the balance for each of the intermediates (by applying relation [5.11] to this intermediate) and let us prove that this balance is zero in order to apply the pseudo-steady state, for instance, to the intermediary  $X_i$  produced by step  $i$  and consumed by step  $i + 1$ :

$$\frac{d\{X_i\}}{dt} = (\beta_{i,i}\phi_i E_i - \beta_{i,i+1}\phi_{i+1}E_{i+1}) n_0 = 0 \quad [7.4]$$

Where  $\lambda_i$  is the multiplying coefficient of step  $i$ , the application of relation [7.1] leads to:

$$\lambda_i \beta_{i,i} = \lambda_{i+1} \beta_{i,i+1} \quad [7.5]$$

By combining [7.4] and [7.5], we can calculate:

$$\phi_1 E_1 = \frac{\beta_{1,2}}{\beta_{1,1}} \phi_2 E_2 = \frac{\lambda_1 \phi_2 E_2}{\lambda_2} \quad [7.6]$$

from which we deduce:

$$\frac{1}{\lambda_1} \phi_1 E_1 = \dots = \frac{1}{\lambda_i} \phi_i E_i = \dots = \frac{1}{\lambda_n} \phi_n E_n = \frac{1}{\lambda_{n+1}} \phi_{n+1} E_{n+1} \quad [7.7]$$

which proves the theorem.

Let us now examine the *reciprocal*. Let us assume that all the absolute speeds are proportional to each other, which means that we have:

$$\frac{1}{\lambda_1} \phi_1 E_1 = \dots = \frac{1}{\lambda_i} \phi_i E_i = \dots = \frac{1}{\lambda_n} \phi_n E_n \quad [7.8]$$

Let us apply [7.8] to the balance of species  $X_i$ :

$$\frac{d\{X_i\}}{dt} = (\beta_{i,i} \phi_i E_i - \beta_{i,i+1} \phi_{i+1} E_{i+1}) n_0 = \phi_i E_i (\beta_{i,i} \lambda_i - \beta_{i,i+1} \lambda_{i+1}) n_0 \quad [7.9]$$

According to [7.5], the last members of the equalities of this type are zero regardless of  $i$  and the mode is in pseudo-steady state, which shows our reciprocal.

Thus, in pseudo-steady state conditions, for a linear mode we obtain:

$$\frac{\phi_\rho E_\rho}{\lambda_\rho} = \text{Const} \quad [7.10]$$

This theorem is sometimes called the equality of speeds theorem because we notice that if all the multiplying coefficients are equal, then the rates and thus the speeds of elementary steps are equal.

#### 7.1.3.3. Reaction speed of a linear sequence in pseudo-steady state mode

Let us reconsider expression [5.11] for the balance of  $A$ . By taking into account [7.10] we obtain:

$$\frac{d\{A\}}{dt} = v_a v_A = \phi_k E_k n_0 \sum_\rho \frac{v_{A,\rho} \lambda_\rho}{\lambda_k} = \frac{\phi_k E_k}{\lambda_k} n_0 \sum_\rho v_{A,\rho} \lambda_\rho \quad [7.11]$$

and by utilizing [7.5], it becomes:

$$v_a = \frac{\phi_k E_k}{\lambda_k} n_0 \quad [7.12]$$

or for the rate:

$$r = \frac{\phi_k E_k}{\lambda_k} \quad [7.13]$$

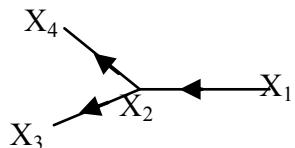
we can therefore state the following theorem.

**THEOREM 7.3.**— The rate of a reaction with a linear mechanism in pseudo-steady state mode is the product of the reactivity of any of its steps times the space function of that step divided by the multiplying coefficient of that step.

**NOTE 7.1.**— In the case of heterogeneous systems that may possibly involve diffusion, let us recall that the space function involves the shape factor  $G$ , which equals one for a reaction and is given by [3.38] for a unidirectional diffusion.

#### 7.1.4. Multipoint sequences in pseudo-steady state mode

Let us now consider a sequence containing a multiple point (see Figure 7.2) that involves four intermediates through the following four steps [7.R1a] to [7.R1d]:



**Figure 7.2. Multipoint sequence**



We see, for example, that intermediate  $X_2$  is produced by reaction [7.R1b] and consumed by two steps: [7.R1c] and [7.R1d].

##### 7.1.4.1. Equality of speeds law for pseudo-steady state multipoint sequences

Let us now examine the conditions of pseudo-steady state. Since the mechanism is no longer linear, we cannot apply the equality of speeds theorem. The mass balances of the intermediates should be cancelled out as follows:

$$\frac{d\{X_2\}}{dt} = n_0 [\beta_{2,2}\phi_2 E_2 - (\beta_{2,3}\phi_3 E_3 + \beta_{2,4}\phi_4 E_4)] = 0 \quad [7.14]$$

however, according to the elimination rule:

$$\beta_{2,2}\lambda_2 = \beta_{2,3}\lambda_3 = \beta_{2,4}\lambda_4$$

so we deduce:

$$\frac{\phi_2 E_2}{\lambda_2} = \frac{\phi_3 E_3}{\lambda_3} + \frac{\phi_4 E_4}{\lambda_4} \quad [7.15]$$

This result is equivalent to the equality of speeds theorem for multiple points.

#### 7.1.4.2. Reaction speed with a multipoint sequence in pseudo-steady state mode

Let us calculate the contribution of the multipoint sequence to the speed of disappearance of reactant  $A$ . From relation [5.11], we obtain:

$$\frac{d\{A\}}{dt} = n_0 (v_{A,2}\phi_2 E_2 + v_{A,3}\phi_3 E_3 + v_{A,4}\phi_4 E_4) \quad [7.16]$$

The pseudo-steady state condition will be expressed by equation [7.14] and we shall take into account that, for the entire reaction, the law of definition of multiplying coefficients [7.3] should be met for each linear sequence.

#### 7.1.5. Experimental research into the pseudo-steady state

Given the simplification introduced by the pseudo-steady state modes, it is important to know experimentally whether such a mode is acceptable for the reaction studied given the precision of experimental data, and this by setting apart any idea about mechanisms. Therefore, the method of two speed measurements is used.

##### 7.1.5.1. Principle of the method

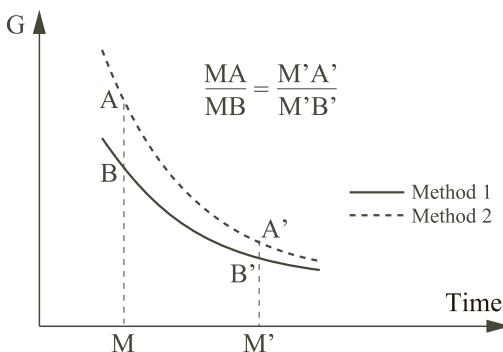
This principle involves using the unique property of the extent or speed of pseudo-steady state (see section 7.1.2) by measuring one of these quantities using two different methods, including the largest number of elementary steps. At least one of these methods is the technique usually used for the study of kinetics. In order to choose these two methods, it is suggested we use the monitoring technique of the chosen reaction, on one hand, and calorimetry, on the other hand, because the

reaction speed expression through calorimetry includes all the elementary steps that feature an enthalpy, which means the greatest number. The choice of the methods used to monitor the reaction enables us to test the confidence interval of this technique and thus to make the test consistent with experimental precision. If the test is positive, it means that a pseudo-steady state mode will be sufficiently good to describe the evolution of the system studied.

NOTE 7.2.— We have seen (see section 4.3) that Bodenstein measured the decomposition of hydrogen iodide by following the iodine released through iodometry, the hydrogen released through volumetry and the hydrogen iodide formed by acidimetry. The results overlap: the author believed that he had verified his results by utilizing three methods. In fact he has proven that he can use the steady state mode to determine the reaction in view of his experiments.

On the same graph we plot the speed obtained through both methods: calorimetry and the method used to monitor the reaction (see below) versus time (see Figure 7.3).

If the ratio of two lengths ( $MA/MB$ ) does not depend on time, the system is in pseudo-steady state. This is seen (Figure 7.4) by calculating the ratio of two measures at a given time and by recalculating one curve from the other applying the preceding ratio at all times. If the two new curves are confounded with one another versus time, then the system is in pseudo-steady state.



**Figure 7.3.** Comparison of two physical measures related to the reaction

#### 7.1.5.2. Experimental method

We chose the heat flow as one of the measures that involves all of the elementary steps that feature a non-zero enthalpy. As a second measure, we utilize the method that has been chosen to monitor the system. Let us assume the following choices:

- in homogeneous kinetics, the speed will be measured through monitoring the concentration of a reactant;
- in heterogeneous kinetics, the variation of solid phases' mass and heat flow is used in both cases.

We will examine the expression of variation in the speeds of these three quantities as a function of the speeds of the elementary steps for a linear reaction mechanism.

#### 7.1.5.2.1. Heat flux during a reaction

A heat flux is involved in each of the steps and is characterized by the step's enthalpy ( $\Delta H_\rho$ ). Therefore, the heat flow (produced or consumed) will be:

$$\frac{dQ}{dt} = n_0 \sum_{\rho} \lambda_{\rho} (\Delta H)_{\rho} \phi_{\rho} E_{\rho} \quad [7.17]$$

In pseudo-steady state condition, by using [7.10] for a linear sequence and denoting an arbitrary step of the mechanism  $i$ , the heat flow (produced or consumed) will be:

$$\frac{dQ}{dt} = n_0 \frac{\phi_i E_i}{\lambda_i} \sum_{\rho} (\Delta H_{\rho}) \lambda_{\rho} \quad [7.18]$$

Despite this, the enthalpy of the overall reaction obeys the following relation:

$$\Delta H = \lambda_{\rho} \sum_{\rho} (\Delta H_{\rho}) \quad [7.19]$$

thus the flow in the pseudo-steady state condition (by using [7.12]) is:

$$\frac{dQ}{dt} = n_0 \frac{\phi_i E_i}{\lambda_i} \Delta H = n_0 r \Delta H \quad [7.20]$$

#### 7.1.5.2.2. Concentration speed of reactant $A$

The concentration speed is obtained through:

$$\frac{d[A]}{dt} = \frac{n_0}{V} \sum_{\rho} v_{A,\rho} \phi_{\rho} E_{\rho} = \sum_{\rho} v_{A,\rho} \phi_{\rho} \quad [7.21]$$

The sum is composed of all the steps in which component  $A$  is involved, which means those for which the stoichiometric coefficient  $v_{A,\rho}$  relative to  $A$  is not zero. In a homogeneous medium, all elementary steps have the same space function, which is the volume per mole occupied by the reaction.

Since the mode is in the pseudo-steady state, the equality of speeds law allows us to replace all the reactivities by the reactivity of any step  $i$ :

$$\frac{d[A]}{dt} = \frac{\phi_i}{\lambda_i} \sum_{\rho} v_{A,\rho} \lambda_{\rho} \quad [7.22]$$

We remember the relation between the stoichiometric coefficients of each step and the stoichiometric coefficient of component  $A$  in the overall reaction:

$$\sum_{\rho} v_{A,\rho} \lambda_{\rho} = v_A \quad [7.23]$$

By including it in [7.22] and including the reactivity  $r$  of the reaction, we obtain:

$$\frac{d[A]}{dt} = \frac{v_A \phi_i}{\lambda_i} = \frac{n_0 r}{V} \quad [7.24]$$

By taking into account [7.20], the ratio  $R$  of the calorimetric speed to the concentration speed gives:

$$R = \frac{\frac{d[A]}{dt}}{\frac{dQ}{dt}} = \frac{\sum_{\rho} v_{A,\rho} \phi_{\rho}}{n_0 \sum_{\rho} \lambda_{\rho} (\Delta H_{\rho}) \phi_{\rho} V} = \frac{v_A}{n_0 V \Delta H} \quad [7.25]$$

It appears that if the reaction is carried out at constant volume during the measurement of the concentrations this ratio  $R$  is independent of time. The same reasoning that would lead to the same qualitative result could be conducted for any quantity: concentration of another reactant but also concentrations of products, density of the medium, etc. Any method (see Chapter 4) to monitor homogeneous reactions.

### 7.1.5.2.3. Mass variation during a heterogeneous gas–solid reaction

$v_{G,\rho}$  will denote the algebraic stoichiometric number of gas  $G$  (which is positive for a gas produced by the reaction and negative for a reactant gas) in the  $\rho$ -th reaction mechanism and of rate  $\phi_\rho E_\rho$ . This stoichiometric number is zero if the gas  $G$  is not involved in this reaction.

From the balances, the speed of mass increase is:

$$\frac{d(\Delta m)}{dt} = M_G \frac{d\{G\}}{dt} = -n_0 M_G \sum_{\rho} v_{\rho} \phi_{\rho} E_{\rho} \quad [7.26]$$

The sum is extended to all the elementary steps in which the gas is involved.

In pseudo-steady state mode, by using expression [7.10] in relation [7.25] and choosing any one of the steps  $i$  of the mechanism, the speed of mass increase becomes:

$$\frac{d(\Delta m)}{dt} = -n_0 \frac{\phi_i E_i}{\lambda_i} \sum_{\rho} (\lambda_{\rho} M_G v_{\rho}) \quad [7.27]$$

However, the stoichiometric coefficients of the gas in the elementary steps and in the overall reaction are connected through:

$$\sum_{\rho} \lambda_{\rho} v_{G\rho} = v_G \quad [7.28]$$

and, by using [7.12], we obtain the expression of the speed of mass variation in a pseudo-steady state system:

$$\frac{d(\Delta m)}{dt} = -n_0 M_G v_G \frac{\phi_i E_i}{\lambda_i} = -n_0 M_G v_G r \quad [7.29]$$

Let us now examine the ratio of the speed of mass variation to the heat flow. According to [7.20] and [7.29], this ratio is usually:

$$R = - \frac{\sum_{\rho} M_G v_{\rho} \phi_{\rho} E_{\rho}}{\sum_{\rho} (\Delta H_{\rho}) \phi_{\rho} E_{\rho}} \quad [7.30]$$

and in pseudo-steady state mode, this ratio becomes:

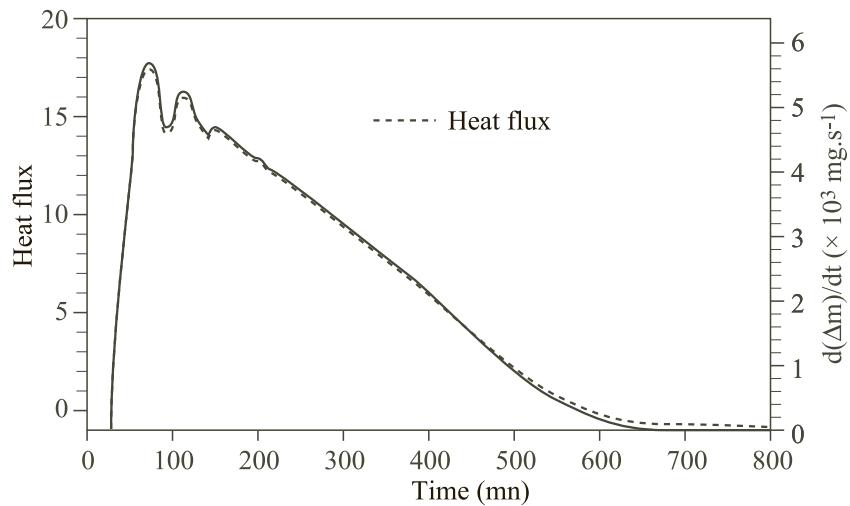
$$R = -\frac{M_{G_i} v_G}{\Delta H} \quad [7.31]$$

Thus this ratio is independent of time (independent of the different reactivities and space functions) and is linked to the ratio of the molar mass of the gas to the enthalpy of the reaction for a pseudo-steady state mode.

NOTE 7.3.— It is necessary to quantitatively examine the value of the ratio because a ratio independent of time can be fortuitously found even if the mode is not in the pseudo-steady state. The experiment should therefore be repeated, not in isothermal conditions but, for example, in linearly increasing temperature because the chances of curves overlapping without being in pseudo-steady state mode become extremely low.

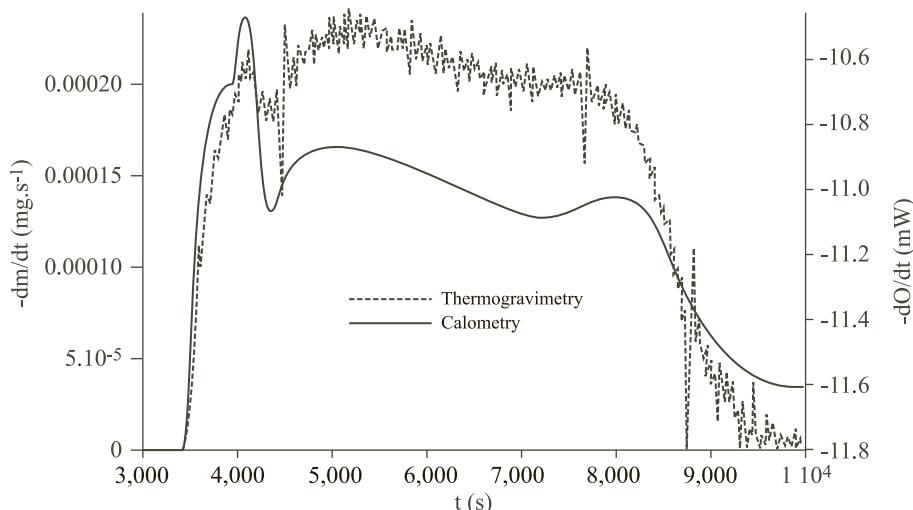
#### 7.1.5.3. Examples

Figure 7.4 shows an example of two curves of the speed of variation of mass and heat flow in the case of magnesium oxidation after application of the overlap ratio. We see that the pseudo-steady state system is quite acceptable and could be retained as a working assumption.



**Figure 7.4.** Examples of a pseudo-steady state mode during magnesium oxidation

Figure 7.5 shows the same curves during the study of triuranium octoxide according to:



**Figure 7.5.** Test of pseudo-steady state during a uranium oxide reduction by hydrogen

We see that the assumption of an overall pseudo-steady state cannot be retained. On the other hand, a detailed review shows that, over time, three successive periods of pseudo-steady state with different ratios can be considered. This suggests the succession of three reactions, each in pseudo-steady state mode.

## 7.2. Pseudo-steady state sequences with constant volume (or surface) – quasi-steady state

### 7.2.1. Quasi-steady state sequences

Let us express the balance of an intermediate as a function of concentration. By definition of the concentration we have:

$$\{X_i\} = V[X_i] \quad [7.32]$$

Through derivation, the following can be written:

$$\frac{d\{X_i\}}{dt} = V \frac{d[X_i]}{dt} + [X_i] \frac{d \ln V}{dt} \quad [7.33]$$

If for all the intermediates, the volumes of their phases do not vary and the mode is in pseudo-steady state, then we obtain:

$$\frac{d[X_i]}{dt} \equiv 0 \quad [7.34]$$

Thus for a homogeneous system operating at constant volume, the pseudo-steady mode gives the same result as the Bodenstein quasi-steady state approximation. We can say that we have a quasi-steady state mode.

Since quasi-steady modes at constant volume are also in pseudo-steady state, they feature all of the latter's properties.

### 7.2.2. Linear sequences in quasi-steady state mode

We will now focus our attention on linear sequences in quasi-steady state mode, which are of great practical importance in homogeneous kinetics.

#### 7.2.2.1. Equality of speeds law for homogeneous linear quasi-steady state sequences with invariant volume

In quasi-steady state mode, for a linear sequence of a homogeneous system we can prove a theorem symmetrical to the very general one obtained for pseudo-steady state modes.

By making the spatial function explicit, it can be written from relation [7.10] that:

$$\frac{\phi_p V}{n_0 \lambda_p} = \text{Const} \quad [7.35]$$

and since the system volume  $s$  is constant, we obtain:

$$\frac{\phi_p}{\lambda_p} = \text{Const} \quad [7.36]$$

### 7.2.3. Speed of a homogeneous linear sequence in quasi-steady state mode with invariant volume

If the system volume is unique, by using [7.12] and by making the spatial function explicit we can write:

$$v_a = \frac{\phi_k V}{\lambda_k} \quad [7.37]$$

So in terms of speed per volume unit:

$$v = \frac{\phi_k}{\lambda_k} \quad [7.38]$$

This is a simple relationship by which to calculate a volumetric speed where we know the reactivity of a single elementary step.

### 7.2.4. Multipoint sequences in quasi-steady state mode

Let us now introduce a multiple point reaction of the type shown in Figure 7.2.

In quasi-steady state mode, for a multipoint sequence of a homogeneous system, we prove a theorem symmetrical to the very general one obtained for pseudo-steady state modes.

By making the spatial function explicit, it can be written from relation [7.15] as:

$$\frac{\phi_2 V_2}{\lambda_2} = \frac{\phi_3 V_3}{\lambda_3} + \frac{\phi_4 V_4}{\lambda_4} \quad [7.39]$$

and since all the volumes are identical, we obtain:

$$\frac{\phi_2}{\lambda_2} = \frac{\phi_3}{\lambda_3} + \frac{\phi_4}{\lambda_4} \quad [7.40]$$

In the case of surface reactions, if the area is the same for all steps, using equation [7.15] yields:

$$\frac{\phi_2 G_2}{\lambda_2} = \frac{\phi_3 G_3}{\lambda_3} + \frac{\phi_4 G_4}{\lambda_4} \quad [7.41]$$

It should be noticed that, in the case of diffusion, the product  $\phi_\rho G_\rho$  is the diffusion flux.

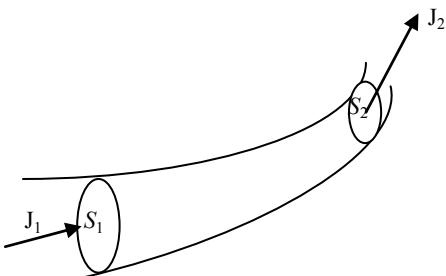
### 7.3. Pseudo- and quasi-steady state of diffusion

Let us consider a diffusion path between two surfaces of areas  $S_1$  and  $S_2$  (see Figure 7.6). The application of pseudo-steady state to diffusion leads to the following invariant:

$$JS = \text{const} \quad [7.42]$$

so in our case:

$$J_1 S_1 = J_2 S_2 \quad [7.43]$$



**Figure 7.6. Diffusion path**

In the case where diffusion is in the quasi-steady state, the flux will be deduced from the following equation:

$$\frac{\partial[X]}{\partial t} = D \frac{\partial^2[X]}{\partial x^2} \approx 0 \quad [7.44]$$

For diffusion between two planes, the steady flux is therefore “quasi-steady” and is obtained from relation [3.38]. Since this flux is independent of the space, its production by a surface that remains constant will be invariant and therefore the quasi-steady diffusion across a constant surface is pseudo-steady.

We will therefore assume that quasi-steady diffusion is generally pseudo-steady.

#### 7.4. Application to the calculation of speeds in pseudo-steady state or quasi-steady state

Experience shows that in many cases pseudo-steady state modes are acceptable solutions for the kinetic results of reactions such as the expression of speed as a function of different variables.

##### 7.4.1. Principle of the method

From an assumed mechanism, after having verified the adequacy of the pseudo-steady state approximation, we will seek the kinetic laws applicable to these pseudo-steady state modes. The results can then be compared with those from the experiment.

Given the growing number of relations that constitute equations [7.3], [7.10], [7.13], [7.15], [7.30], [7.37], [7.39] and [7.40] – which are individual cases – special attention to their application is required. Generally, for heterogeneous reactions, we recommend making general relation [7.4] void for each intermediate in order to calculate a speed. In the context of homogeneous reactions taking place at constant volume, provided that we remain aware of these restrictions we can apply the concentration balance.

##### 7.4.2. Example 1: dinitrogen pentoxide decomposition

We will reconsider reaction [2.R3] from section 5.4 with its three steps [5.R8a], [5.R8b] and [5.R8c]. We see that the three multiplying coefficients are equal to one.

Since the reaction is homogeneous, the three steps take place in the same invariant volume and we make the concentration balances of both intermediates void in order to apply the pseudo-steady state. Thus by making [5.20] and [5.21] void, we obtain:

$$\frac{d[NO]}{dt} = k_2 [NO_2] [NO_3] - k_3 [NO] [N_2O_5] = 0 \quad [7.45]$$

$$\frac{d[NO_3]}{dt} = k'_1 [N_2O_5] - k''_1 [NO_2] [NO_3] - k_2 [NO_2] [NO_3] = 0 \quad [7.46]$$

We deduce:

$$[\text{NO}_3] = \frac{k'_1 [\text{N}_2\text{O}_5]}{(k''_1 + k_2)[\text{NO}_2]} \text{ and } [\text{NO}] = \frac{k'_1 k_2}{k_3(k'_1 + k_2)} \quad [7.47]$$

The speed is obtained from [5.24]:

$$v = \frac{d[\text{O}_2]}{dt} = k_2 [\text{NO}_2][\text{NO}_3] \quad [7.48]$$

therefore:

$$v = k'_1 [\text{N}_2\text{O}_5] = k [\text{N}_2\text{O}_5] \text{ and } E_a = E'_1 \quad [7.49]$$

We thus obtain a volumetric speed that is proportional to nitrogen pentoxide concentration as if the overall reaction [2.R4] was elementary, except that the coefficient  $k$  is not a rate coefficient and does not follow Arrhenius' law since constants  $k'_1 k''_1$  and  $k_2$ , which are rate coefficients, follow it. However if:

$-k''_1 \ll k_2$  we obtain  $k = k'_1$  which becomes an rate coefficient, and Arrhenius' law is followed with an activation energy equal to that of step 1 from left to right:

$$v = k'_1 [\text{N}_2\text{O}_5] = k [\text{N}_2\text{O}_5] \quad [7.50a]$$

$-k''_1 \gg k_2$  we obtain  $k = k'_1 k_2 / k''_1$  and Arrhenius' law is followed with an apparent activation energy equal to:

$$E_a = E'_1 + E_2 - E''_1 \quad [7.50b]$$

In the general case, the global constant  $k$  no longer obeys Arrhenius law. If the experiment gives a correct agreement with this law, the temperature coefficient no longer carries any physical meaning.

#### 7.4.3. Example 2: hydrogen bromide synthesis

We refer to section 5.5.1 and, by making them void, reconsider expressions [5.27] and [5.28]. We obtain:

$$\frac{d[H]}{dt} = k'_2 [Br] [H_2] - k''_2 [H] [HBr] - k_3 [H] [Br_2] = 0 \quad [7.51]$$

$$\frac{d[Br]}{dt} = 2k'_1 [Br_2] - k'_2 [H_2] [Br] + k_3 [H] [Br_2] - 2k'_1 [Br]^2 = 0 \quad [7.52]$$

which enables us to deduce that:

$$[Br] = \sqrt{\frac{k'_1 [Br_2]}{k''_1}} ; [H] = \frac{k''_1 [Br] [H_2]}{k'_2 [HBr] + k_3 [Br_2]} \quad [7.53]$$

By including this in [5.29] and [5.32], the volumetric speed of hydrogen bromide formation is obtained using:

$$v = \frac{k'_1 \sqrt{k_3} [H_2] [Br_2]^{1/2}}{\sqrt{k_4} \left( 1 + \frac{k''_1 [HBr]}{k_2 [Br_2]} \right)} \quad [7.54]$$

NOTE 7.4.— It should be seen that, as in the previous example, the calculation of the formation speed from any reactant or product of the reaction leads to the same results.

We can now examine the influence of temperature on speed.

Let us reconsider expression [7.54]. Coefficients  $k'_1$ ,  $k''_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  are all rate coefficients that obey Arrhenius' law with a temperature coefficient equal to the activation energy of the corresponding steps. The speed will not obey Arrhenius' law. However, if the experimental results agree with each other, and with a straight line in coordinates ( $\ln v$ ,  $1/T$ ), the calculated temperature coefficient will carry no physical meaning.

On the other hand, it should be noted that the initial speed (without hydrogen bromide) is written as follows:

$$v = \frac{k'_1 \sqrt{k_3} [H_2] [Br_2]^{1/2}}{\sqrt{k_4}} \quad [7.55]$$

Hence the reaction admits orders 1 and 1/2 with respect to hydrogen and bromine, respectively. Depending on the temperature, we will find Arrhenius' law with an apparent activation energy, which is:

$$E_a = E'_1 + \frac{E_3}{2} - \frac{E_4}{2} \quad [7.56]$$

#### 7.4.4. Example 3: polymerization

We refer to section 5.5.2, and in order to apply the pseudo-steady state, we will cancel out expressions [5.34] to [5.37]:

$$\frac{d[M]}{dt} = v_i + k_P [M] \sum_j [R_j^\circ] = 0 \quad [7.57]$$

$$\frac{d[R_1^\circ]}{dt} = v_i - k_P [M] [R_1^\circ] - k_t [R_1^\circ] \sum_j [R_j^\circ] = 0 \quad [7.58]$$

$$\frac{d[R_2^\circ]}{dt} = k_P [M] \{ [R_1^\circ] - [R_2^\circ] \} - k_t [R_2^\circ] \sum_j [R_j^\circ] = 0 \quad [7.59]$$

$$\frac{d[R_j^\circ]}{dt} = k_P [M] \{ [R_{j-1}^\circ] - [R_j^\circ] \} - k_t [R_j^\circ] \sum_j [R_j^\circ] = 0 \quad [7.60]$$

By adding all these new equalities separately, which gives:

$$v_i - k_t \left( \sum_j [R_j^\circ]^2 \right) = 0 \quad [7.61]$$

and incorporating it into [5.34], the speed of decrease of the monomer concentration becomes:

$$-\frac{d[M]}{dt} = v_i + k_P [M] \sqrt{\frac{v_i}{k_t}} \quad [7.62]$$

By analogy, we pose:

$$v_P = k_P [M] \sqrt{\frac{v_i}{k_t}} \quad [7.63]$$

This reveals the speed of monomer disappearance as the sum of two terms:

- the initiation speed  $v_i$ ; and
- the “propagation speed”  $v_P$ .

Depending on the case,  $v_i$  could be ignored compared to  $v_P$ . If this is the case, which is very common in practice, we can write:

$$-\frac{d[M]}{dt} = v_P = k_P [M] \sqrt{\frac{v_i}{k_t}} \quad [7.64]$$

hence, through integration, the variation of monomer concentration over time ( $v_i$  being practically independent of time) will be:

$$[M] = [M]_0 \exp \left\{ -k_P \sqrt{\frac{v_i}{k_t}} t \right\} \quad [7.65]$$

This relation can easily be compared to the experiment.

By incorporating this expression into [5.43], we calculate  $p$  from [5.44] and the average degree of polymerization:

$$\bar{N} = \frac{2 \left\{ v_i + k_P [M] \sqrt{\frac{v_i}{k_t}} \right\}}{v_i} \quad [7.66]$$

and in the case where the initiation speed is negligible compared with propagation speed, for the average degree of polymerization we obtain:

$$\bar{N} = \frac{2 k_P [M]}{\sqrt{v_i k_t}} \quad [7.67]$$

Thus the average degree of polymerization varies with the monomer concentration and by using [7.62] we obtain the average length of the polymer at a given time:

$$\bar{N} = \frac{2k_P[M]_0}{\sqrt{v_i k_t}} \exp\left\{-k_P \sqrt{\frac{v_i}{k_t}} t\right\} \quad [7.68]$$

This relation can be compared to the experiment by measuring the molar mass of the polymer formed through osmotic pressure, for instance.

NOTE 7.5.— By also applying the pseudo-steady state to relation [5.33], we obtain:

$$v_i = 2k_i[S] \quad [7.69]$$

and thus  $v_i$  will be practically independent of time if a small amount of the initiator is consumed, which is the case if  $v_i$  is small.

#### 7.4.5. Example 4: application of the pseudo-steady state to a heterogeneous catalytic reaction

Here we will use the example of the catalysis discussed in section 6.4. We will ignore the reactions from right to left ( $k''_2 = k''_3 = k''_4 = 0$ ). We will also ignore the portion of the catalyst surface occupied by an adsorbed gas compared with the free surface ( $\theta_A + \theta_A' \ll 1$ ).

By applying the pseudo-steady state to the diffusion of  $A$  and  $B$ , we calculate:

$$J_A = D_A \frac{[(A)_h] - [(A)_e]}{h - e} \quad [7.70]$$

$$J_B = D_B \frac{[(B)_e] - [(B)_h]}{h - e} \quad [7.71]$$

We will assume that the diffusion coefficients of the two gases are identical and equal to  $D$ .

Applying the pseudo-steady state by setting equations [6.42] to [6.44] to zero and by taking into account relations [6.17] to [6.19], [7.70] and [7.71], we get:

$$\frac{d\theta_A}{dt} = \phi_2 - \phi_3 = 0 \quad [7.72]$$

$$\frac{d\theta_B}{dt} = \phi_3 - \phi_4 = 0 \quad [7.73]$$

$$\frac{d[(B)_e]_s}{dt} = \phi_4 - D \frac{\left( \frac{\partial [(B)_e]}{\partial y} \right)_e}{e} = 0 \quad [7.74]$$

We then calculate:

$$[(A)_e] = \frac{(A)_h}{1 + \frac{k'_2(h-e)}{D}} \quad [7.75]$$

$$[(B)_e] = [(B)_h] + \frac{k'_2[(A)_h]}{1 + \frac{k'_2(h-e)}{D}}(h-e) \quad [7.76]$$

$$\theta_A = \frac{k'_2[(A)_h]}{k'_3 \left( 1 + \frac{k'_2(h-e)}{D} \right)} \quad [7.77]$$

and:

$$\theta_B = \frac{k'_2[(A)_h]}{k'_4 \left( 1 + \frac{k'_2(h-e)}{D} \right)} \quad [7.78]$$

The speed of production of  $B$  is obtained from the flux of  $B$  at the exit of the crucible:

$$(J_B)_h = D \frac{[(B)_e] - [(B)_h]}{(h-e)} = \frac{k'2[(A)_h]}{\left(1 + \frac{k'2(h-e)}{D}\right)} = k[(A)_h] \quad [7.79]$$

We thus obtain a first order reaction with respect to the reactant, but coefficient  $k$  is not a factor of speed and therefore the speed does not obey Arrhenius' law with temperature. The ratio  $\frac{k'2(h-e)}{D}$  is called Damkhöler's number.

Two extreme cases of Damkhöler's number are of interest:

- if  $\frac{k'2(h-e)}{D} \ll 1$ , the speed becomes:

$$(J_B)_h = D \frac{[(B)_e] - [(B)_h]}{h-e} = k'2[(A)_h] = k[(A)_h] \quad [7.80]$$

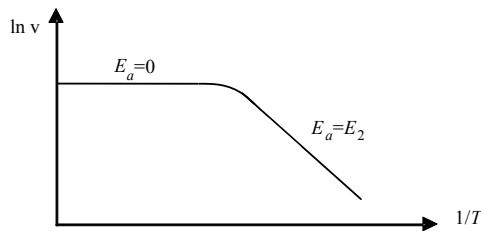
Coefficient  $k$  is now the rate coefficient of the adsorption step of  $A$ . The speed will then obey Arrhenius' law with temperature, with an activation energy equal to that of the adsorption of  $A$ ;

- if  $\frac{k'2(h-e)}{D} \gg 1$ , the speed becomes:

$$(J_B)_h = D \frac{[(B)_e] - [(B)_h]}{h-e} = \frac{D[(A)_h]}{h-e} = k[(A)_h] \quad [7.81]$$

Coefficient  $k$  is now the ratio of the diffusion coefficient of the gas over the crucible height, but the diffusion activation energy of a gas is zero and the diffusion coefficient is practically unaffected by temperature (it varies in the range of  $T^{3/2}$ ).

We see that only the temperature and depth of the crucible can affect Damkhöler number, and thus enable a reaction to go from zero activation energy to a non-zero value. Figure 7.7 gives the pace of an Arrhenius plot showing the changes between the two cases under the influence of temperature. We say that we have a mode change because the solution for the speed is changed (we do not have a change of mechanism, this one is always the same).



**Figure 7.7. Change of mode detected on an Arrhenius curve in a catalytic reaction**

We already noted the same phenomenon of a possible change of activation energy according to temperature range in the study of dinitrogen pentoxide decomposition between relations [7.49] and [7.50].

NOTE 7.6.— Despite the change in activation energy, there is absolutely no change of mechanism in function of temperature in either case. Changes of modes very easily explain disruptions of an Arrhenius line.

### 7.5. Pseudo-steady state and open or closed systems

In the examples of pseudo-steady state solutions that we have computed above, we have never used the equations of conservation of elements, which means we have never needed to specify whether our calculation was valid in a closed system, an open or a partially open system. This comes from the fact that we have only established speed-concentration relations and have not considered the effect of time. If we wished to integrate the resulting speed expressions, some differences would emerge. We should not include a pseudo-steady state condition for an intermediate in order to deduce that its concentration (or amount) is constant in closed system. Similarly the integration of the speed equation cannot be performed in closed system if we do not know the law of the variation of the concentrations with time.

This integration can be performed if the speed-concentration curve is transposed into rate-fractional extent curve.

#### 7.5.1. Kinetics law in homogeneous closed systems

We write the rate as follows:

$$r = \frac{vV}{\{A_1\}_0} \quad [7.82]$$

However, for ideal mixtures, if  $v_k^0$  is the molar volume of component  $A_k$ , the total volume at time  $t$  is:

$$V = \sum_k V_k = \sum_k v_k^0 \{A_k\} \quad [7.83]$$

By expressing the amounts through [1.15], it becomes:

$$V = \{A_1\}_0 (\alpha - \alpha_0) \sum_k v_k v_k^0 + \sum_k v_k^0 \{A_k\}_0 \quad [7.84]$$

and by incorporating it into [7.79], we obtain:

$$r = \frac{d\alpha}{dt} = \frac{v \left( \{A_1\}_0 + (\alpha - \alpha_0) \sum_k v_k v_k^0 + \sum_k v_k^0 \{A_k\}_0 \right)}{\{A_1\}_0} \quad [7.85]$$

hence the volumetric speed:

$$v = \frac{\{A_1\}_0}{\{A_1\}_0 + (\alpha - \alpha_0) \sum_k v_k v_k^0 + \sum_k v_k^0 \{A_k\}_0} \frac{d\alpha}{dt} \quad [7.86]$$

Moreover in the second part of the speed–concentration relation, we can replace each concentration by using relation [1.30]. We are thus led to a differential expression with a single function: the fractional extent and a variable, whose integration time gives the variation of fractional extent with time. It is then possible to return to [1.30] in order to obtain the variation of all the principle components (reactants and products).

To illustrate this, we apply this method to hydrogen bromide synthesis for which the volumetric speed–concentration relation is relation [7.54], which will be written as follows:

$$v = \frac{k[H_2][Br_2]^{1/2}}{k' \left( 1 + \frac{k''[HBr]}{[Br_2]} \right)} \quad [7.87]$$

Let us assume that at the initial time the fractional extent is zero. There is no hydrogen bromide and the reactants are in the stoichiometric proportions. Thus:

$$\text{if } t=0, \alpha=0, [H_2]_0 = [Br_2]_0 \text{ and } [HBr]_0 = 0$$

This is a gas-phase reaction with conservation of the number of moles of gas. The volume therefore remains constant and thus, from [7.82] and [7.87], we obtain:

$$\frac{d\alpha}{dt} = V_0 \frac{k(1-\alpha)\{[Br_2]_0(1-\alpha)\}^{1/2}}{k' \left\{ 1 + \frac{2k''\alpha}{(1-\alpha)} \right\}} = \frac{kV_0 [Br_2]_0^{1/2} (1-\alpha)^{5/2}}{k' [1 + (2k'' - 1)\alpha]} \quad [7.88]$$

This expression can then be integrated, but it is much easier to keep it in the derivative form in order to compare it with experimental experience. Moreover digital methods enable us to transform any experimental integral curve into its derivative curve. The fitting of this derivative curve with equation [7.8] allows us to calculate the values of the constants  $k$ ,  $k'$  and  $k''$ . Then it is possible to integrate equation [7.8] and knowing  $\alpha(t)$ , calculate the concentrations of each reactant and product with the following equations:

$$[HBr] = 2\alpha[Br_2]_0 \quad [Br_2] = [Br_2]_0(1 - \alpha) = [H_2]$$

### 7.5.2. Kinetics law in heterogeneous closed systems

We replace [7.82] by:

$$r = \frac{vS}{\{A_1\}_0} \quad [7.89]$$

The surface variation with reaction speed is then evaluated through a relation of the same type as those encountered in [6.60] and [6.61]. We then find ourselves at the same point as in homogeneous systems.

For example, we reconsider the catalytic reaction for which we have the very simple function [7.79]. By taking in account the partial pressure of  $A$  in the chamber, this can be written:

$$v = k[(A)_h] = k \frac{P_A}{RT} \quad [7.90]$$

By including it in [7.86], we obtain:

$$r = \frac{d\alpha}{dt} = \frac{kP_A S_0}{R T \{[A]_h\}_0} = \frac{kP_A S_0}{(P_A)_0} = kS_0(1-\alpha) \quad [7.91]$$

which through integration gives:

$$\alpha = 1 - \exp(-kS_0 t) \quad [7.92]$$

### 7.5.3. Kinetic laws of open systems with constant concentrations

In systems with concentrations that are held constant, the speeds with constant space function – which is the term  $\phi$  of product  $\phi E$  – are independent of time in isothermal conditions. This is true for the volumetric speed of a homogeneous system as well as for the areal speed of a catalytic system. This will be also true in the case of a strictly heterogeneous reaction that obeys the law of  $\phi E$ . Space functions are, however, frequently a function of time, which leads to absolute speeds or to rates that vary with time through this space function.

## 7.6. Conclusion

Finally we see that the real simplification in the resolution of systems is based on the existence of pseudo-steady state modes. It is the latter that enable us to replace the differential equations of intermediate balance with algebraic equations. Hence the interest in experimentally showing the adequacy introduced with experimental data.

The notion of quasi-steady state, without being combined to a single and invariant volume, however, provides only little interest in itself in the end because it is not equivalent to the pseudo-steady state, which enables the true simplifications.

We could have got along very well without the notion of quasi-steady state. We have stated this as the reader might cling to other books relating to kinetics that are too often, and wrongly, focused on the quasi-steady state, which implies that the volume or surface are invariant. The difference in volume and surface do, however, become paramount when mainly heterogeneous systems are tackled.

### 7.7. Important figure in pseudo-steady state

Max Bodenstein was the first to introduce the quasi-steady state approximation to determine a reaction in view of experimental results.



**Max Bodenstein**  
(1871-1942)

**Figure 7.8.** *Important chemist*



## Chapter 8

# Modes with Rate-determining Steps

We will devote this chapter to a particular class of pseudo-steady state modes that are known as modes with rate-determining steps in which one or several steps will determine the entire kinetics of a reaction. In other words, these are modes in which one or several steps have rate coefficients so great that we consider them to be infinite compared with those of the other steps. These other steps will be the rate-determining steps or determining steps in the context of the pseudo-steady state. When a single step is determining, we have a pure Besson mode. If two steps are determining, according to the same author, the mode is known as “mixed”.

We may ask where the interest lies in examining pseudo-steady state mode while the treatment of the general pseudo-steady state mode is relatively easy, as we have shown through some examples in Chapter 7. In fact this mode is interesting in two aspects. On one hand, it allows us to sometimes have simpler expressions and yet keep a good agreement with the experiment considering the accuracy of measurements. On the other hand, such modes are essential in heterogeneous kinetics because they are the only ones that lead to kinetics that obey the law of  $\phi E$ , which allows us to establish a parallel with homogeneous reactions. Moreover they appear to be sufficient in the vast majority of heterogeneous reactions.

NOTE 8.1.– It is wrong to talk about slow steps and fast steps or a speed-limiting step instead of a speed-determining step because being in the context of pseudo-steady state, by considering for example relation [7.7] for a linear sequence, all steps have practically the same speed when rounded to a coefficient (the ratio of multiplying coefficients).

## 8.1. Mode with one determining step

### 8.1.1. *Definition*

One rate-determining step or “pure” will be called a mode if it satisfies the following assumptions:

- the mode is in the pseudo-steady state;
- the direct and reverse rate coefficients (and hence the speed factors) of the different elementary steps are infinite except for one, whose coefficients are finite and which is called the determining step.

### 8.1.2. *Concentrations theorem for linear sequences*

We will first state and verify a very important theorem that connects the concentrations of intermediate species to those of the main components of the reaction (reactants and products).

**THEOREM 8.1.–** In a mode with one rate-determining step, each intermediate species is in physico-chemical equilibrium with the main components of the reaction (reactants and/or products). Therefore the concentration of each intermediate is linked to the concentrations of some of the main components.

We cannot provide general proof of this theorem because there is no general linear mechanism. We shall verify it on a simple linear mechanism, but it is easy to prove it in each individual case of linear mechanism.

Let us consider a simple linear mechanism with consecutive steps named [8.R1a], [8.R1b]..., [8.R1 $\rho$ ]..., [8.R1 $n + 1$ ] of a reaction that produces  $B$  from  $A$ .

We will use speed factors  $f'_\rho$  and  $f''_\rho$  for a reaction  $\rho$  and its opposite (see section 3.3.2).

Let us write the reactivity of the the first step of the mechanism by taking into account of the reverse step:

$$\phi_1 = f'_1 - f''_1 [X_1]^{\beta_{1,1}} = f'_1 \left\{ 1 - \frac{f''_1}{f'_1} [X_1]^{\beta_{1,1}} \right\} \quad [8.1]$$

If this reaction is at equilibrium, then we can show that the concentration of  $X_1$  is:

$$[X_1]_{equ} = \left( \frac{f'_1}{f''_1} \right)^{\beta_{1,1}} \quad [8.2]$$

hence the reactivity of the first step:

$$\phi_1 = f'_1 \left\{ 1 - \frac{[X_1]^{\beta_{1,1}}}{[X_1]_{equ}^{\beta_{1,1}}} \right\} \quad [8.3]$$

Let us examine the  $\rho$ th chain reaction, [8.R1  $\rho$ ]. Its reactivity is written as follows:

$$\phi_\rho = f'_\rho [X_{\rho-1}]^{\beta_{\rho-1,\rho}} \left\{ 1 - \frac{f''_\rho}{f'_\rho} \frac{[X_\rho]^{\beta_{\rho,\rho}}}{[X_{\rho-1}]^{\beta_{\rho-1,\rho}}} \right\} \quad [8.4]$$

At the equilibrium of this step we have:

$$\frac{[X_\rho]^{\beta_{\rho,\rho}}}{[X_{\rho-1}]^{\beta_{\rho-1,\rho}}} = \frac{f'_\rho}{f''_\rho} \quad [8.5]$$

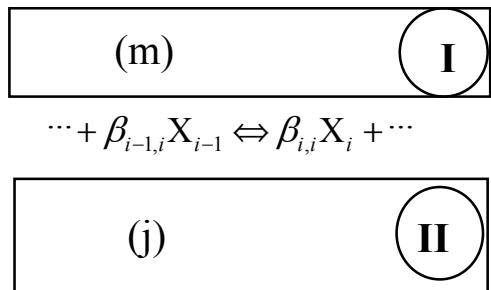
and therefore the reactivity of such a step becomes:

$$\phi_\rho = f'_\rho [X_{\rho-1}]^{\beta_{\rho-1,\rho}} \left\{ 1 - \left( \frac{[X_{\rho-1}]^{\beta_{\rho-1,\rho}}}{[X_\rho]^{\beta_{\rho,\rho}}} \right)_{equ} \cdot \frac{[X_\rho]^{\beta_{\rho,\rho}}}{[X_{\rho-1}]^{\beta_{\rho-1,\rho}}} \right\} \quad [8.6]$$

Finally, for the last step [8.R1n + 1], in the same way we obtain:

$$\phi_{n+1} = f'_{n+1} [X_n]^{\beta_{n,n+1}} \left\{ 1 - \frac{[X_n]_{equ}^{\beta_{n,n+1}}}{[X_n]^{\beta_{n,n+1}}} \right\} \quad [8.7]$$

Let us now assume that the rate coefficients  $k'_\rho$  and  $k''_\rho$  are infinite except those of step  $i$  for which coefficients  $k'_i$  and  $k''_i$  are finite. The concentrations of the reactants and products are not zero (hence the importance of setting the reactant and product concentrations of the reaction during experiments), so the speed factors  $f'_\rho$  and  $f''_\rho$  are thus also infinite, whereas for  $i$  steps the factors  $f'_i$  and  $f''_i$  have finite values.



**Figure 8.1.** Subsets I and II of the steps surrounding the rate-determining step

Let us now group together all the steps of the mechanism with infinite coefficients into two subsets (Figure 8.1). Subset I will include all the steps preceding step  $i$  of finite coefficients; their rank is  $m$ , such that:  $m < i$ . Subset II will include all the steps following step  $i$ , and their rank  $j$  will be such that:  $j > i$ .

Let us first consider subset I. Step [8.R1a] is part of this and its reactivity cannot be infinite (otherwise it would take place instantaneously and  $X_1$  would no longer be an intermediate, but almost a reactant). We can therefore see, by looking at expression [8.4], that the only solution in which the reactivity of this step will be finite with infinite  $f'_1$  and  $f''_1$ , is when the term in square brackets is zero. More formally, we should have:

$$[X_1] = [X_1]_{equ} = \left( \frac{f'_1}{f''_1} \right)^{\frac{1}{\beta_{1,1}}} \quad [8.8]$$

This means that step [8.R1a] will always be at equilibrium.

Step [8.R1b] also belongs to subset I. Let us apply relation [8.6] for  $\rho = 2$ . By canceling out the square bracket term, we obtain:

$$\frac{[X_2]^{\beta_{2,2}}}{[X_1]^{\beta_{1,2}}} \left( \frac{[X_1]^{\beta_{1,2}}}{[X_2]^{\beta_{2,2}}} \right)_{equ} = 1 \quad [8.9]$$

hence by using the previous expression:

$$[X_2]^{\beta_{2,2}\lambda_2} = \left( \frac{f'_1}{f''_1} \right)^{\lambda_1} \left( \frac{f'_2}{f''_2} \right)^{\lambda_2} \quad [8.10]$$

By going through this reasoning for all of subset I, we obtain:

$$[X_m]^{\beta_{m,m}\lambda_m} = \prod_{\rho=1}^{\rho=m} \left( \frac{f'_\rho}{f''_\rho} \right)^{\lambda_\rho} \quad [8.11]$$

and we finally reach:

$$[X_{i-1}]^{\beta_{i-1,i-1}\lambda_{i-1}} = \prod_{\rho=1}^{\rho=i-1} \left( \frac{f'_\rho}{f''_\rho} \right)^{\lambda_\rho} \quad [8.12]$$

Thus any intermediate formed by a step belonging to subset I is only expressed through the ratios of speed factors of pairs of opposite steps. It is therefore in equilibrium with the reactants and main products involved in its production step and the steps that precede it.

Let us now consider subset II and follow the same reasoning as for I, but this time starting from the last step [8.R1n + 1]. For this step, we are led to:

$$[X_n] = [X_n]_{equ} = \left( \frac{f''_{n+1}}{f'_{n+1}} \right)^{\frac{1}{\beta_{n,n+1}}} \quad [8.13]$$

By rolling back step-by-step we obtain:

$$[X_j]^{\beta_{j,j+1}\lambda_{j+1}} = \prod_{\rho=j+1}^{\rho=n+1} \left( \frac{f_\rho''}{f_\rho'} \right)^{\lambda_\rho} \quad [8.14]$$

and thus we reach:

$$[X_i]^{\beta_{i,i+1}\lambda_{i+1}} = \prod_{\rho=i+1}^{\rho=n+1} \left( \frac{f_\rho''}{f_\rho'} \right)^{\lambda_\rho} \quad [8.15]$$

Each intermediate of subset II is therefore in equilibrium with the reactants and main products involved in the steps following that of its production, and the theorem is verified.

A consequence of this theorem is that if we work in isothermal conditions and the concentrations of the reactants and products are held constant, the mode is in steady state. In fact, the concentration of each of the intermediates remains constant over time because the speed factors are also constant (see Note 3.4).

### 8.1.3. Reactivity of the rate-determining step

In what follows,  $\phi_{j,[i]}$  will denote the reactivity of a step  $j$  in a system determined by step  $i$ .

As previously, we will reason on the same linear chain.

According to the previous theorem, the reactivity of each step has an indeterminate form  $0.\infty$  except that of the determining step  $i$ , which is written as follows:

$$\phi_i = f_i' [X_{i-1}]^{\beta_{i-1,i}} \left\{ 1 - \frac{f_i''}{f_i'} \frac{[X_i]^{\beta_{i,i}}}{[X_{i-1}]^{\beta_{i-1,i}}} \right\} \quad [8.16]$$

By referring to the concentration expressions [8.12] and [8.15], and by taking into account relations of definitions of multiplying coefficients:

$$\beta_{i-1,i}\lambda_i = \beta_{i-1,i-1}\lambda_{i-1} \text{ and } \beta_{i,i+1}\lambda_{i+1} = \beta_{i,i}\lambda_i \quad [8.17]$$

As all other reactivities are at equilibrium, for the reactivity of step  $i$  we obtain:

$$\phi_i = \phi_{i,[i]} = f_i \prod_{\rho=1}^{\rho=i-1} \left( \frac{f_\rho'}{f_\rho''} \right)^{\frac{\lambda_\rho}{\lambda_i}} \left\{ 1 - \prod_{\rho=1}^{\rho=n+1} \left( \frac{f_\rho''}{f_\rho'} \right)^{\frac{\lambda_\rho}{\lambda_i}} \right\} \quad [8.18]$$

NOTE 8.2.– It can be seen in the above expression that, if the intensive properties of the reaction (temperature and concentrations of reactants and main products) are kept constant, the various speed factors are independent of time and, therefore, the reactivity remains constant. In pure mode, the reactivity of the rate-determining step only depends on time if the intensive properties vary with time (temperature programming or closed systems).

#### 8.1.4. Rate of reaction

THEOREM 8.2.– During a mode with one determining step, the rate of the reaction is the product of the reactivity of the determining step (the other steps are at equilibrium) by the space function relative to the zone where the determining step takes place; this product is weighted by the inverse of the multiplying coefficient of this determining step.

To calculate the rate of our reaction, since the mode is in pseudo-steady state, relation [7.13] should be applied by choosing the step that determines the speed to be step  $i$ . Therefore we will have:

$$\eta_{[i]} = \frac{\phi_{i,[i]}}{\lambda_i} E_i = \phi_{i,[i]} E_i \quad [8.19]$$

In this expression,  $\phi_{i,[i]}$  is the reactivity of the determining step. All others are considered to be at equilibrium.  $E_i$  is the space function where the determining step takes place.

Thus, we can write the solution as follows:

$$\eta_{[i]} = \phi_{[i]} E_i \quad [8.20]$$

This form is thus the product of a reactivity  $\phi_{[i]} = \frac{\phi_{i,[i]}}{\lambda_i}$ , which only depends

on physico-chemical conditions (such as the reactivity of an elementary step), with a space function that depends only on the nature, shape and size of the zone where the elementary determining step takes place.

The product of [8.20] enables us to say that, for a linear sequence that occurs in pure mode determined by one step, the rate is separable.

This reactivity  $\phi_{[i]}$  is a volumetric speed in a homogeneous reaction. In the case of a heterogeneous reaction, however, it is an areal speed. Despite this, we have kept the name “reactivity” for it because it is often viewed as (if  $\lambda_i = 1$ ) a reactivity of an elementary step.

**NOTE 8.3.–** If the reaction is carried out by keeping all the concentrations of the main components constant and in isothermal conditions, the reactivity  $\phi_{[i]}$  is independent of time and the rate (or speed) only depends on time if the space function depends on it, which means if the corresponding zone has sizes that vary due to the progress of the reaction.

Thus, through this method of the determining process, as many solutions (modes) can be obtained as there are steps in the mechanism.

### 8.1.5. Calculation of speed of a linear sequence in pure mode determined by one step

#### 8.1.5.1. Calculation method

In light of the above, we can now give a speed calculation method.

To apply the method of pure kinetics, we have to:

- write the mass action law for the equilibria of the different steps, except for the determining step;

– deduce the concentrations of the various intermediates, especially, those that are involved in the expression of the reactivity of the determining step, as a function of the equilibrium constants of the other steps and concentrations (and/or partial pressures) of reactants and main products of the overall reaction;

– include these concentrations in the expression of the reactivity of the determining step.

We finally obtain the reactivity of the determining step as a function of temperature and concentrations (and/or partial pressures) of the main components.

By multiplying it by the space function of this determining step and by taking into account its multiplying coefficient, we obtain the rate of the considered mode [8.20].

#### 8.1.5.2. Example of the magnesium oxidation reaction

Let us reconsider the example discussed in section 6.5 of oxidation [6.R4] of the magnesium plate whose mechanism is given by steps [6.R4a] to [6.R4d]. We have seen that the multiplying coefficients are:  $\lambda_1 = 1/2$ ,  $\lambda_2 = \lambda_3 = \lambda_4 = 1$ . We will calculate the four possible pure modes, which are the solutions when the determining step is successively [6.R4a], [6.R4b], [6.R4c] and [6.R4d].

In our case, the initial solid  $A$  is magnesium. Therefore the rate is obtained through its consumption, which only occurs through step [6.R4d]. The reaction's rate is thus:

$$r = \phi_4 E_4 \quad [8.21]$$

In order to simplify the calculations and the expressions, we will make the approximation that the oxygen vacancies  $V_O$  in magnesium oxide are highly diluted.

The equilibrium constants of the different steps (where  $K_3 = 1$  because it involves diffusion) are written as follows:

$$K_1 = \frac{\theta^2}{P(1 - \theta)^2}; K_2 = \frac{(1 - \theta)}{\theta [V_O]_{ext}}; K_4 = [V_O]_{int} \quad [8.22]$$

We verify that the overall equilibrium has a coefficient  $K$  such that:

$$K = \frac{1}{\sqrt{P^0}} = \sqrt{K_1} \cdot K_2 \cdot K_4 \left[ = \prod_{\rho=1}^{n+1} \left( K_\rho^{1/\lambda_\rho} \right) \right] \quad [8.23]$$

#### 8.1.5.2.1. Step [6.R4a] is determining

According to [6.50], the reactivity of the determining step is written as follows:

$$\phi_1 = k'_1 (1 - \theta)^2 P \left\{ 1 - \frac{\theta^2}{K_1 (1 - \theta)^2 P} \right\} \quad [8.24]$$

By using relations [8.22], we calculate the concentrations of the intermediates:

$$\theta = \frac{1}{1 + K_2 K_4} \text{ and } [V_O]_{int} = [V_O]_{ext} = K_4 \quad [8.25]$$

By including this in the reactivity of [8.24], we obtain:

$$\phi_{1,[1]} = k'_1 \frac{K_2^2 K_4^2 P}{(1 + K_2 K_4)^2} \left\{ 1 - \frac{P^0}{P} \right\} \quad [8.26]$$

We have seen that the rate of the reaction under such a mode is given by [8.21]. This expression is indeterminate, however, because the reactivity  $\phi_4$  appears as the product of an infinite speed factor by a null term in the square brackets. In order to evaluate the indeterminate form, we apply the pseudo-steady state by setting relations [6.34], [6.34], [6.35] to zero and using a null diffusion gradient. Thus, we recursively reach:

$$r = \phi_4 E_4 = \phi_3 E_3 = \phi_2 E_2 = \frac{\phi_1 E_1}{2} \quad [8.27]$$

and therefore the rate under this mode determined by step [6.R4a] is the following:

$$\eta_{[1]} = \frac{\phi_{1,[1]} E_1}{2} = k'_1 \frac{K_2^2 K_4^2 P}{(1 + K_2 K_4)^2} \left\{ 1 - \frac{P^0}{P} \right\} \frac{S_e}{2} \quad [8.28]$$

We will return to the calculation of the area of the outer surface  $S_e$  in section 8.1.5.2.5.

#### 8.1.5.2.2. Step [6.R4b] is determining

According to [6.51], the reactivity of the determining step is written as follows:

$$\phi_2 = k'_2 \theta \left[ V_O \right]_{ext} \left\{ 1 - \frac{(1 - \theta)}{K_2 \theta \left[ V_O \right]_{ext}} \right\} \quad [8.28]$$

By using relations [8.22], we calculate the intermediates:

$$\theta = \frac{\sqrt{K_1 P}}{1 + \sqrt{K_1 P}} \text{ and } \left[ V_O \right]_{int} = \left[ V_O \right]_{ext} = K_4 \quad [8.29]$$

By including the reactivity of step [8.28], we obtain:

$$\phi_{2,[2]} = k'_2 \frac{\sqrt{K_1 P}}{1 + \sqrt{K_1 P}} K_4 \left\{ 1 - \sqrt{\frac{P^0}{P}} \right\} \quad [8.30]$$

Likewise, as above, we evaluate the indeterminate form through:

$$\begin{aligned} 2\phi_1 E_1 &= \phi_2 E_2 = \phi_3 E_3 = \phi_4 E_4 \\ \text{or } 2\phi_1 S_e &= \phi_2 S_e = \phi_3 G_3 S_i = \phi_4 S_i \end{aligned} \quad [8.31]$$

hence the rate:

$$\eta_{[2]} = \phi_2 E_2 = \phi_{2,[2]} E_2 = \frac{k'_2 \sqrt{K_1 P}}{1 + \sqrt{K_1 P}} K_4 \left\{ 1 - \sqrt{\frac{P_0}{P}} \right\} S_e \quad [8.32]$$

We will return to the calculation of the area of the outer surface  $S_e$  and therefore  $E_2$  in section 8.1.5.2.5.

## 8.1.5.2.3. Step [6.R4c] is determining

According to relation [3.42], by arbitrarily setting  $l_0 = 1$  m, the reactivity of this diffusion step is:

$$\phi_3 = D_4'' \left[ V_O \right]_{ext} \left\{ 1 - \left[ V_O \right] \right\} \quad [8.33]$$

By using relations [8.22], we calculate the intermediates:

$$\theta = \frac{\sqrt{K_1 P}}{1 + \sqrt{K_1 P}}, \left[ V_O \right]_{ext} = \frac{1}{K_2 \sqrt{K_1 P}} \text{ and } \left[ V_O \right]_{int} = K_4 \quad [8.34]$$

By including it in the reactivity of step [8.33], we obtain:

$$\phi_{3[3]} = D_4'' K_4 \left\{ 1 - \sqrt{\frac{P^\theta}{P}} \right\} \quad [8.35]$$

As previously, we evaluate the indeterminate form through [8.31], and the reactivity becomes:

$$\phi_{[3]} = \phi_{3[3]} = D_4'' K_4 \left\{ 1 - \sqrt{\frac{P^\theta}{P}} \right\} \quad [8.36]$$

By using relation [3.44] (by setting  $l_0 = 1$  m), we calculate the rate by:

$$\begin{aligned} \eta_{[3]} &= \phi_{[3]} E_3 = \frac{\phi_{[3]} G_3 S_i}{n_0} \\ &= D K_4 \left\{ 1 - \sqrt{\frac{P^\theta}{P}} \right\} E_3 = D K_4 \left\{ 1 - \sqrt{\frac{P^\theta}{P}} \right\} \frac{S_i}{n_0 X} \end{aligned} \quad [8.37]$$

We will return to this expression in section 8.1.5.2.5.

#### 8.1.5.2.4. Step [6.R4s] is determining

According to [6.52], the reactivity of the determining step is written as follows:

$$\phi_4 = k'_4 - k''_4 \left[ V_O \right]_{int} \quad [8.38]$$

By using relations [8.22], we calculate the intermediates:

$$\theta = \frac{\sqrt{K_1 P}}{1 + \sqrt{K_1 P}} \text{ and } [V_O]_{ext} = [V_O]_{int} = \frac{1}{K_2 \sqrt{K_1 P}}$$

By including the reactivity of step [8.38], we obtain:

$$\phi_{4[4]} = k'_4 \left\{ 1 - \sqrt{\frac{P^\theta}{P}} \right\} \quad [8.39]$$

According to [8.21], the rate of the reaction immediately becomes:

$$\eta_{[4]} = \phi_{4[4]} S_i = \phi_{[4]} S_i = k'_4 \left( 1 - \sqrt{\frac{P^0}{P}} \right) S_i \quad [8.40]$$

#### 8.1.5.2.5. Calculation of space functions

In the case of a plate, the areas of both the inner  $S_i$  and outer  $S_e$  interfaces are equal to each other and to the initial area of the plate  $S_0$ .

We can link the thickness of the layer formed X (see Figure 6.5) to the extent of the reaction. For this, let us write that the magnesia volume formed is obtained from:  $S_0 X$ . It corresponds to the transformed magnesium volume if  $z$  is the expansion coefficient of magnesia with respect to magnesium, i.e. the ratio of magnesia to the volume of magnesium that produced it:

$$S_0 \left( \frac{e}{2} - Y \right) = \frac{S_0 X}{z} \quad [8.41]$$

Therefore, the portion of the magnesium transformed will be:

$$\alpha = \frac{S_0 \left( \frac{e}{2} - Y \right)}{S_0 \frac{e}{2}} = \frac{e - 2Y}{e} \quad [8.42]$$

It is deduced from [8.41] and [8.42] that:

$$X = \frac{ze\alpha}{2} \quad [8.43]$$

Mode determined by	Rate
[6.R4a]	$\frac{d\alpha}{dt} = r_{[1]} = k_1' \frac{K_2^2 K_4^2 P}{(1 + K_2 K_4)^2} \left\{ 1 - \frac{P^0}{P} \right\} \frac{V_{m(Mg)}}{e}$
[6.R4b]	$\frac{d\alpha}{dt} = r_{[2]} = k_2' \frac{\sqrt{K_1 P}}{1 + \sqrt{K_1 P}} K_4 \left\{ 1 - \sqrt{\frac{P_0}{P}} \right\} \frac{2V_{m(Mg)}}{e}$
[6.R4c]	$\frac{d\alpha}{dt} = r_{[3]} = \frac{Dz K_4}{2\alpha} \left\{ 1 - \sqrt{\frac{\mathbf{P}^0}{P}} \right\} \frac{4V_{m(Mg)}}{ze^2 \alpha}$
[6.R4d]	$\frac{d\alpha}{dt} = r_{[4]} = k_4' \left( 1 - \sqrt{\frac{P^0}{P}} \right) \frac{2V_{m(Mg)}}{e}$

**Table 8.1.** Pure cases of the determining step with the oxidation of a magnesium plate

If the rate-determining step is a reaction [6.R4a], [6.R4b] or [6.R4d], the space function is:

$$E_1 = E_2 = E_4 = \frac{S_0}{n_0} = \frac{\frac{S_0}{eS_0}}{\frac{2V_{m(Mg)}}{e}} = \frac{2V_{m(Mg)}}{e}$$

These space functions do not depend on the fractional extent  $\alpha$ .

If the rate-determining step is the diffusion [6.R4c], the space function is:

$$E_3 = \frac{S_0 G}{n_0} = \frac{\frac{S_0}{eS_0}}{\frac{2V_{m(Mg)}}{eX}} = \frac{2V_{m(Mg)}}{eX} = \frac{4V_{m(Mg)}}{ze^2 \alpha}$$

This space function depends on the fractional extent.

Table 8.1 summarizes the rates of the four modes with one determining step for magnesium oxidation with electrically-neutral oxygen vacancies. The integration of these speed equations with respect to  $\alpha$  leads to linear laws of variation of fractional extent with time, except in the case of the mode determined by diffusion [6.R4c], which leads to the parabolic law:

$$\alpha^2 = k_p t \quad [8.44]$$

Finally, a solution corresponding to a pure mode leads to an expression of the rate as a function of the partial pressures, concentrations of the main components of the reaction and fractional extent.

#### 8.1.6. Pure modes away from equilibrium for linear sequences

We know that the speed of an elementary step contains the distance term of experimental conditions relative to the equilibrium (relation [3.14]) which for a step  $i$  is:

$$\varepsilon_i = 1 - \exp \frac{\Delta G_i}{RT} \quad [8.45]$$

However, the Gibbs free energy of the reaction is given as a function of the Gibbs free energies of the elementary steps through:

$$\Delta G = \sum_{\rho} \lambda_{\rho} \Delta G_{\rho} \quad [8.46]$$

but in a mode determined by one step, all the steps other than the one that determines the speed are assumed at equilibrium and therefore their Gibbs free energy is zero, which leads to:

$$\Delta G = \lambda_i \Delta G_{i,[i]} \quad [8.47]$$

Thus, for the speed of a reaction determined by step  $i$ , the distance between the actual conditions and the equilibrium conditions is obtained through:

$$\varepsilon_{[i]} = 1 - \exp \frac{\Delta G}{\lambda_i RT} \quad [8.48]$$

The latter term corresponds to the term in square brackets of relations [8.30], [8.32], [8.36] and [8.40].

If the experimental conditions are such that we are a long way from equilibrium conditions (which means, since all the steps except the determining one are always at equilibrium, the determining step is itself far away from equilibrium and its opposite reaction speed can therefore be ignored) then the exponential of the previous expression is negligible compared to one.

Everything goes as if the steps that follow the determining step are no longer involved. The speed is completely determined by the first  $i$  steps. Thus the partial pressure or concentration of a main component of the reaction will only affect the speed if that constituent is involved in the steps that precede the step that determines the speed.

### 8.1.7. Influence of temperature on linear sequences

As for the influence of temperature, by deriving the rate, *with constant space function*, we can write:

$$\frac{\partial \ln r_{[i]}}{\partial (1/T)} = \frac{\partial \ln \phi_{[i]}}{\partial (1/T)} \quad [8.49]$$

Let us reconsider the example of relation [8.40]:

$$\frac{\partial \ln r[4]}{\partial(1/T)} = \frac{\partial \ln \phi[4]}{\partial(1/T)} = \frac{\partial \ln \left\{ k'_4 \left( 1 - \sqrt{\frac{P^0}{P}} \right) \right\}}{\partial(1/T)} = \frac{\partial \ln \left\{ k'_4 \varepsilon_4 \right\}}{\partial(1/T)} \quad [8.50]$$

This relation is not a simple equation. Let us look at the ratio of the reactivity to the distance between the actual conditions and the equilibrium conditions. Equation [8.50] becomes:

$$\frac{\partial \left( \ln \frac{\phi[4]}{\varepsilon[4]} \right)}{\partial(1/T)} = \frac{d \ln k'_4}{d(1/T)} \quad [8.51]$$

however, it is known that the rate coefficient  $k'_4$  follows Arrhenius' law, so we deduce:

$$\frac{\partial \ln \left( \frac{\phi[4]}{\varepsilon[4]} \right)}{\partial(1/T)} = \frac{d \ln \left\{ k'_4 \right\}}{d(1/T)} = -\frac{(E_a)_4}{R} \quad [8.52]$$

Thus we realize that the ratio of the reactivity to the distance between the actual conditions and the equilibrium conditions follows Arrhenius' law with a temperature coefficient that is an apparent activation energy and, in the case of the example chosen, is the activation energy of the rate-determining step. We will see, in other examples, that this is not always the case. Table 8.2 summarizes Arrhenius' temperature coefficient (or apparent activation energy), when it exists, as a function of the activation energies and enthalpies of the elementary steps.

It should be noted that a diffusion step occurs with a null enthalpy. The sign of the apparent activation energy, if it exists, unlike the sign of a real activation energy, is not necessarily positive due to possible negative enthalpic terms, i.e. due to the presence of highly exothermic steps that precede the determining step.

NOTE 8.4.– We see that the influence of temperature can be complex and that a similar calculation should be performed for each mechanism studied. In particular, it should be noted that the second solution corresponding to the second mode does not enable us to separate the variables of pressure and temperature.

Speed-determining step	Arrhenius coefficient
[6.R3a]	Exists only if $K_2K_4 \gg 1$ <b>then</b> $\Xi_a = (E_a)_1$ or $K_2K_4 \ll 1$ <b>then</b> $\Xi_a = (E_a)_1 + 2\Delta H_2 + 2\Delta H_4$
[6.R3b]	Exists only if: $\sqrt{K_1P} \gg 1$ then $\Xi_a = (E_a)_2 + \Delta H_4$ or $\sqrt{K_1P} \ll 1$ then $\Xi_a = (E_a)_2 + \Delta H_4 + \frac{\Delta H_4}{2}$
[6.R3c]	$\Xi_a = (E_a)_3 + \Delta H_4$
[6.R3d]	$\Xi_a = (E_a)_4$

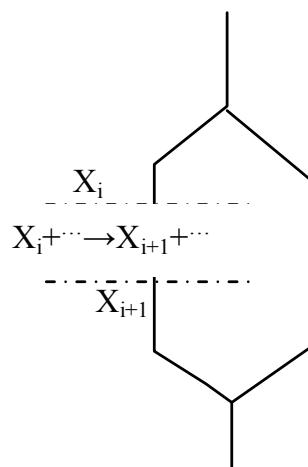
**Table 8.2.** Arrhenius coefficients of the different modes determined by a step in magnesium oxidation

### 8.1.8. Cyclic sequences

Until now, we have chosen the rate-determining step in a linear sequence. Let us now examine the case where the determining step is chosen within a loop.

Figure 8.2 represents a step that enables us to go from intermediate  $X_i$  to  $X_{i+1}$  in the loop of a Semenov diagram. If this step determines the speed, which means that all the others are practically at equilibrium, then species  $X_i$  and  $X_{i+1}$  are in equilibrium with the other side of the loop, regardless of its direction of traversal. Therefore, the speed of the determining step will be zero because it is the product of a finite rate with null distance between the actual conditions and the equilibrium conditions.

It follows that it is impossible to envisage a mode with a rate-determining step if this step is placed inside a loop because the reaction would be instantaneous.



**Figure 8.2. Determining step inserted in a loop**

### 8.1.9. Conclusion on modes with a single determining step

From our study of pseudo-steady state modes whose speed is determined by a single step, we can draw the following conclusions:

- A pseudo-steady state solution determined by a single step is only conceivable for the steps taken outside of a Semenov cycle diagram.
- In practice, in order to seek a solution related to a determining step, we just have to perform the speed calculation by considering the direct reaction of the rate-determining step and, if it is not negligible, add the distance term between the actual conditions and the equilibrium conditions obtained from relation [8.47] by taking into account the multiplying coefficient of the step. It is useful to make the Gibbs free energy explicit in terms of concentrations and temperature.

The review of many general results enables us to deduce the following properties of modes with one rate-determining step that are important in the choice of mechanism:

- The resulting rate is always separable and the space function only depends on the size of the zone where the determining step takes place. Thus, steps [6.R4a] and [6.R4b] occur in zones that always maintain identical sizes and so the space function is the same for these two steps.

- We see that if the rate-determining step does not belong to a catalytic cycle, which means that it does not involve species whose concentrations are complementary (constant sum – step [6.R4c] and [6.R4b] in the previous example), the mode of the determining step enables us to reach a solution in which the ratio of the reactivity to distance between the actual conditions and the equilibrium conditions is a function in which the concentration variables are separated from each other and from the temperature. In this function only the concentrations of the reactants and products used in the first members of the determining step and steps that precede the determining step in the mechanism are involved. This function obeys Arrhenius' law and its temperature coefficient, which is an apparent activation energy, is the sum of the activation energy of the determining step and the enthalpies of the steps that precede it, each multiplied by its multiplying coefficient.

We deduce from these observations that a speed that obeys an order with respect to a reactant can be explained if the following conditions are met:

- the reaction is carried out under conditions that are a long way from equilibrium;
- the determining step does not belong to a catalytic cycle;
- this step, or at least one of those that precedes it in the mechanism, involves that reactant.

Likewise, the speed obeys Arrhenius' law and the temperature coefficient is an apparent activation energy if the following conditions are met:

- the reaction is carried out under conditions that are a long way from equilibrium;
- the determining step does not belong to a catalytic cycle.

Furthermore, this apparent energy is only a true activation energy if no step precedes the rate-determining step in the mechanism.

For example, we see that in the magnesium oxidation reaction, the reactivity is a function in which the temperature is a separate variable only if the steps [6.R4c] or

[6.R4d] are determining (steps [6.R4a] and [6.R4b] belong to a catalytic cycle with the sum of the concentrations of empty and occupied sites, which is constant). These steps are of zero order with respect to the gas because the chain of the mechanism, which is a convergent linear mechanism, has a branch that starts in [6.R4d] and then [6.R4c] and neither of these steps reacts with oxygen. They both lead to apparent activation energies but only the mode determined by step [6.R4d] gives a true activation energy because this step is not preceded by any other in the chain.

## 8.2. Pseudo-steady state mode with two determining steps

### 8.2.1. Definition

A pseudo-steady state mode is said to have two rate-determining steps or be in the mixed pseudo-steady state if it meets the following assumptions:

- the mode is in the pseudo-steady state;
- the rate coefficients (and hence the speed factors) of the different elementary steps are infinite except for two of them whose coefficients are finite and are called the rate-determining steps.

### 8.2.2. Mathematical formulation of a mixed pseudo-steady state mode

The simplest method for the mathematical formulation of such a mode is the following and it is based on the one that has been used for pure modes with a single rate-determining step.

First, we write the mass action law for all the non-determining steps and we deduce the concentrations of all the intermediates except one: the one that is involved in both determining steps.

NOTE 8.5.– If the two chosen steps are not immediately consecutive, we obtain a relation between the concentrations of the intermediate produced by the first and the intermediate for the second through the equilibria of the intermediate steps by applying the mass action law to the steps located between the two determining steps.

Then we write two equations, by applying [8.19], each expressing that the rate is given by the rates of each of the determining steps. We replace there the concentrations calculated earlier. This gives a system of two equations with two unknowns, which are the rate of the system and the unknown concentration of the intermediate. The resolution of this system enables us to determine the rate as a function of concentrations, temperature (through the rate coefficients of both non-

determining steps and the equilibrium constants of the others) and morphological data in the zones where the determining steps take place.

We will apply the method to such a mode in the case of magnesium oxidation [6.R4] with the magnesium sample plane whose mechanism is given by steps [6.R4a] to [6.R4b]. We will choose the mixed mode determined by the outer interface reaction [6.R4b] and diffusion [6.R4c].

By using the first and third equation in [8.22], the equilibria of steps [6.R4a] and [6.R4d], we calculate:

$$\theta = \frac{\sqrt{K_1 P}}{1 + \sqrt{K_1 P}} \text{ and } [V_O]_{\text{int}} = K_4 \quad [8.53]$$

We can express the system rate  $r_{[2,3]}$  in two different ways by applying relation [7.15] to each of the determining steps [6.R4b] and [6.R4c]. Therefore we will have:

$$r_{[2,3]} = \phi_2 E_2 = \left\{ \frac{k'_2 \sqrt{K_1 P}}{1 + \sqrt{K_1 P}} [V_O]_{\text{ext}} - \frac{k''_2}{1 + \sqrt{K_1 P}} \right\} E_2 \quad [8.54]$$

$$r_{[2,3]} = \phi_3 E_3 = \{ D K_4 - D [V_O]_{\text{ext}} \} E_3 \quad [8.55]$$

The system consisting of equations [8.54] and [8.55] has two unknowns: the rate  $r$  and the outer concentration in oxygen vacancies. The resolution of this system gives the solution to the corresponding mixed mode.

### 8.2.3. Linear sequences: inverse rate law or the law of slowness

Through the addition of [8.54] and [8.55], after having multiplied the first by  $K_4 D E_3$  and the second by  $E_2 \frac{k'_2 \sqrt{K_1 P}}{1 + \sqrt{K_1 P}}$ , we cancel the concentration in outer oxygen vacancies and we obtain:

$$\frac{1}{r} = - \frac{1}{k'_2 \frac{\sqrt{K_1 P}}{1 + \sqrt{K_1 P}} K_4 \left\{ 1 - \sqrt{\frac{P_0}{P}} \right\} \frac{2V_{m(Mg)}}{e}} + \frac{1}{Dz K_4 \left\{ 1 - \sqrt{\frac{P^0}{P}} \right\} \frac{4V_{m(Mg)}}{ze^2 \alpha}} \quad [8.56]$$

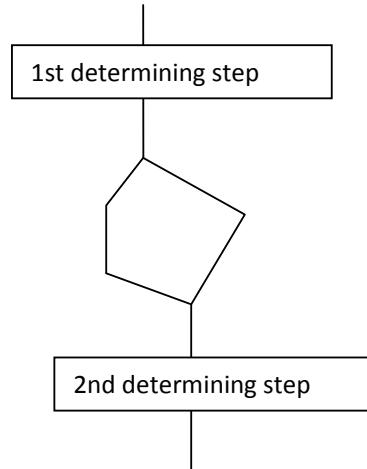
If we compare the latter relation with the expressions of the second and third row of Table 8.1, we can see that the following result is obtained:

$$\frac{1}{\eta_{[2,3]}} = \frac{1}{\eta_{[2]}} + \frac{1}{\eta_{[3]}} = \frac{1}{\phi_{[2]}E_2} + \frac{1}{\phi_{[3]}E_3} \quad [8.57]$$

The inverse of the rate in a mixed pseudo-steady state mode is the sum of the inverse rates of both pure modes corresponding to the two determining steps. This theorem constitutes what is called the inverse rate law.

It is proved and we assume that this theorem is general for the mixed pseudo-steady state modes of a linear sequence, even if the two determining steps are not immediately consecutive, as in the previous example, *provided that both determining steps have the same multiplying coefficient*. If the latter condition is not met, relation [8.57] is not usable.

We cannot take a determining step in a loop and one outside the loop, but it is possible to have a loop between the two rate-determining steps, like in the scheme below.



NOTE 8.6.— This theorem, which has often been viewed as an inverse (or conductance) addition law for series reactions (by analogy to the electrical conductances), is not one of them. This is because the addition does not concern the rates of the inverses of both determining steps (which are equal), but the solutions of the modes with one determining step.

NOTE 8.7.— We can write relation [8.57] as follows:

$$r = \frac{\phi_{2[2]}\phi_{3[3]}E_2E_3}{\phi_{2[2]}E_2 + \phi_{3[3]}E_3} \quad [8.58]$$

This relation shows that in general the mixed pseudo-steady state mode does not follow the law of  $\phi E$ , except when both determining steps have the same space function. In this case the reactivities follow the inverse rate law.

If the two determining steps do not have the same multiplying coefficient, the system of the two equations is less straightforward and does not allow elimination of the concentration by simple addition. Therefore, the inverse rate law is no longer met.

The solution is thus obtained with steps close to equilibrium. If the overall reaction is carried out a long way from equilibrium conditions, this does not mean that each of the rate-determining steps is also distant from equilibrium. In order to avoid mistakes, we lead the calculations in the general case with the actual conditions not far from the equilibrium conditions and we apply the approximation only on the final result. For example in relation [6.55] we will ignore  $\sqrt{P^0/P}$  compared with 1.

#### 8.2.4. Cyclic sequences

In the case of a loop, two cases arise:

- both determining steps belong to the same branch of the loop, but the equilibrium between all the species due to the other branch of the loop and the reaction is instantaneous; or
- each of the determining steps belongs to one branch of the loop and, in this case, a simple rate addition law is obtained. To sum up, whenever at least one of the determining steps belongs to a loop or a set of parallel paths, the application of the inverse rates law will be avoided.

#### 8.2.5. Law of characteristic times

Let  $\Delta\tau$  denote the time needed for the fractional extent to go from zero to a value  $\alpha$ , which represents a variation  $\Delta\alpha$  in a mixed pseudo-steady state mode of a linear

sequence and let  $\Delta\tau_{[i]}$  and  $\Delta\tau_{[j]}$  denote the time needed to obtain the same fractional extent of variation  $\Delta\alpha$  in a pure mode of  $i$  and  $j$ , respectively. If  $\Delta t$  is not too large, by using [8.57] we can write:

$$\frac{1}{\eta_{[i,j]}} = \frac{\Delta t}{\Delta\alpha} = \frac{1}{\eta_{[i]}} + \frac{1}{\eta_{[j]}} = \frac{\Delta\tau_{[i]}}{\Delta\alpha} + \frac{\Delta\tau_{[j]}}{\Delta\alpha} \quad [8.59]$$

from which we deduce:

$$\Delta\tau_{[i,j]} = \Delta\tau_{[i]} + \Delta\tau_{[j]} \quad [8.60]$$

This law is called the law of addition of characteristic times. It is applied under the same conditions as the inverse rates law from which it is directly derived and is recalled in the following:

- pseudo-steady state mode;
- linear sequence;
- the same multiplying coefficients for all the determining steps.

### 8.3. Generalization to more than two determining steps

It is easily conceivable that choosing three, four, or more determining steps and, ultimately, taking all the steps as determining can complicate the mode. We then obtain the general pseudo-steady state mode.

The previous generalization leads to a generalization of the inverse rates law in the case of linear sequences and with the condition that all the steps involved have the same multiplying coefficient. Thus we have:

$$\frac{1}{r} = \sum_i \left( \frac{1}{\eta_{[i]}} \right) = \sum_i \left( \frac{1}{\phi_{[i]} E_i} \right) \quad [8.61]$$

This generalized inverse rates law only leads to a form  $\phi E$  if all the space functions are identical, as is the case in a homogeneous system.

Similarly, a generalized law of the addition of characteristic times would be obtained.

#### 8.4. Conclusion to the study of modes with one or several rate-determining steps

We deduce from the systematic review of many cases and assume an extremely important property of modes with one or several determining steps and other modes, that a reaction rate is expressed as a product of two functions:

- $\phi$ , which only depends on intensive physico-chemical variables; and
- $E$ , which only depends on the textural characteristics of reaction zones.

This is the case only for modes belonging to the following families:

- modes with one rate-determining step; and
- modes with several rate-determining steps and more generally all pseudo-steady state modes, with the condition that the space functions of all the steps are identical.

This property, which is sometimes known as the law of  $\phi E$ , is extremely useful in heterogeneous kinetics because the experimental verification of this property, which is very common, greatly simplifies the research into mechanisms.

This property applies to all homogeneous systems in pseudo-steady state modes. Here, the function  $\phi$  is the volumetric speed and the unique space function is the ratio of the phase volume to the amount of reference substance chosen.

#### 8.5. First order mode changes

Let us reconsider Table 8.1 and imagine that in a certain range of temperatures step 3 of diffusion is determining, and in the following temperature range – due to a different action of temperature on the rate coefficients – step 2 of the outer interface reaction becomes determining. In each of the temperature ranges we will therefore obtain two kinetic laws versus time. If we look at Table 8.2, we will probably have a different temperature coefficient for each range. This is what is called a first order change of mode.

This change results in a break in the Arrhenius line. This is what we have already seen in the example of  $\text{N}_2\text{O}_5$  decomposition (see section 7.4.2) and in the catalysis example (section 7.4.5 and Figure 7.7), in which the resulting two extreme cases were the two modes with a single determining step.

The space between the two modes with one determining step is the corresponding mode with two determining steps.

This phenomenon is particularly expanded in the oxidation reaction of a sheet of tantalum by oxygen gas, for which with the increase in temperature we pass from an inverse logarithmic-type law of extent as a function of time to a logarithmic law, then a cubic law, parabolic law, and finally a linear law at the highest temperatures.

### 8.6. Conclusion

Pseudo-steady state modes with rate-determining steps are specifically useful in heterogeneous kinetics for which we see that a very broad majority of reactions are adequately represented. They lead to simple expressions of speed that often admit an order with respect to some reactants.



## PART 2

# Reaction Mechanisms and Kinetic Properties



## Chapter 9

# Establishment and Resolution of a Reaction Mechanism

It is known that most chemical reactions do not occur in a single step but are the result of combinations of simpler reactions called “elementary steps”. In a reaction, all these elementary steps combine to produce its overall reaction mechanism.

### 9.1. Families of reaction mechanisms

There are two large families of reactions.

- *Reactions with a unique sequence* limited to a few elementary steps.
- *Reactions with an infinite number of elementary steps*, which include two distinct families:
  - chain reactions in which, in addition to a number of single-sequence steps (initiations and terminations), a small number of steps (the link) are repeated a theoretically infinite number of times;
  - reactions producing macromolecules in which each step periodically increases a pattern that is the length of a molecule with a periodic pattern.

It is extremely difficult to prove the elementary status of a reaction. Knowing examples and following some principles allows us to appreciate the elementary status of a reaction.

## 9.2. Different categories of elementary steps

There are numerous types of elementary reactions involving the use of different types of reaction intermediates.

With regard to the type of reaction zone, we can distinguish volume reactions that occur in a certain volume and interface reactions that take place at the interface between two phases: solid–gas, solid–solid, solid–liquid or liquid–gas.

Reactions are classified according to the type of intermediate processes involved and the nature of the chemical bond altered during the elementary step. As we shall see in section 9.3.3, an elementary step only involves the modification of a single bond.

### 9.2.1. Homolytic bond breaking

In this type of breaking, two parts of the molecule take an electron away from the electron pair, which leads to the formation of two radicals, such as for example the dissociation of bromine during the first step of hydrogen bromide synthesis:



### 9.2.2. Heterolytic bond breaking

In such breaking, one side of the molecule takes both electrons away from the electron pair. This leads to the formation of both positive and negative ions on two parts of the molecule. This can be seen, for example, during the breaking of organometallic compounds such as organomagnesium:



### 9.2.3. Ion dissociation

When ions are formed, these may have an internal energy that is higher than the energy required to induce fragmentation, thus leading to dissociation reactions such as:



This is in fact a type of homolytic ion dissociation that is classified separately because, unlike the homolytic breaking previously shown, this dissociation does not originate from molecules.

#### 9.2.4. Radical reactions

This combination involves the addition of reacting radicals, such as for example between two ethyl radicals to give *n*-butane:



Radical–radical reactions are simply the “marriage” of two unpaired electrons by anti-parallel spin coupling; they therefore need little or no activation energy but are highly exothermic. With the exception of a few cases, radical–radical reactions are more likely than radical–molecule reactions, provided the radical concentrations are suitable.

The majority of radicals reacting with each other form what is called combination products, whereas a minority form dismutation (disproportionation) products.

There is, however, an example where radicals do not react with each other when radical concentrations are extremely low. The radicals then have the opportunity to survive long enough to diffuse up to the walls of the reactor, where they are either adsorbed or recombine due to their proximate high concentration.

#### 9.2.5. Ion–molecule reactions

The electrical influence of an ion disturbs the charge distribution inside a molecule, which is even more prevalent with electron bonds. This electric polarization effect will give specific properties to the ion when attacking a molecule, which will not require a thermal energy bigger than the average surrounding molecule to react. This interaction may result in different effects.

##### 9.2.5.1. Ion–molecule reactions with charge transfer

In this case, the charge of the ion is transferred to the molecule. These are reactions of the following type:



These reactions are very efficient and generally have no parallel reaction.

### 9.2.5.2. Ion–molecule reactions with proton transfer

In these reactions, the ion loses a proton to the molecule. The proton affinity (AP) of a neutral molecule  $M$  is defined as being equal to the enthalpy (except for the sign) of the reaction:



or:

$$A.P.(M) = \Delta H_f(M) + \Delta H_f(H^+) - \Delta H_f(MH^+)$$

NOTE 9.1.– The proton affinity of  $M$  is therefore the opposite to the enthalpy of the reaction of the  $MH^+$  species formation. If we consider the following equilibrium:



this equilibrium will shift so that the reaction is exothermic. In other words, the proton moves towards the entity with the highest proton affinity.

These reactions are also very effective and it can be said that virtually every clash leads to a proton transfer.

### 9.2.5.3. Ion–molecule reactions with negative ion transfers

Various types of negative ion transfers have been observed in the gas phase as well as in the condensed phase. For example, the transfer of the  $H^+$  ion is a fast process, provided that the reaction is exothermic:



These reactions are also very effective and can occur at virtually every clash.

### 9.2.5.4. Ion–molecule reactions with condensation

Condensation reactions are also possible with ions. Ionic polymerization is a common example:



In some cases the reaction is accompanied by the elimination of an electron or a small molecule:



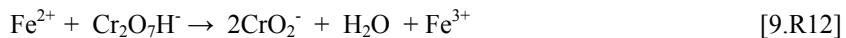
### 9.2.6. Reactions between ions

We must distinguish reactions between ions of the same sign, such as the dismutation of the hypochlorite ion according to:



These reactions generally have very high activation energy.

The reactions between ions of opposite signs have *a priori* very low activation energy, such as the reaction between the iron (II) and chromium (VI) ions:



This reaction is a step in the oxidation of iron (II) into iron (III) by chromium (VI). In the mechanism, the chromium goes through all its levels of oxidation.

### 9.2.7. Interface reactions

In heterogeneous systems, particularly those involving a solid phase, reactions happen at the interface between the gaseous medium and the solid phase. The most important are those involving adsorption. When gas is in the presence of a solid, some of its molecules bind to the solid surface. These bonds can sometimes be of comparable force to covalent bonds. This is described as the process of chemisorption, where the gaseous molecules linked to the solid are called adsorbed molecules.

#### 9.2.7.1. Simple adsorption

If  $s$  denotes a site on the surface of the solid that can fix a gas molecule, the adsorption step is often considered elementary and for a gas  $G$  is written:



#### 9.2.7.2. Dissociative adsorption

In some cases the distance between two sites on which two parts of a molecule are linked is such that true dissociation of the gaseous molecule occurs during the adsorption. In the hypothesis of identical sites for both fractions, this can be written:



### 9.2.7.3. Reactions between adsorbed species or adsorbed species and molecules

In heterogeneous catalysis, two types of reactions involving the absorbed molecules are possible, which result in two distinct families of mechanisms. Either the reactions between adsorbed molecules give rise to a new adsorbed molecule, such as:



or, the reaction between an adsorbed molecule and a gas molecule gives rise to a new adsorbed molecule, such as:



Reactions such as [9.R15] are characteristic of the Langmuir–Hinshelwood catalysis mechanism (see section 13.2.3.2.1). Reactions such as [9.R16] are characteristic of the Rideal–Riley mechanism (see section 13.2.3.2.2).

### 9.2.8. Reaction between structure elements in the solid state

This reaction produces or consumes vacancies or ions within the interstitial position at the interface between a solid phase and another solid or gaseous phase, such as those found at an oxide–metal interface during the oxidation of zinc by oxygen. This can be written using Kröger's notation (see Appendix 1):



### 9.2.9. Reactions between adsorbed species and point defects

In heterogeneous reactions involving a stoichiometric solid, defects of the solid can react with adsorbed species. Hence the oxidation of zinc by oxygen, in which a reaction between adsorbed oxygen and zinc cations at the interstitial position leads to the growth of the zinc oxide network at the surface of the zinc oxide solid. This can be written using Kröger's notation (see Appendix 1):



The wide variety of elementary reactions hitherto examined is far from covering all possible stages. Insufficient experimental data often result in researchers settling for hypotheses that are compatible with the overall process of the reaction. Often,

the proposed mechanism is a possible mechanism; others are also likely, but the adoption of a new mechanism can only result from new experimental data.

A step during which two intermediates react with each other is sometimes called a quadratic step.

### 9.3. Establishment of a reaction mechanism

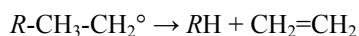
There is no foolproof and generic methodology that allows us to find the mechanism of a reaction. We therefore take an intuitive approach. Some rules must be respected, however. For writing the process itself, we generally use personal knowledge about a number of already known mechanisms, and therefore the more the researcher knows, the more likely he or she will be effective. A number of common mechanisms generic to an entire family of reactions are often good starting points. There are many examples of such generic mechanisms. One is the Rice–Herzfeld mechanism, which is used to account for the decomposition of saturated hydrocarbons. It is generally accepted as following a chain of radical mechanisms. This includes the three classic phases of chain reactions:

- *Initiation*: free radicals are initiated by rupture of the molecule at its weakest bond.

- *Chain propagation* takes place in two phases:

- one of the radicals extracts one hydrogen atom from the initial hydrocarbon to form a small molecule and a new radical; the two families of radicals formed can in turn react the same way,

- free radicals of the type  $R\text{-CH}_3\text{-CH}_2^\circ$  can be stabilized by ethylene elimination, such as:



- *Termination*: chain termination happens by radical combination.

This type of reaction mechanism applied to different saturated hydrocarbons highlights the extraordinary complexity of the distribution of products formed during numerous pyrolyses.

#### 9.3.1. Methodology

We use the trial and error method, which is a permanent back-and-forth between writing the mechanism and carrying out experiments to validate it.

First, we must propose a possible mechanism satisfying a certain number of rules (five in total, see sections 9.3.2 to 9.3.6). Once the mechanism hypothesis is proposed, all the consequences including kinetics are drawn. Thereafter, we can come up with complementary experiments to prove the mechanism incorrect. A mechanism can never be proved correct. We can only prove the opposite, hence discarding a mechanism that would not be consistent with observations.

It follows from this that the conclusion always leads to the availability of a mechanism accounting for known facts, but others may exist and therefore “*a*” mechanism and not “*the*” mechanism of the reaction is identified. Sometimes, we can suggest several mechanisms that are compatible with all of the experimental observations. New experiments or methods of investigation must be set up to decide between these mechanisms. However, even if only one mechanism is compatible with all experimental data, it should always be considered a hypothesis.

### **9.3.2. Rule no. 1: the law of elimination of intermediates**

For elementary steps, it is possible to write a balanced equation. Any intermediary must be produced and consumed during the overall mechanism, so there will be one or more combinations of elementary steps leading to the final balanced equation by eliminating all of the intermediates (sometimes this result is called the *law of elimination of intermediates*). To perform this combination, it is sometimes necessary to multiply some of the elementary steps by coefficients. Remember that these act as the *multiplying coefficient* of the step.

A review of the different reaction schemes is given in the following subsections.

#### **9.3.2.1. Open sequences**

In this case, a linear combination of the elementary steps must eliminate the intermediary species. In other words, for a main reactant of reaction  $k$  (reactant or product) involved in step  $\rho$  with the algebraic stoichiometric coefficient  $v_{k,\rho}$ , the following relationship can be written:

$$\sum_{\rho} \lambda_{\rho} v_{k,\rho} = 0 \quad [9.1]$$

#### **9.3.2.2. Case of single looped sequences**

This is a case where two linear combinations pass either side of the loop (in the correct direction).

### 9.3.2.3. Case of chain reactions

In this case, the linear combination must involve the link of the chain as well as at least one of the initiation and rupture steps. In the case of several parallel rupture steps, each step enters a different linear combination.

Moreover, in a chain reaction, the propagation steps must obey the elimination of intermediates rule by repeating them an infinite number of times. This is called the alternation of steps of the chain link.

**NOTE 9.2.–** As the stoichiometric coefficients of the balanced equation are only defined to the nearest coefficient, which is not the case with elementary steps, there are an infinite number of coefficient sets for a reaction, all of which are in proportion to each other. This is what is chosen when writing the overall equation that sets the range of coefficients chosen.

### 9.3.3. Rule no. 2: the rule of the least change of structure (in the case of a single bond)

An elementary reaction must only modify a small number of covalent or dative bonds, as the probability of several bonds rupturing simultaneously is extremely low, especially in the case of very high-energy bonds. To break several bonds, suitable levels of energies are required to spread within the molecule in given directions, which is very unlikely.

For example, during the combustion of propane:



it is necessary to break three carbon–carbon and eight carbon–hydrogen bonds. To imagine a simultaneous rupture of all these bonds would be contrary to common sense.

This rule does not apply to ionic bonds, which are distant and not oriented. The displacement of an ion can lead to the deep mutation of several bonds.

### 9.3.4. Rule no. 3: the rule of the greatest simplicity of elementary reactions (bimolecular)

This principle, which is applied within fluid, gaseous and liquid phases, comes from the commonly agreed fact that for one elementary reaction to happen, molecules must “meet” – at least in the energetic sense of the word. This means that

they must come into close contact with each other. Moreover, the collision of two particles is much more likely than the simultaneous collision of three particles. We will accept as a general rule that elementary reactions involve only two molecules, also called bimolecular reactions.

Returning to the previous example of propane combustion, a single-step reaction would require collisions between six non-random molecules, which is highly unlikely and would result in a very low reaction rate in reality.

### **9.3.5. Rule no. 4: the rule involving a single jump into the solid state**

This rule is the same as the previous one for the solid state. We will see that the elementary act during solid state reactions is the activated jump of a particle from a departure to an arrival site. A reaction involving the simultaneous jump of several particles or multiple jumps of the same particle would be very unlikely.

Transcribed as a quasi-chemical reaction using Kröger's notations, one jump can lead to the reactant stoichiometric coefficients, with a high sum greater than two. We must remember that in the solid state, these coefficients have no relationship with the number of particles involved in single collision, as in the fluid phase. For example, reaction [9.R14] only requires the two necessary sites to be adjacent at the surface of the solid.

### **9.3.6. Rule no. 5: the law of micro-reversibility**

This is a consequence of the second law of thermodynamics. The development of a reaction must in some way follow the same mechanical pathway as the reverse reaction.

This principle, which must be respected at the scale of an elementary step, is not valid when considering the overall reaction, as shown in the example of calcium carbonate decomposition:



In this decomposition reaction, it is evident that the lime formed will be on the surface of the carbonate grains (between the carbonate and the gas), whereas in the reverse reaction the carbonate would be on the surface of the lime (between the lime and the gas). In the first case, carbon dioxide has to go through the lime, whereas in the second case, it has to go through the carbonate. These paths are not the reverse

of each other, but this does not contradict the principle of micro-reversibility because reaction [9.R20] is not elementary.

#### 9.4. Research into a mechanism: intermediary reactions

If a mechanism includes several steps, this means that it involves relatively stable intermediary compounds, which can be classified in two large families based on their relative duration of existence:

- intermediates with long lifetimes that will eventually be detected by classic analytical methods, as if they were stable, final products of reactions;
- intermediates with short lifetimes for which additional experiments – often sophisticated – are necessary for detection.

##### 9.4.1. Reaction filiations: primary and non-primary products

As well as the reactants, several products can simultaneously be present with relative stability, even if these are no longer present in the reaction. These products are known as intermediates with a long lifetime. The research into reaction filiations is the first step in a kinetic study because it allows us to define chemical reactions that actually happen in a medium while producing long lifetime intermediates.

###### 9.4.1.1. Filiation schemes

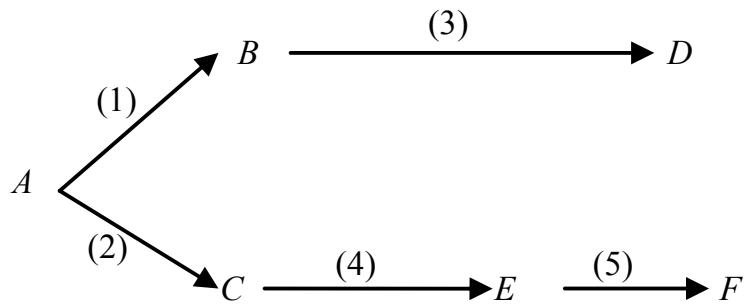
If several products are present at a sensible level in a medium, and some are “stable” intermediates that will no longer be present at the end of the reaction, it is important to build-up the filiations of different products. We need to know each of their immediate precursors. To achieve this, we must proceed in two steps. In the first instance, we must consider the possible filiations that are reactions. If some can be achieved on their own, we will analyze them separately to check them. In the second instance, we must try to distinguish primary and non-primary products.

###### 9.4.1.2. Primary and non-primary products

It is important to know the order in which these intermediates appear as well as their filiations. We must distinguish the primary products directly resulting from reactants from the non-primary products that result directly or non-directly from the primary products.

To illustrate this, consider the simple reaction as shown in Figure 9.1 in which only one reactant, *A*, is included and gives two stable products, *D* and *E*.

Compounds *B* and *C* are the primary products, whereas *D*, *E* and *F* are the secondary products.



**Figure 9.1.** Reaction scheme with primary and non-primary products

With homogeneous kinetics, the initial reaction rates allow us to distinguish the primary products – whose initial rate of formation is finite and not zero – from the non-primary products – whose initial speeds of formation are zero and the precursors are not present in the initial medium. This rule is no longer true with heterogeneous kinetics, including the formation of new solid phases, since the competitive nucleation-growth reactions (see Chapter 14) have an initial rate of zero, even for primary products.

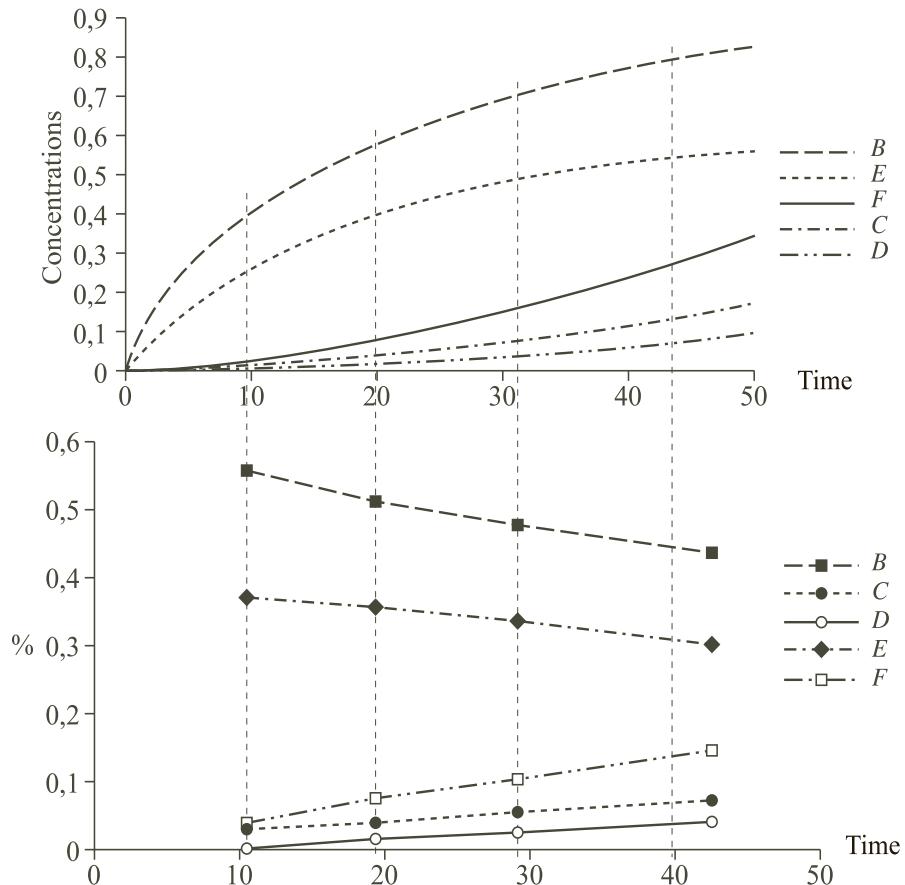
#### 9.4.1.3. Experimental determination of the primary or non-primary character of a product

We have seen that the initial rates are not always reliable, even in the case of homogeneous kinetics with low initial rates. To establish the primary or secondary nature of a mixture of reaction products, the “horizontal diagram” is used.

Consider the evolution curves of the five products from the previous reaction as a function of time (see Figure 9.2a). The percentage of each of product present in the medium is normalized to 100 by products, not reactants, and at a given time  $t_1$ , must be taken into account. Percentages are recorded as a function of time on a graph (Figure 9.2b). This is repeated for different times:  $t_2$ ,  $t_3$ ..., which gives rise to the curves in Figure 9.2b. At the first time,  $t_1$ , the primary products are the only ones present in the medium and correlate with a high proportion of the non-primary products.

Let us see the example of the reduction of uranyl fluoride by pyrolysis during which the uranyl fluoride is heated in the presence of both water and hydrogen

vapors. Two uranium oxides,  $\text{UO}_2$  and  $\text{UO}_3$ , are present in the reaction medium. It would take a long time to determine whether the final product is  $\text{UO}_2$  or  $\text{UO}_3$ .

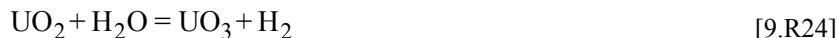


**Figure 9.2.** Construction of the horizontal diagram

Two filiations are possible. The first in which  $\text{UO}_3$  is the intermediary:



or the in which  $\text{UO}_2$  is the intermediary:



Experimentally, mixing the fluoride with water vapor alone exclusively results in  $\text{UO}_3$ ; the first filiation is therefore the correct one, since water vapor does not reduce  $\text{UO}_3$ .

#### **9.4.2. Labile intermediates**

Most of the time, research into labile intermediates involves the use of very sophisticated techniques that require experts in the technique being used. The kinetics researcher rarely leads this research on his/her own, but his/her input is important for the suggestions that can be brought forward with respect to the possible presence of some of the compounds. Two main methods are used: chemical and physics methods.

##### **9.4.2.1. Chemical methods**

Radicals or ions react with the suitable reactants in order to follow the disappearance or appearance of one substance resulting from the action of the intermediary on the reactant.

###### **9.4.2.1.1. Paneth's mirror method**

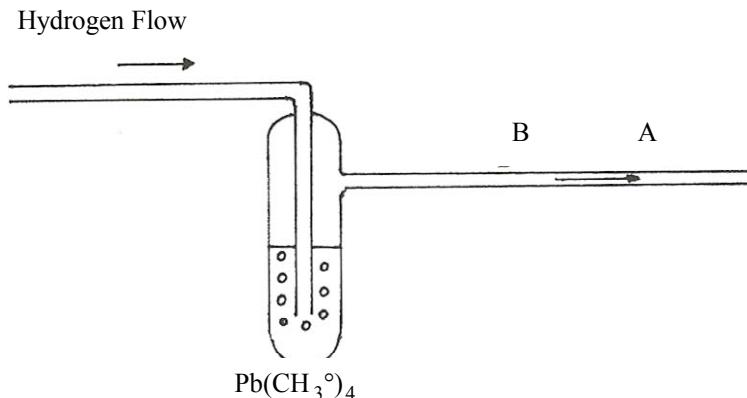
In 1930, Paneth's experiment allowed the existence of free radicals to be demonstrated. A hydrogen flow (see Figure 9.3) drives away the tetramethyl lead vapors. The wall of the tube in which the vapors circulate is heated at a specific point, A. The thermal decomposition of the tetramethyl lead results in the formation of a lead mirror at point A. If the wall is heated at another point, B, mirror A disappears and a new mirror appears at point B.

The process can be explained by the formation of methyl radicals,  $\text{CH}_3^\circ$ , coming from the decomposition of the tetramethyl lead:



When radicals are in the presence of lead, tetramethyl lead is renewed.

The average lifetime of free radicals can be measured if the gas flow and the required time to reform mirrors located at increasing distances from the production zone are known. This average lifetime value is about  $10^{-2}$  seconds.



**Figure 9.3.** Paneth's mirror experiment

Substances ( $M$ ), such as arsenic, sodium, zinc and mercury, are usually used instead of lead. Quantitative measurements are carried out using the dosing of the compound  $M(R^\circ)_n$ .

#### 9.4.2.1.2. Other examples of chemical methods

Here we will mention two families for dosing radicals in a liquid medium:

- The use of iodine or iodhydric acid as radical traps by using fixation or one iodine atom on one radical:



The disappearance of di-iodine is followed using calorimetry of iodometry. An acid–base titration and the following reaction can also be used:



- Colorimetric quantitative analysis by the diphenylpicrylhydrazyl (DPPH) radical. The purple color of this reactant can disappear to become colorless, reflecting the formation of the colorless compound.

#### 9.4.2.2. Physics methods

As reaction intermediates are often present at very low levels or with a very short lifetime (or both at the same time), physics-based methods are more suitable for their analysis, especially methods focused on the use of spectroscopy and resonance. Among the most frequently used methods are:

- absorption or emission spectroscopy;
- electronic paramagnetic resonance; and
- Fourier transform infrared spectroscopy of an adsorbed phase.

With heterogeneous reactions leading to the formation of a solid, the reaction intermediates, including adsorbed gases, are temporary defects. This knowledge was gained by the use of physics-based methods: electric conductivity, Hall effect, spectroscopies, etc.

As already mentioned, the use of different techniques to the full extent of their capacities requires experts who are often associated with studies of kinetics.

### 9.5. Back to the modes and laws of kinetics

The main kinetic modes provide comparatively complex reaction rate laws, the results of which depend on the type of mode chosen. The experimental comparison of these laws is one of the aspects of mechanism validation.

#### 9.5.1. Modes with a single rate-determining step

Such modes are obtained by writing the pseudo-steady state and that each step, except the rate-determining step, are at equilibrium.

Such a mode provides a rate law that is the product of one kinetic term and the distance from the equilibrium conditions, with the kinetic term being the reaction rate when the reaction is far from the equilibrium.

By applying the law of mass action for all the non-rate-determining steps, the reaction rate far from the equilibrium is such that it often admits an order with respect to some reactants and/or products. In this case, concentrations of the different reagents and products are separate variables apart from each other and from temperature. Only “catalytic” sequences such as adsorption disturb these properties.

### 9.5.2. Modes with multiple rate-determining steps

With these modes, two (or more) steps are rate-determining, with others having infinite rate coefficients and so are always at equilibrium. The mode is either in a pseudo-steady state or not.

It is known that for some reactions, the reaction rates of such pseudo-steady state modes are given by the overall rate law (the law of the slowness) for a reaction. This law says that the reverse rate of the reaction is the sum of the reverse of the rates of the determining step modes.

This law of the slowness step is only valid if the reaction mechanism follows some conditions:

- the rate-determining steps belong to a linear sequence not involved in a loop;
- every rate-determining step has the same multiplying coefficient.

The law of the slowness involves the “sum” function, so the result may contain numerous sums, meaning that concentrations are not separated from each other and the temperature.

### 9.5.3. Pseudo-steady state modes

The form of the expression of the rate of such modes can be complex nevertheless a category of modes is like those described above and obeys the law of the slownesses (usable under the same conditions) the sum corresponding then including all the determining modes made possible by the mechanism.

Having the same form as the previous (see section 9.5.2), the expression of rates will have the same characteristics.

There is therefore some correlation between the form of rate law and acceptable modes, hence the importance of what we call the test experiments.

### 9.5.4. Link between the form of the rate equation and the presence of some elementary steps

The presence of the concentration of a species in a certain form indicates a strong probability of certain types of elementary reactions:

- the square root of a concentration most likely involves the symmetric dissociation of the corresponding compound;

- the influence of a product concentration implies that one of the products is the reactant of one of the elementary steps. This reaction is therefore either the rate-determining step or is occurring before the rate-determining step;
- the presence of a homographic term of a partial pressure indicates a step in which the adsorbed molecule is the reactant of one of the elementary steps.

## 9.6. Experimental tests

Having identified the reaction mechanism and stoichiometric coefficients, the experimental values (measured rate, measured fractional extent) can be used to determine the kinetic values, including the fractional extent and the rate (or reactivity). To do this, it is crucial for a reaction to undergo the pseudo-steady state test. Indeed, it is only when this test has been satisfied that the reaction will be defined by the reaction rate only, whatever the component or measurement analyzed. If this test is not satisfied, we will have to remember that each measurement is defined by its own fractional extent or a combination of several fractional extents. In the search for a kinetic mode, several methods are used. These will now be reviewed.

### 9.6.1. *Experimental methods*

These methods use techniques involved in following the extent of a reaction under specific conditions or with data analyzed differently.

#### 9.6.1.1. *Ostwald's isolation method*

In a closed system, this method aims to “isolate” the variations in the quantity of one of the reactants. The reaction is occurring in a mix, where each reactant except one is present in great excess. Hence, the amount (and concentrations, eventually) and influence of all the reactants in excess are considered constant during the measurement. The amount of the isolated reactant will be the only thing changing as a function of the fractional extent.

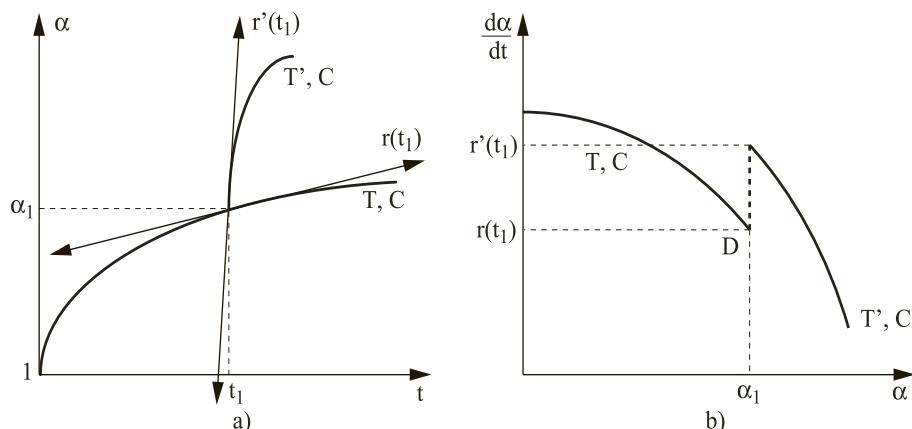
Products formed are also among the reactants to be taken into account.

A variation of this method consists of carrying out the reaction without the isolation of a component, i.e. using a large amount for each component so that all the amounts remain constant during the whole reaction. In this case, the reaction occurs within an extremely small fractional extent.

### 9.6.1.2. The switch method

The switch method consists of a sudden change in the value of one of the intensive quantities (temperature, concentration of one of the reactants, or partial gas pressure) during the reaction. Its effect is evaluated on an integral or derived curve (fractional extent against time, rate against time or rate against fractional extent).

Figure 9.4 shows an example of a switch in temperature on an integrate curve (a) and the deriveate curve (b). At the switch point, D, the spatial function has a given value,  $E_D$ . The volumic rate (rate per unit of volume – or surface rate) on the left of point D are defined by the physico-chemical conditions (temperature  $T$ , concentration  $C$ ) preceding the switch. The one on the right side of point D is calculated considering the physico-chemical conditions (temperature  $T'$  and concentration  $C$ ) after the switch point.



**Figure 9.4. a) Integral; and b) derived forms of a temperature switch**

### 9.6.1.3. Separated variables

With the aim of modeling a reaction, it is interesting to know which separate variables define the reaction rate. These include the concentration and partial pressure as well as the fractional extent of every separate variable included in the expression of a reaction's rate. If the rate can be written as a product of several functions, each of them being one of the variables, the reaction's rate would be written as:

$$r = f([A_1], \dots, [A_i], T, \alpha) = g_1([A_1]) \dots g_i([A_i]).h(T).m(\alpha) \quad [9.2]$$

The method applies the *theorem of separated variables*, which is defined as: if two curves representing function  $y$  with variable  $x$  obtained for two values of parameter  $a$  are subtracted from each other by an orthogonal affinity of axis  $Ox$ , orientation  $Oy$  and ratio  $k$ ; in the expression of the function, variable  $x$  is separated. Hence, if  $k$  is independent from  $x$ , we can write:

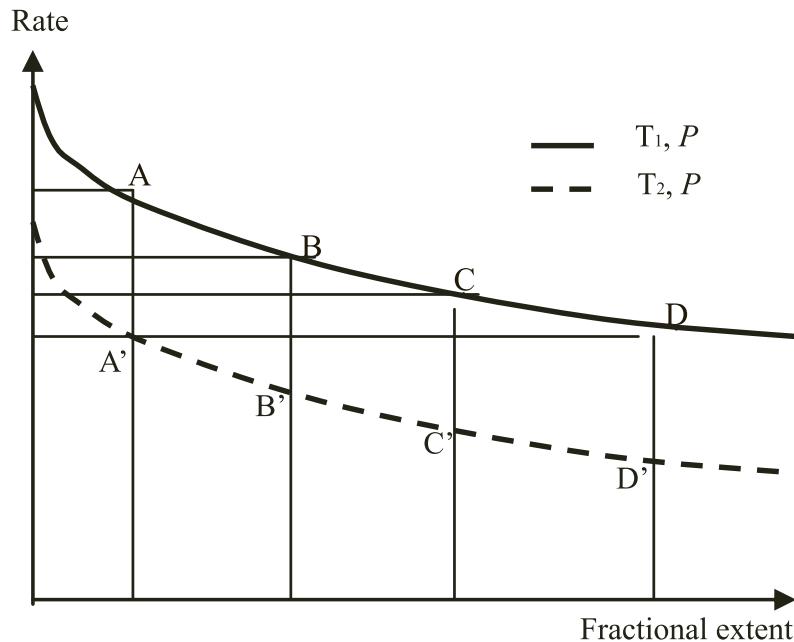
$$\frac{y_1}{y_2} = \frac{f(a_1, x)}{f(a_2, x)} = k \quad [9.3]$$

thereby:

$$y = f(a, x) = g(a).h(x) \quad [9.4]$$

and vice versa.

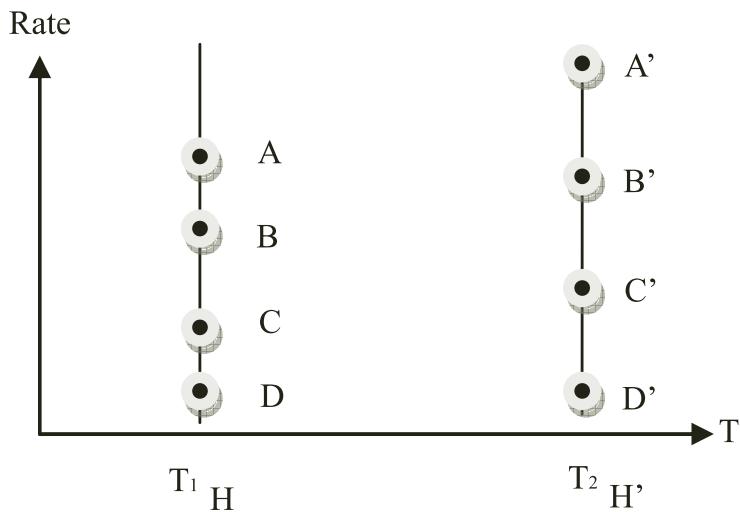
Suppose that we want know whether the temperature variable is a separated variable. Two experimental curves of rate versus fractional extent must be plotted for the same pressure and two separate temperatures (see Figure 9.5).



**Figure 9.5.** Experimental curves at two separate temperatures

From the first curve at pressure  $P$  and temperature  $T_1$ , four points of fractional extents A, B, C and D (distant enough from each other) and four rate values must be chosen. Using the same points of fractional extent on the second curve for a pressure  $P$  and temperature  $T_2$ , four other points A', B', C' and D', and four new rates values are obtained.

On a set of rate/temperature axes the rate for each point A, B, C and D as well as A', B', C' and D' for each temperature,  $T_1$  and  $T_2$  is plotted (see Figure 9.6).



**Figure 9.6.** Determination of the separation of variable  $T$

If the temperature is a variable separated from  $P$  and  $\alpha$ , the series of points A and A', B and B', C and C', and D and D' belong to four curves – iso-concentrations with an iso-extent – in the axis system  $v(T)$  that can be deduced from each other by the orthogonal affinity of temperatures axis and the rate axis orientation. This means that there is the following relation between distances:

$$\frac{HA}{HB} = \frac{H'A'}{H'B'} \quad \frac{HA}{HC} = \frac{H'A'}{H'C'} \quad \frac{HA}{HD} = \frac{H'A'}{H'D'} \quad [9.5]$$

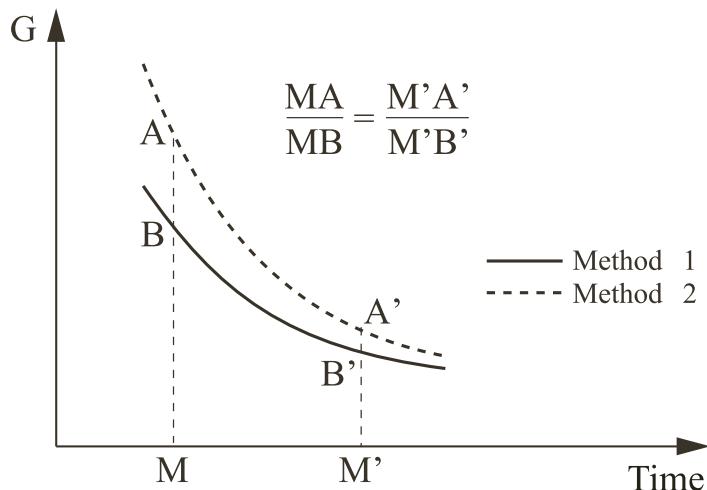
and the rate can be written:

$$v(T, P, \alpha) = h(P, \alpha) \cdot g(T) \quad [9.6]$$

### 9.6.2. The pseudo-steady state mode test

To prove the pseudo-steady state mode, two methods are used to determine the reaction rate and the measured rate. The first method is simultaneously compared to the one measured by calorimetry.

If the ratio of both rate measurements is the same at any time, the system is pseudo-steady state. To visualize it (see Figure 9.7), the ratio of two measurements is calculated at a given time and one of the two curves is re-calculated using the other one and the ratio value. If both curves obtained merge as a function of time, the system is pseudo-stationary.



**Figure 9.7. Comparison of two physics measurements related to the reaction**

### 9.6.3. Research into the uniqueness of the space function mechanism or $\phi E$ test

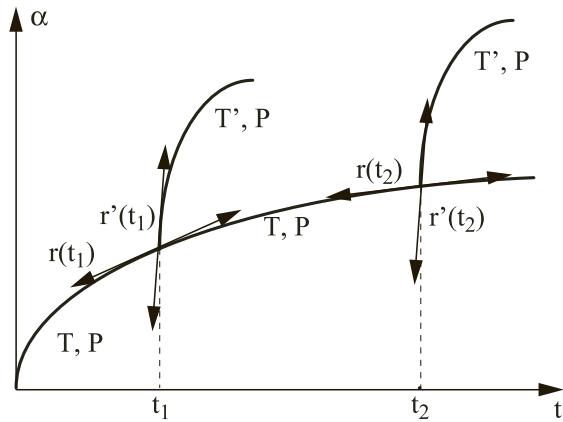
This test is carried out after the pseudo-steady state test, since it is only valid if the former is satisfied.

The  $\phi E$  test aims to determine whether the rate measured is written as a product of a function of only physico-chemical variables (temperature, concentrations, partial pressure, etc.) by a function of the morphological characteristics of a medium (surface-to-volume ratio, area of interfaces, volumes of the phases, etc.).

In homogenous kinetics the method is used to prove that there is only one way, without parallel ways, for the reaction to happen. This is no longer true if a reaction occurs simultaneously within and on the walls of the reactor.

With heterogeneous kinetics, a positive result means the mode has one or several rate-determining steps with the same space function. If the result is negative, it means the reaction does not occur within one rate-determining step.

This test is performed using constant concentrations in either an open or closed system using a concentrated medium and undergoing temperature switches.



**Figure 9.8. Principle of the  $\phi E$  test**

The first experiment is carried out (see Figure 9.8) at temperature  $T$  and at a given time  $t_1$ , the temperature is changed to  $T'$  with all other variables being kept constant. The same experiment is then repeated, but the temperature change is carried out at a different time,  $t_2$ . If the test is satisfied, we must have:

$$\frac{r(t_1)}{r'(t_1)} = \frac{\phi(T, P, \dots) E(t_1)}{\phi(T', P, \dots) E(t_1)} = \frac{\phi(T, P, \dots)}{\phi(T', P, \dots)} \quad [9.7]$$

$$\frac{r(t_2)}{r'(t_2)} = \frac{\phi(T, P, \dots) E(t_2)}{\phi(T', P, \dots) E(t_2)} = \frac{\phi(T, P, \dots)}{\phi(T', P, \dots)} \quad [9.8]$$

Hence the quotient of the rate on the left- and right-hand side of the switch point must not depend on time. To verify the test, we need to carry out several switches at

different times and plot the quotient of the right- over left-hand side rates as a function of time, obtaining a horizontal line.

## 9.7. Looking for the type of rate law

The type of rate law as a function of the different variables (concentrations, temperature and fractional extent) can be quite diverse. For this reason, some additional experiments will provide extra information about the form of law involved. These additional experiments are carried out according to specific methodologies.

### 9.7.1. Research into the influence of concentrations

The law of rates as a function of concentrations is the basic element of mechanism verification. For many years, researchers have worked on the integrated curves of fractional extent as a function of time. Indeed, the experiment generally gives these data directly. We must notice, however, that modeling leads to relations derived from the rate as a function of concentrations and that the integration of such an expression is often difficult or even impossible. With the rise of the digital era, it is now easy to obtain both derived and integrated experimental curves. The first experimental curves are then compared to the modeling results.

#### 9.7.1.1. Qualitative research

The first piece of information that needs to be obtained on the function of a reactant is whether its concentration affects the rate of reaction. This qualitative information can be simply obtained using a concentration switch.

In a gaseous medium, the switch is achieved by replacing a portion of the inert gas with high concentration of the gas being studied.

In solution, the addition of the reactant being studied must be done while keeping the concentrations of all the other reactants at the same level. There are two possible ways to do this:

- using the isolation method, starting with a low concentration of the reactant being studied and adding a small amount of pure reactant or concentrate in solution; or
- adding a solution identical to the one obtained at the switch point, except for the concentration of the reactant being studied. The additions will be done at the same temperature.

In any case, the influence of a reactant – if its concentration has an influence – induces a sudden change in the reaction rate.

#### 9.7.1.2. Quantitative research

To carry out quantitative research, the isothermal rate curves must be plotted for separate values of the concentration being studied. The isolation method must be used so the other reactant concentrations are kept constant during the reaction.

##### 9.7.1.2.1. Is the reactant concentration a separate variable?

Using the previous curves, the method from section 9.6.1.3 is used if the concentration is a separate variable in the expression of the rate. Using the result, a mechanism model is obtained, and so is the rate–concentration relationship. If the concentration is not a separate variable, the model must take that into account, and the law given by the model has to be compared with the rate–concentration curves obtained for different fractional extents.

If the concentration is a separate variable, the order of the reaction must be determined for one of the reactants. This is achieved using van 't Hoff's differential method.

##### 9.7.1.2.2. Determination of the reaction rate order

If the reaction has an order for reactant  $A_i$ , the rate can be written:

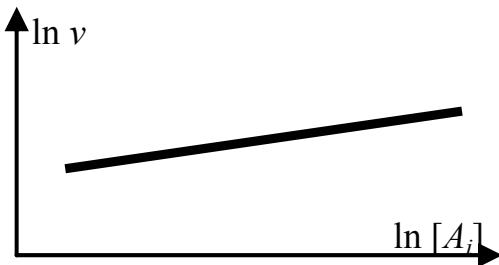
$$v = k[A_i]^{\beta_i} \quad [9.9]$$

where  $k$  is the pseudo-coefficient of the rate and includes all the other concentrations and temperatures.

This equation can be tested using decimal, entire or quotient values, or by using the logarithm scale:

$$\ln v = \ln k + \beta_i \ln[A_i] \quad [9.10]$$

By plotting the logarithm of the rate as a function of the logarithm of the concentration, a straight line of a gradient representing the partial order of the reaction is obtained (see Figure 9.9).



**Figure 9.9.** Determining of the order of a reaction by the differential method

Considering the variations caused by the logarithm scale, it is important to double-check the order determined by plotting the rate against the concentration at the power of the order determined. This should result in a straight line.

### 9.7.2. Research into the influence of temperature

Research into the influence of temperature involves:

- determining a quantitative expression using one or several “temperature coefficients”, allowing us to obtain the reaction rate for a different temperature to those used during the experiments; and
- confirming the model hypothesis.

#### 9.7.2.1. Research into the temperature coefficient

The temperature coefficient only exists if the temperature is a separate variable, which must be verified using the method detailed in section 9.6.1.3. If this is the case, the Arrhenius coordinates must be used by plotting the logarithm of the rate against the reverse of the temperature (see Figure 9.10). These curves often result in a straight line of gradient  $m$ . The temperature coefficient is the measure  $\Xi$  defined from the following expression of the volumic (or surface) rate:

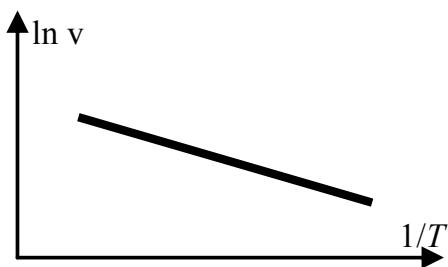
$$v = A \exp - \frac{\Xi}{RT} \quad [9.11]$$

where  $A$  is called the pre-exponential factor. Here, we can write:

$$\Xi = -Rm \quad [9.12]$$

where  $\Xi$  has the same units as the activation energy (joule.mole<sup>-1</sup>), but it is too early to merge both as the activation energy is only defined for the elementary steps.

If the temperature is not a separate variable, a possible temperature coefficient is of little interest to us as it has many chances to be a function of all the rate variables: concentrations, time, etc.



**Figure 9.10.** Use of the Arrhenius coordinates to determine the temperature coefficient of a reaction

#### 9.7.2.2. Model and influence of temperature

When a model hypothesis is available, various modes of the expression of the rates-concentrations can be deduced. These expressions usually involve rate coefficients from elementary steps and, eventually, equilibrium constants. At this stage, Arrhenius' law can be applied to the rate coefficients, with an activation energy for each. For the equilibrium constants, van't Hoff's law, which involves reaction enthalpy, can be applied and written as:

$$K = K^0 \exp - \frac{\Delta H^0}{RT} \quad [9.13]$$

It is only after introducing these substitutions that the rate law according to the temperature can be obtained. Arrhenius' law can thus be checked to see whether the theory is correct. If this is the case, a physics-based definition can be given to the temperature coefficient as a function of the activation energies and enthalpy of the elementary steps.

If the temperature coefficient has several values according to the temperature, we will determine whether the changes in the Arrhenius curve correlate with a change of mode, especially a change in the rate-limiting steps with temperature.



## Chapter 10

# Theory of the Activated Complex in the Gas Phase

This chapter presents modeling of the elementary steps in the gas phase. Its aim is to determine the reactivity of an elementary reaction step, the expression of the rate coefficient and its variation with temperature.

### **10.1. The notion of molecular energy: energy of a group of atoms**

An elementary reaction is in effect only the result of the re-distribution of energies within a group of atoms, which explains the importance of the molecular energy approach.

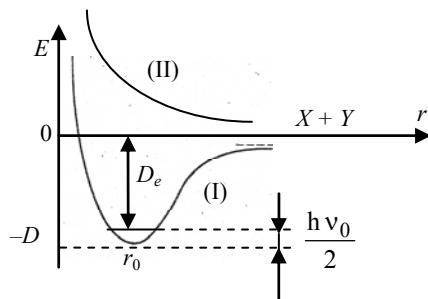
To determine the “reaction pathway”, we must determine the energy of a system made up of a certain number of atoms, of which the molecule is a specific case. It is not our intention to present quantic modeling, which leads to the calculation of energies, but to summarize the results that will be used later.

#### **10.1.1. Energy of a group of two atoms**

The theoretical studies of molecular bonds of molecules made of only two atoms can be classified in two categories according to the complexity of the atoms involved:

– the theoretical studies are mostly carried on the hydrogenoid ion,  $\text{H}_2^+$ , for which it is possible to follow rigorous calculations;

– semi-empirical studies that, taking into account the result obtained in the prior study, can be generalized to other molecules without permitting a complete calculation. This is the result presented here.



**Figure 10.1. Energy of a set of two atoms**

Based on the Heitler–London model, when two hydrogen atoms located slightly away from each other (origin of energies) move closer, there are two possibilities:

– If the two atoms have electrons spinning in opposite directions, they attract each other to form a chemical bond and the energy changes depending on the distance  $r$  separating them following curve I of Figure 10.1. Thus the energy can be written:

$$E_I = \frac{Q + \alpha}{1 + \Delta} \quad [10.1]$$

In this equation,  $Q$ ,  $\alpha$  and  $\Delta$  are integrals defined for the distance  $r$  and issued from the Schrödinger equation.  $Q$  is called Coulomb's integral and  $\alpha$  is the exchange integral. The value  $\Delta$  varies only a little and is often considered to be zero.

– If the atoms getting closer have parallel electron spins, this results in a repulsive energy following curve II on Figure 10.1, which is defined by the following relationship:

$$E_{II} = \frac{Q - \alpha}{1 - \Delta} \quad [10.2]$$

Curve I can be plotted experimentally using spectroscopic observations for any bi-atomic molecule. This cannot be done for curve II.

Equations [10.1] and [10.2] do not show the inter-atom distance  $r$  and therefore do not allow calculation of the energy for two atoms according to distance. This led Morse and Sato to propose simpler functions including  $r$  to represent curves I and II.

Morse's law represents curve I and is written as:

$$E_I = D \{ 1 + \exp - [2a(r - r_0)] - 2 \exp - [a(r - r_0)] \} \quad [10.3]$$

In this equation,  $D$  is the difference between the origin of energies and the minimum value of the curve.  $D_e$  is the residual energy, which is the vibration energy at absolute zero:  $h\nu_0/2$ ,  $r_0$  is the inter-atom distance for the minimum energy, which is the equilibrium distance of the molecule. Constant  $a$  depends on the light speed  $c$ ; molecule reduced mass  $\mu$  ( $\mu$  is related to the atomic masses by the equations in [10.5]); Plank's constant  $h$ ; and value  $x$  as defined by [10.5]. Constant  $a$  is written:

$$a = \sqrt{8\pi^2 c \mu \nu_0} \frac{x}{h} \quad [10.4]$$

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B} \text{ and } x = \frac{h\nu_0}{4D} \quad [10.5]$$

We assume that curve II in Figure 10.1 is correctly represented by Sato's function, also called the anti-Morse function:

$$E_{II} = D \{ 1 + \exp - [2a(r - r_0)] + 2 \exp - [a(r - r_0)] \} \quad [10.6]$$

Assuming  $\Delta = 0$ , equations [10.1], [10.2], [10.3] and [10.6] can be used to calculate the value of two integrals  $Q$  and  $\alpha$  for every distance,  $r$ , and therefore obtain  $\alpha(r)$  and  $Q(r)$ :

$$\alpha = \frac{E_{II} - E_I}{2} \text{ and } Q = \frac{E_{II} + E_I}{2} \quad [10.7]$$

### 10.1.2. Energy of an even number of atoms

We now consider a molecule with four atoms represented in Figure 10.2 (the atoms are not necessarily co-planarians).

Let us assume that the values of Coulomb's integrals (determined by the previous method)  $A_1, A_2, B_1, B_2, C_1$  and  $C_2$  and the exchange integrals  $\alpha_1, \alpha_2, \beta_1, \beta_2$ ,

$\gamma_1$  and  $\gamma_2$  of all bi-atomic couples  $XZ$ ,  $XW$ ,  $YZ$ ,  $YW$ ,  $XY$  and  $WZ$  as a function of the different inter-atomic distances  $r_1$ ,  $r_2$ ,  $r_3$ ,  $r_4$ ,  $r_5$  and  $r_6$  are known. London has established the energy of a group of four atoms as:

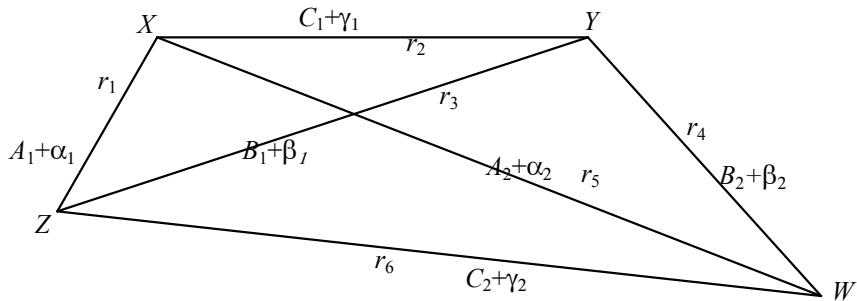
$$E_p = Q - \left\{ \frac{1}{2} \left[ (\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2 \right] \right\}^{1/2} \quad [10.8]$$

with:

$$Q = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 \quad [10.9]$$

and:

$$\alpha = \alpha_1 + \alpha_2 \quad \beta = \beta_1 + \beta_2 \quad \gamma = \gamma_1 + \gamma_2 \quad [10.10]$$



**Figure 10.2.** A four-atom interaction

The origin of energies is always taken for atoms located at quite a distance from each other. This equation allows the calculation of the energy of a group of four atoms as a function of their system internal position coordinates  $r_1$ ,  $r_2$ ,  $r_3$ ,  $r_4$ ,  $r_5$  and  $r_6$ .

This relationship can be generalized to any even number of atoms.

### 10.2.3. Energy of an odd number of atoms

Consider a system with three atoms, as represented in Figure 10.3. This can be deduced from the system in Figure 10.2 by sending one of the atoms ( $W$  for example) an infinite distance from the others so that  $r_5$  and  $r_6$  tend to infinity, which has the consequence of cancelling the terms  $A_2 + \alpha_2$ ,  $B_2 + \beta_2$  and  $C_2 + \gamma_2$ .

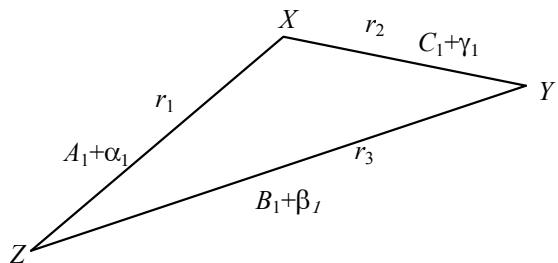
The energy of the system will be given again by equation [10.8], but in this case:

$$Q = A_1 + B_1 + C_1 \quad [10.11]$$

and:

$$\alpha = \alpha_1 \quad \beta = \beta_1 \quad \gamma = \gamma_1 \quad [10.12]$$

We thus can obtain the expressions for a system with an odd number of atoms from the expressions available for the system with the greatest even number of atoms by cancelling the energetic terms involving the cancelled atom.



**Figure 10.3.** Interactions between three atoms

## 10.2. Bimolecular reactions in the gas phase

Early on, researchers thought that the reaction between two substances required a meeting between the molecules of these two reactants. Early theories attempting to explain the reaction rate naturally relied on encounters between molecules. Collision theory does so by treating the molecules as rigid spheres and, in addition to the clash, imposing a minimum energy required for the molecules to meet. Thus Trautz's calculations in Germany and Mac Lewis' calculations in the United States, in 1917, independently accounted for both the influence of temperature by Arrhenius' law and the proportionality of reaction rate to the concentration of both reactants (second-order reaction). Alas, calculations based on the classical mechanics of the collision of rigid spheres led to values for reaction rates that were generally much too high compared with experimental measurements. The difference of a ratio of up to several orders of magnitude was bigger, since the molecules involved were more complex. In this chapter and Chapter 11 we chose to present the theory of activated complex obtained from Eyring and Polanyi's seminal works in the 1940s.

### 10.2.1. Postulate of the activated molecular collision

Modern theories, if they retain the notion of an encounter between molecules, have profoundly changed the nature of the meeting. We now call collision between two molecules,  $A$  and  $B$ , the establishment of energy interaction between these molecules over time. This interaction can have multiple consequences and thus lead to various phenomena, such as the deviation of molecules from their initial trajectories, the transfer of energy from one molecule to another, breaking a bond in a molecule, the melting of the two molecules into one, etc.

Consider an immobile molecule  $B$  surrounded by a gas of molecules  $A$  with a relative flow  $J$ . The efficient section  $Q_i$  of  $B$  for one of the previous phenomena is  $dJ$ . This is the number of encounter molecules  $A$  per unit of time and of area with a unit flux  $J$  and undergoes the shock with the concerned phenomena. We can see that  $Q_i$  (the efficient section) has area units. In the given conditions, the value of the efficient section evidently depends on the phenomenon concerned.

We will admit the following postulation as the basis of the modeling of elementary reactions.

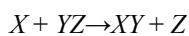
**POSTULATION 10.1.**— An elementary reaction between two molecules,  $A$  and  $B$ , requires a collision, in the sense given above to this term, between a molecule of  $A$  and a molecule of  $B$ . The collision must occur in the geometrical conditions (relative position between the two molecules) and at a given energy level. Under the effect of the collision, there is a redistribution of energies within the molecules that leads to the final products of the reaction.

The modeling of a reaction then appears like the evolution of a system made of nuclei and electrons of mass  $m_j$  over time. This evolution will be entirely defined by the wave function  $\Phi$ , which is the solution of the corresponding Schrödinger's equation, in which  $E_p$  is the potential energy of the system and is written as:

$$-\frac{\hbar^2}{8\pi^2} \sum_j \left[ \frac{1}{m_j} \left( \frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial^2 \Phi}{\partial z^2} \right) \right] + E_p \Phi = -\frac{\hbar}{2\pi i} \frac{\partial \Phi}{\partial t}$$

Alas, there is no method allowing the calculation of the wave function during a molecular collision, although we use approximate methods, of which the most advanced is the Eyring's activated complex theory.

Within the scope of this theory, we will look at the case of a reaction between an atom  $X$  and a bi-atomic molecule  $YZ$  of the following type:



[10.R1]

For this, we will write that the system evolves in a way that constantly minimizes its potential energy.

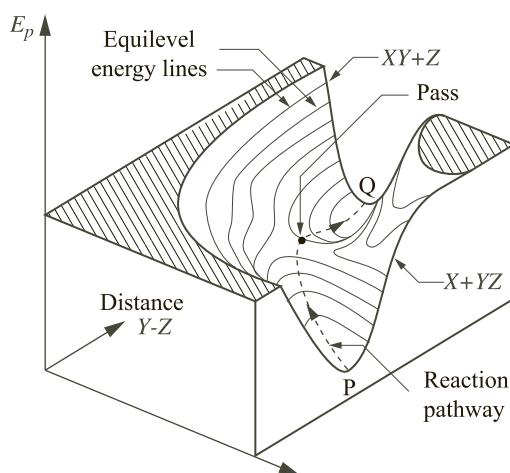
### 10.2.2. Potential energy surface

Here again, we consider a system with three atoms and will calculate its potential energy for different configurations. These configurations could be of any form, but in our case it will be enough to look at the case where the three atoms are aligned (we show that it corresponds to the case of minimal energies, see Figure 10.4). The configuration is therefore characterized by the inter-atomic distances  $r_1$  between atoms  $X$  and  $Y$ , and  $r_2$  between atoms  $Y$  and  $Z$ .

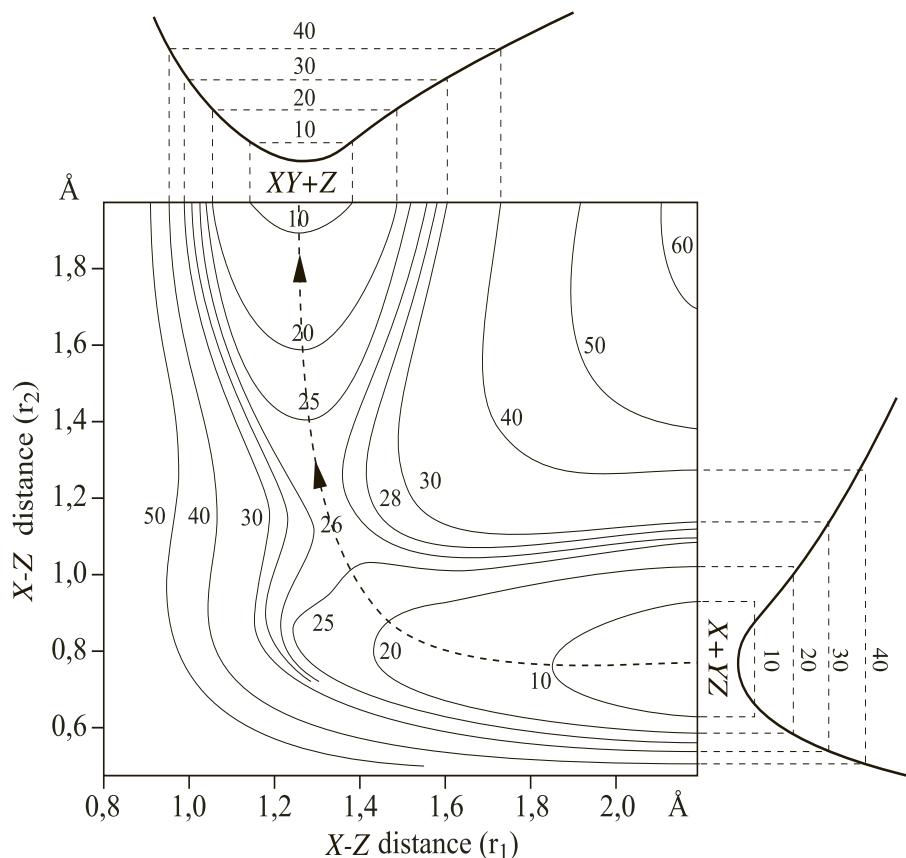


**Figure 10.4.** System with three atoms in a line

By plotting the potential energy on the z-axis and the two inter-atomic distances on the x and y-axes, we obtain the potential-energy surfaces, which are represented in Figure 10.5.



**Figure 10.5.** Potential energy surface in a system including three atoms in alignment



**Figure 10.6.** Potential energy diagram of a system with three atoms in alignment

As shown in Figure 10.6, we can plot the equienergy curves seen on these surfaces and transpose them onto a 2D plot and thereby establish the potential energy curves in the system of axis  $r_1 - r_2$ . We obtain the potential-energy diagram of the system considered. The origin of energies is often taken for the  $X$  atom located at an infinite distance from the bi-atomic  $YZ$  molecule, which requires some changes to London's equation.

With an infinite  $r_2$  value, the  $XY$  molecule and the  $Z$  atom are again infinitely distant from each other. With an infinite  $r_1$  value, however, we find the Morse's curve of the  $YZ$  molecule.

The same type of diagram can be produced whatever the number of atoms involved. However, the representation will not be easy because of the complexity. We often plot the diagram for configurations leading to minimal energies (three atoms aligned and four co-planar atoms).

### 10.2.3. Reaction pathways and the equivalent “mass point”

We have shown that we can change the axes of the potential energy curves in Figure 10.6 so that we have a system of axes Oxy, not necessarily orthogonal, is the evolution of energy for a set of three atoms moving along the valley, which have kinetic energy in the form:

$$E_c = \frac{1}{2\mu} \left[ \left( \frac{dx}{dt} \right)^2 + \left( \frac{dy}{dt} \right)^2 \right] \quad [10.13]$$

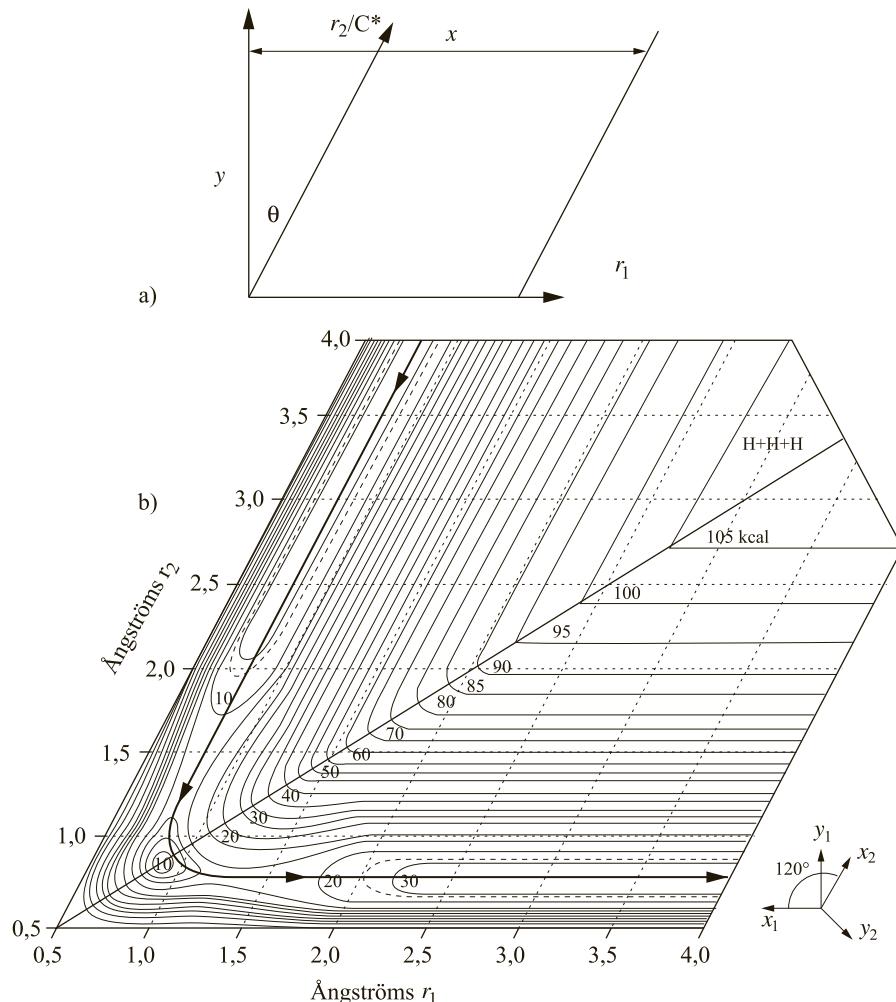
So in this representation the three-atom system is energetically equivalent to a “mass point” of mass  $\mu$ , sliding without friction along the valley. The kinetic energy of this particle is given by equation [10.13] and its potential energy is given by the z-axis in the new potential-energy diagram. We show that the new system of axis ( $E_p, r_1, r_2/c^*$ , see Figure 10.7a) is such that:

$$\sin \theta = \left[ \frac{m_X m_Z}{(m_X + m_Y)(m_Y + m_Z)} \right]^{1/2} \quad [10.14]$$

$$\mu = \frac{m_X(m_Y + m_Z)}{(m_X + m_Y + m_Z)} \quad [10.15]$$

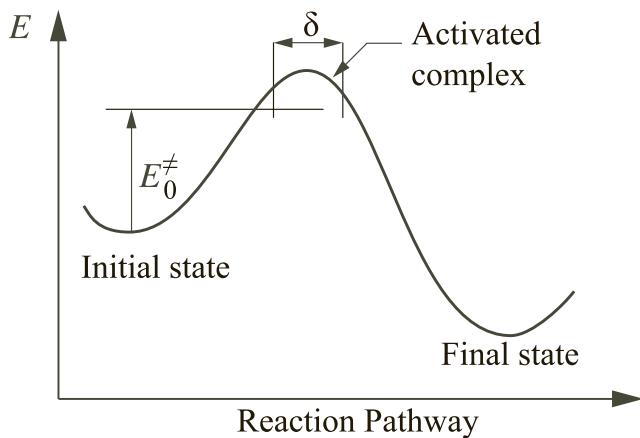
$$c^* = \frac{m_X(m_Y + m_Z)}{m_Z(m_X + m_Y)} \quad [10.16]$$

$$y = E_p = E$$



**Figure 10.7.** Three-atom system: a) definition of skewed coordinates; and b) definition of a reaction pathway

The new diagram therefore has the shape shown in Figure 10.7b. The pathway on which the mass point is climbing is the reaction path. We notice that the point starts from the initially low position and climbs along the valley. If it has enough initial kinetic energy, it will be able to overcome the pass separating the two valleys and go back down to the final state.



**Figure 10.8.** Classic activation energy and pathway energy curves

We usually represent this energetic climb on a two-axis plot (see Figure 10.8) with the potential-energy on the y-axis and the position of the mass point on the reaction pathway on the x-axis. This course shows that the point must overcome an energetic barrier with the height,  $E_0^{\ddagger}$ , called the classic activation energy at absolute zero. The group of atoms in the associated configuration at the top of the pass is called the activated complex.

#### 10.2.4. Absolute expression of the reaction rate

We will now calculate the number of “mass points” that cross the pass per time unit in order to express the reaction rate.

It is presumed that the activated complex is located within a box of arbitrary width  $\delta$ , which is located at the top of the barrier. The net reaction rate is defined by the average speed at which the activated complex surmounts the barrier. The probability  $p(v)$  for our mass point to have a speed between  $v$  and  $v + dv$  along a degree of freedom, with  $k_B$  being the Boltzman’s constant, is:

$$p(v) = \text{Const.} \exp\left(-\frac{\mu v^2}{k_B T}\right) dv \quad [10.17]$$

The average mass point speed of the activated complex at the top of the barrier, in the sense of crossing, is:

$$\bar{v} = \frac{\int_0^{\infty} \exp\left(-\frac{\mu v^2}{k_B T}\right) v dv}{\int_{-\infty}^{\infty} \exp\left(-\frac{\mu v^2}{k_B T}\right) dv} \quad [10.18]$$

The integration limits of the denominator are between  $-\infty$  and  $+\infty$  because the mass point can move in both directions, but only one direction is efficient so the numerator integration limits are between 0 and  $+\infty$ . The calculation of the average passing speed of our “mass point” at the top of the barrier is:

$$\bar{v} = \left( \frac{k_B T}{2\pi\mu} \right)^{1/2} \quad [10.19]$$

The duration of the passage  $\tau$  is given by the average lifetime of our activated complex, which is defined by the quotient of the length of the barrier over the average speed of passage:

$$\tau = \frac{\delta}{\bar{v}} = \delta \sqrt{\frac{2\pi\mu}{k_B T}} \quad [10.20]$$

The reaction rate is given by the quotient of the activated complex concentration in the box over the average lifetime duration  $\tau$ :

$$v = \frac{[XYZ^\#]}{\tau} = \frac{[XYZ^\#]}{\delta} \sqrt{\frac{k_B T}{2\pi\mu}} \quad [10.21]$$

We have assumed so far that all the mass points reaching the top of the pass cross it. It is conceivable that some of them may fall back on the same side, hence the introduction of a transmission coefficient,  $\alpha$ . It is also conceivable that the value of  $\alpha$  may depend on the shape of the summit, in particular the reaction path (Figure 10.8). In the absence of a more accurate initial value, the approximation of  $\alpha = 1/2$  may be selected for an almost symmetrical barrier. It appears that this value can be much lower for reactions involving the exchange of electrons.

Moreover, the reaction rate is assumed to be of second order. If  $k$  is the rate coefficient, the rate can be defined as:

$$v = k[X][YZ] \quad [10.22]$$

By joining expressions [10.21] and [10.22], we have:

$$k[X][YZ] = \alpha \frac{[XYZ^*]}{\delta} \sqrt{\frac{k_B T}{2\pi\mu}} \quad [10.23]$$

At equilibrium between the activated complex and the initial state, we have an equivalence relationship:

$$k_{eq}[X]_{eq}[YZ]_{eq} = \alpha \frac{[XYZ^*]_{eq}}{\delta} \sqrt{\frac{k_B T}{2\pi\mu}} \quad [10.24]$$

Yet at equilibrium, we can apply the law of mass action [A2.53] (see Appendix 2) by introducing the partition function of our mass point for both the initial state and activated complex  $Z^*$ :

$$\frac{[XYZ^*]_{eq}}{[X]_{eq}[YZ]_{eq}} = \frac{Z^*}{Z_X Z_Y Z_Z} \exp\left(-\frac{E_0^*}{RT}\right) \quad [10.25]$$

For our point at the top of the barrier, the degree of freedom of translation crossing the pass plays a specific role. Therefore by taking into account [A2.34] (see Appendix 2), the partition function of the activated complex can be written as:

$$Z^* = Z^* \frac{\sqrt{2\pi\mu k_B T}}{h} \delta \quad [10.26]$$

Otherwise we accept the assumption that the rate coefficient at equilibrium is the same as when it is far from equilibrium or:

[10.27]

By combining [10.23], [10.24], [10.25] and [10.26], the rate coefficient becomes:

$$k = \frac{\alpha k_B T}{h} \frac{Z^*}{Z_X Z_Y Z_Z} \exp\left(-\frac{E_0^*}{RT}\right) \quad [10.28]$$

The term  $k_B T/h$  is a frequency with a value of  $2.10^{10} T$ .

We thereby obtain the rate coefficient of the reaction rate of a bimolecular reaction of second order.

NOTE 10.1.— Although never written, the result of equation [10.28] is identical to the one that would have been obtained by writing the equilibrium between activated complex and reactants and deducting the activated complex concentration from the mass action law [10.21]. Numerous authors calculate the reaction rate in this way. Note that the rigorous calculation that we did does not involve any equilibrium, as theoretical considerations show that this cannot exist. The method involving the equilibrium between reactants in an activated complex is actually a mnemonic device to achieve the same result.

### 10.2.5. Partition functions of the activated complex

To calculate the partition functions, we abandon our mass point and go back to molecules and atoms. The use of the equation [10.25] is required to calculate the partition functions of both the reactants and the activated complex. If the reactant partition functions can be calculated without problem using their characteristics (see Appendix 2), we must spend time calculating the partition function of the activated complex.

The partition functions of the activated complex are calculated using partition functions related to each degree of freedom and applying equation [A2.27] (see Appendix 2) for the characteristics of the activated complex.

#### 10.2.5.1. Translation function of partition

With the activated complex, the bond dimensions are given by the coordinates of the pass of the potential energy diagram. This complex has three degrees of freedom of translation and the term corresponding to volume  $V$  is:

$$Z_t = \left[ \frac{2\pi(m_X + m_Y + m_Z)k_B T}{h} \right]^{3/2} V \quad [10.29]$$

#### 10.2.5.2. Rotation function of partition

In our particular case, the activated complex is linear and therefore has two degrees of freedom of rotation, and the rotation contribution is:

$$Z_r = \frac{8\pi^2 I k_B T}{h^2} \quad [10.30]$$

The momentum of inertia is calculated from the masses and already known dimensions.

#### 10.2.5.3. *Vibration function of partition*

The activated complex molecule theoretically has  $9 - 3 - 2 = 4$  degrees of freedom of vibration. In fact, the molecule cannot vibrate in the same direction as the  $Y-Z$  bond, which is breaking down, and only has three degrees of freedom of vibration. The contribution of vibration will be:

$$Z_v = \prod_{i=1 \text{ to } 3} \left[ 1 - \exp\left(-\frac{hv_i^\neq}{k_B T}\right) \right]^{-1} \quad [10.31]$$

The calculation of this term requires the vibration frequency  $v_i^\neq$  of the activated complex. The mechanics of small movements allows us to calculate the vibration frequency from the potential energy diagram (see Appendix 3). Plotting the diagram of the potential energies will allow us to calculate all the characteristics of the activated complex. The activation energy value can also be read directly from the plot.

#### 10.2.6. *Evaluation of the pre-exponential factor*

Now consider a reaction between polyatomic molecules. As a first approximation, we can consider the partition functions of each type of energy as consisting of terms for a degree of freedom equal to  $z_t$ ,  $z_r$  and  $z_v$ , depending on whether it is a translation, rotation or vibration. The partition function of a molecule per unit of volume will be:

$$Z = z_t^t + z_r^r + z_v^v \quad [10.32]$$

where  $t$ ,  $r$ ,  $v$  are the numbers of the degree of translation, rotation and vibration, respectively.

Thus, in the case of the previous example of an atom  $X$  with its diatomic molecule  $YZ$ , we would have:

$$Z_X = z_t^3, Z_{YZ} = z_t^3 z_r^2 z_v \text{ and } Z^\ddagger = z_t^3 z_r^2 z_v^3 \quad [10.33]$$

According to [10.28], the pre-exponential factor of the rate coefficient is:

$$k_0 = \alpha \frac{k_B T}{h} \frac{Z^\ddagger}{Z_X Z_{YZ}} = \frac{k_B T}{2h} \frac{z_r^2}{z_t^3} \quad [10.34]$$

Now consider the example of a reaction between molecule *A* containing *a* number of atoms and molecule *B* containing *b* number of atoms. The activated complex will have *a + b* atoms.

Molecule *A* will have three degrees of both translation and rotation, and  $9a - 6$  degrees of vibration.

Molecule *B* will have three degrees of both translation and rotation, and  $9b - 6$  degrees of vibration.

The activated complex, which has one degree of freedom less than the normal molecule with the same dimensions, will have three degrees of both translation and rotation and  $9(a + b) - 6 - 1$  degrees of vibration.

The pre-exponential factor will therefore be:

$$k_0 = \alpha \frac{k_B T}{h} \frac{Z^\ddagger}{Z_X Z_{YZ}} = \frac{k_B T}{2h} \frac{z_v^5}{z_t^3 z_r^3} \quad [10.35]$$

We can go further by using terms of the partition functions with the order of magnitudes listed in Table A2.2 (see Appendix 2). Using equations [10.34] and [10.35] leads to the following:

– for a reaction of one atom with a bi-atomic molecule:

$$k_0 = \frac{k_B T}{2h} \frac{z_r^2}{z_t^3} \approx 3.10^{-10} T \text{ to } 3.10^{-8} T \quad [10.36]$$

– for a reaction between molecules *A* and *B*:

$$k_0 = \frac{k_B T}{2h} \frac{z_v^5}{z_t^3 z_r^3} \approx 3.10^{-20} T \text{ to } 3.10^{-23} T \quad [10.37]$$

These equations allow us to reach orders of magnitudes for the pre-exponential factors that are compatible with experimental values.

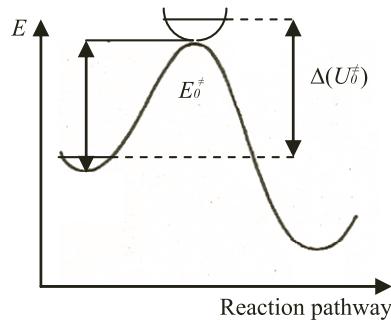
### 10.2.7. Activation energies

#### 10.2.7.1. Classic activation energy and point zero

The classic activation energy  $E_0^\ddagger$  at absolute zero temperature (0 K), which is provided from the potential energy diagram, does not take into account the residual energy of vibration at this temperature and is defined for each vibration of frequency  $v$  by:  $h/2v_i$ .

Figure 10.9 uses Figure 10.8 and adds the residual energies of the reactants and the activated complex. The true activation energy  $E_0^\ddagger$  at 0 K can easily be calculated with the following relationship:

$$E_0^\ddagger = \Delta(U_0^\ddagger) + \sum \frac{hv_i^\ddagger}{2} - \sum \frac{hv_r}{2} \quad [10.38]$$



**Figure 10.9.** Difference between classic activation energy and the free energy of a true activation

In this equation, the first sum is expanded to all frequencies of vibration of the activated complex and the second sum to all frequencies of vibration of all reactants.

#### 10.2.7.2. Thermodynamic formulation of the reaction rate

Using equation [10.28], we can express the rate constant by adding the equilibrium constant,  $K_c^\ddagger$ :

$$k = \frac{\alpha k_B T}{h} K_c^\neq \quad [10.39]$$

The constant  $K_c^\neq$  issued from the partition function would be the constant of an “equilibrium” between the activated complex and reactants. Considering the definitions of equilibrium constants, the free energy related to the reaction can be introduced and the reaction rate coefficient becomes:

$$k = \frac{\alpha k_B T}{h} \exp\left(-\frac{\Delta(F_0^\neq)}{RT}\right) \quad [10.40]$$

The standard free activation energy is  $\Delta(F_0^\neq)$ . This free energy can be expressed as a function of the internal energy  $\Delta(U_0^\neq)$  and the activation entropy as:

$$\Delta(F)_0^\neq = \Delta(U_0^\neq) - T\Delta(S_0^\neq) \quad [10.41]$$

Thereby the reaction rate coefficient becomes:

$$k = \frac{\alpha k_B T}{h} \exp\left(\frac{\Delta(S_0^\neq)}{R}\right) \exp\left(-\frac{\Delta(U_0^\neq)}{RT}\right) \quad [10.42]$$

The activation entropy can be introduced by the equation:

$$\Delta(H_0^\neq) = \Delta(U_0^\neq) + P\Delta(V_0^\neq) \quad [10.43]$$

The volume associated with the activation energy is represented by  $\Delta(V_0^\neq)$ . With perfect gases, if  $(\sum n_i^\neq)$  is the sum of algebraic stoichiometric coefficients of the activated complex reaction formation, we will have:

$$P\Delta(V_0^\neq) = RT(\sum n_i^\neq) \quad [10.44]$$

and the reaction rate coefficient therefore becomes:

$$k = \frac{\alpha k_B T}{h} \exp\left(\frac{\Delta(S_0^\ddagger)}{R}\right) \exp\left(-\frac{\Delta(U_0^\ddagger)}{RT}\right) \exp\left(\sum n_i^\ddagger\right) \quad [10.45]$$

In the case of reaction [10.R1], where  $\sum n_i^\ddagger = -1$ , the reaction rate coefficient becomes:

$$k = \frac{\alpha k_B T}{h} \exp\left(\frac{\Delta(S_0^\ddagger)}{R}\right) \exp\left(-\frac{\Delta(U_0^\ddagger)}{RT}\right) \exp(-1) \quad [10.46]$$

#### 10.2.7.3. Activation energy of the elementary step

By using the natural logarithm of the reaction rate coefficient definition [10.42], we have:

$$\ln k = \ln \frac{\alpha k_B T}{h} + \ln T + \frac{\Delta(S_0^\ddagger)}{R} - \frac{\Delta(U_0^\ddagger)}{RT} \quad [10.47]$$

From derivation of the temperature, we obtain:

$$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{\Delta(U_0^\ddagger)}{RT^2} \quad [10.48]$$

This derivation defines the “experimental” activation energy  $E_a$  of the elementary step, therefore:

$$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{\Delta(U_0^\ddagger)}{RT^2} = \frac{E_a}{RT^2} \quad [10.49]$$

from which the activation energy of the elementary step is defined:

$$E_a = RT + \Delta(H_0^\ddagger) - P\Delta(V_0^\ddagger) \quad [10.50]$$

In the case of perfect gases, the activation energy is:

$$E_a = RT \left[ 1 - \left( \sum n_i^\ddagger \right) \right] + \Delta(H_0^\ddagger) \quad [10.51]$$

In the case of reaction [10.R1], where  $\left(\sum n_i^{\neq}\right) = -1$ , the activation energy becomes:

$$E_a = \Delta(H_0^{\neq}) + 2RT \quad [10.52]$$

All these expressions eventually provide a definition of the activation energy of the elementary step that varies slightly with temperature. These variations are nearly impossible to detect experimentally, since the range of variations for one reaction is usually quite narrow in order to keep reaction rates measurable.

### 10.2.8. Units and other forms of the reaction rate coefficient

#### 10.2.8.1. Other expressions of the reaction rate coefficient

The examination of equation [10.22] shows that the units of the reaction rate coefficient  $k$  are  $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ .

If we take into account equation [10.39], the reaction rate coefficient can also be written as:

$$k = \frac{\alpha k_B T}{h} K_p^{\neq} (PV)^{\sum n_i^{\neq}} = \frac{\alpha k_B T}{h} K_p^{\neq} (RT)^{\left(\sum n_i^{\neq}\right)} \quad [10.53]$$

In the case of reaction [10.R1], this equation becomes:

$$k = \frac{\alpha k_B T}{h} \frac{K_p^{\neq}}{RT} \quad [10.54]$$

#### 10.2.8.2. Other forms of the reaction rate coefficient

Using equation [10.22], we have defined the reaction rate coefficient of the volumic rate of a bimolecular reaction, such as reaction [10.R1], as a function of concentration. In some cases with gases, we prefer to define the reaction rate using the partial pressure instead of the concentration, which is described by a new reaction rate coefficient,  $k_p$ , in:

$$v = k_p \frac{P_x P_{yz}}{P_0^2} \quad [10.55]$$

where  $P_0$  represents the reference pressure. If we choose a reference pressure of one atmosphere, the reaction rate becomes:

$$v = k_p P_X P_{YZ} \quad [10.56]$$

If the pressure units are in atmospheres, the reaction rate coefficient is therefore expressed in mol.s<sup>-1</sup>.m<sup>-3</sup>.atm.<sup>-2</sup>.

The new reaction rate coefficient can be linked to the one defined by concentration by writing:

$$k_p = k(RT)^2 \quad [10.57]$$

A new apparent activation energy  $E'_a$  corresponds to a new reaction rate coefficient, such as:

$$\frac{d \ln k_p}{dT} = \frac{E'_a}{RT^2} \quad [10.58]$$

or by using equations [10.48] and [10.58]:

$$E'_a = E_a + 2RT \quad [10.59]$$

### 10.3. Monomolecular reactions in the gas phase

By definition, a monomolecular reaction must involve only one molecule, like for example decomposition and isomerization reactions. Such a reaction will therefore be written:



We accept that the reaction does not occur at an infinite rate (i.e. the decomposition is not spontaneous for the group of molecules), but that it would be better if at each instant only one fraction of the molecule was ready to break down. Thus we derive the idea that only one fraction of molecule  $A$  acquires enough energy to spontaneously trigger bond breakage. Moreover, with a reaction that is temperature-activated (without any radiation intervention), it is known that only a bimolecular collision permits the energy transfer from one molecule to the other, and thereby can result in some molecules having higher energies than others. How is it therefore possible to explain that a bimolecular collision can lead to a first order reaction rate with respect to the reactant? The response is defined by the first condition, that modeling will have to obey the knowledge that normally, as we have seen before, the bimolecular collision results in a second order reaction rate.

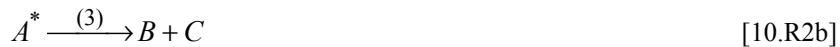
The second challenge for modeling is to report experimental results incorporating the reaction order for a high enough pressure and the knowledge that at lower pressure the reaction is second order in relation to the reactants.

Lindemann proposed the following model, which takes into account these two requirements. Lindemann concedes that a monomolecular reaction is not elementary, but the result of a mechanism including three steps:

- a first activation step in which the collision between two  $A$  molecules allows one of them (the activated molecule labeled  $A^*$ ) to acquire enough energy to break down;
- a second step, which is the reverse of the first step, which deactivates the molecule by a collision with another  $A$  molecule:



- the third step is the decomposition of the activated molecule to give the products of the reaction,  $B$  and  $C$ :



This set of steps is then treated according to the classical part of the pseudo-steady state (here a quasi-steady state) by writing the balance of activated molecules and eliminating it according to:

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_2[A][A^*] - k_3[A^*] = 0 \quad [10.60]$$

The concentration of the activated molecule is then deduced:

$$[A^*] = \frac{k_1[A]^2}{k_2[A] + k_3} \quad [10.61]$$

From this, the rate of decomposition is measured in the third step:

$$v = v_3 = \frac{k_3 k_1 [A]^2}{k_2 [A] + k_3} \quad [10.62]$$

By using low pressures (low reactant concentration), we can approximate  $k_2 [A] \ll k_3$ , which according to equation [10.53] leads to a second order reaction rate:

$$v = v_3 = k_1 [A]^2 \quad [10.63]$$

If a high pressure is used, the approximation  $k_2 [A] \gg k_3$  is remembered, which results in a first order reaction rate:

$$v = v_3 = \frac{k_1 [A]}{k_2} \quad [10.64]$$

This basic model allows us to satisfy the two required conditions. From this fundamental model that was originally used for the approximation of a simple molecular collision between two rigid spherical molecules, authors have developed models intended to refine the development of the previous steps and remained within the scope of the mechanic collision postulate. Hence Hinshelwood explains how the energy provided during the first collision is eventually transferred into the bond that will be broken. Slater had an interest in the third step, which models the frequency of bonds breaking having acquired enough energy. These different derivations resulted in increasingly complicated equations showing the influence of temperature over the reaction rate, for which sadly no experiments allow us to distinguish from Arrhenius' law and the different models.

For the sake of homogeneity, more time will be spent looking at how Eyring's activated complex theory, which is the only one able to give orders of magnitude to the pre-exponential terms in the bimolecular reactions, deals with monomolecular reactions.

This time, the collision hypothesis is conserved in the energetic sense and involves two reactant molecules forming the activated complex, but the latter only contains one molecule  $A$ , and the second molecule is used to transfer energy. The crossing of the pass will therefore lead to the reaction product provided a transmission coefficient exists. We will later return to this. Thus, the elementary reaction will be represented by:



A mnemonic method is used to express the reaction rate coefficient (see Note 10.1). This involves writing the “equilibrium” between the reactant and the activated complex, resulting in the constant being:

$$K_c^{\ddagger} = \frac{[A^{\ddagger}][A]}{[A]^2} \quad [10.65]$$

The volumic rate is then:

$$v = \frac{\alpha k_B T}{h} [A^{\ddagger}] = \frac{\alpha k_B T}{h} K_c^{\ddagger} \frac{[A]^2}{[A]} \quad [10.66]$$

By taking [10.65] into account and the definition of the equilibrium constant of the activated complex using the complex partition functions of reactant  $A$ , as well as excluding a degree of freedom of vibration and taking into account the energy corrections at 0 K, the rate is defined as:

$$v = \frac{\alpha k_B T}{h} \frac{F^{\ddagger}}{F_A} [A] \exp\left(-\frac{E_a}{RT}\right) \quad [10.67]$$

The reaction rate is therefore proportional to the pressure (concentration of  $A$ ) despite a bimolecular collision, which implies that the activated complex does not include two particles from the collision.

A first order monomolecular reaction has been reported here. Nothing from the equations obtained, however, allows us to predict that both first and second order reactions are limited to the high and low pressure respectively.

In the previous case, no particular attention was given to the transmission coefficient,  $\alpha$ . This plays a very important role in monomolecular reactions. There are apparently two steps in reaction [10.R3]:

- first, the activation process that involves the transfer of energy from the collision into a vibration energy suitable for the bond to break;
- second, the activated complex surmounting the barrier leading to the decomposition reaction.

Consequently, it is necessary to introduce a transmission coefficient into expression [10.67]. It will have values that are lower than one unit and depend on the pressure.

The transmission coefficient must be the same for the forward and reverse reaction (this vanishes in the equilibrium constant definition, which is the ratio of two rate coefficients). Useful information regarding  $\alpha$  can therefore be deduced from the study of the reverse reaction. It has led authors to define the theoretical transmission coefficient as:

$$\alpha = \frac{\alpha_e v_e}{\frac{k_B T}{h} + \alpha_e v_e} \quad [10.68]$$

In this expression,  $v_e$  is the frequency of collisions between activated molecules and normal molecules and  $\alpha_e$  is the probability of deactivation after the collision, which is considered independent from the pressure. Naturally,  $v_e$  is proportional to the gas pressure (the concentration of  $A$ ):

$$v_e = \phi[A] \quad [10.69]$$

Substituting  $v_e$  into [10.68] and [10.69], we get:

$$v = \frac{\alpha_e \phi k_B T F^\#}{h} \frac{[A]^2}{F_A \frac{k_B T}{h} + \alpha_e \phi [A]} \exp\left(-\frac{E_a}{RT}\right) \quad [10.70]$$

With high pressure, a first order reaction rate is obtained:

$$v = \frac{k_B T F^\#}{h F_A} [A] \exp\left(-\frac{E_a}{RT}\right) \quad [10.71]$$

and at low pressure, we get a second order reaction rate:

$$v = \alpha_e \phi \frac{F^\#}{F_A} [A]^2 \exp\left(-\frac{E_a}{RT}\right) \quad [10.72]$$

These results are valid for a decomposition reaction such as [10.R3]. In the case of an isomerization of the form:



there is only one molecule of product and the transmission coefficient no longer depends on the pressure. Relation [10.58] would be valid whatever the value of this variable. This has been observed in *cis-trans* isomerization.

#### 10.4. Photochemical elementary reactions

Photochemistry is the contribution of the energy needed, in the form of electromagnetic radiation, for a reaction system to react.

In general, as for thermally-activated reactions, photochemical reactions are complex and distinct from the basic steps. In general, only one is photochemical and is called the primary act, the rest being conventional thermal steps.

In an experiment, the primary act is almost never separable from the other elementary steps.

Photochemical reactions are governed by two very old laws: a qualitative and a quantitative law.

##### 10.4.1. Grotthus–Draper quantitative law

Under this law a reaction can only be caused by radiation if it is absorbed by a molecule. This law reflects the need for interaction between the wave and the molecule. If the absorption of light is necessary, this law is not broad enough because radiation can be absorbed without causing a chemical change.

The development of photochemistry is actually closely connected to the interpretation of the spectra of light absorption by molecules, which explains whether absorption causes a chemical change or not.

First, qualitatively it is clear that radiation with greater energy will have a higher chance of causing a reaction, which is to say that in relation [10.73] its frequency is greater or its wavelength is smaller according to [10.74]:

$$E = N_a h\nu \quad [10.73]$$

$$E = \frac{118}{\lambda(\mu)} \text{ kJ} \quad [10.74]$$

Domain	Wavelength	Energy
Extreme red	$\lambda = 0.8 \mu$	148 kJ
Extreme violet	$\lambda = 0.4 \mu$	297 kJ
Ultraviolet	$\lambda = 0.284 \mu$	418 kJ

**Table 10.1.** Energies matching visible and ultraviolet wavelengths

#### 10.4.2. Energetic paths of molecule dissociation

With spectroscopy, there are three distinct paths of molecule dissociation.

##### 10.4.2.1. Molecule dissociation by vibration

If we consider the energy curve of a bi-atomic molecule (curve I in Figure 10.1), the absorption of energy has the effect of increasing the vibratory state to reach the dissociation energy. The series of different vibrational states, their limit and dissociation of the molecule are manifested spectrally by a succession of bands of increasing closeness, each corresponding to a vibrational state up to a limit corresponding to the dissociation of the molecule. Any excess energy supplied to the molecule is lost as unquantified kinetic energy, hence a continuous spectrum.

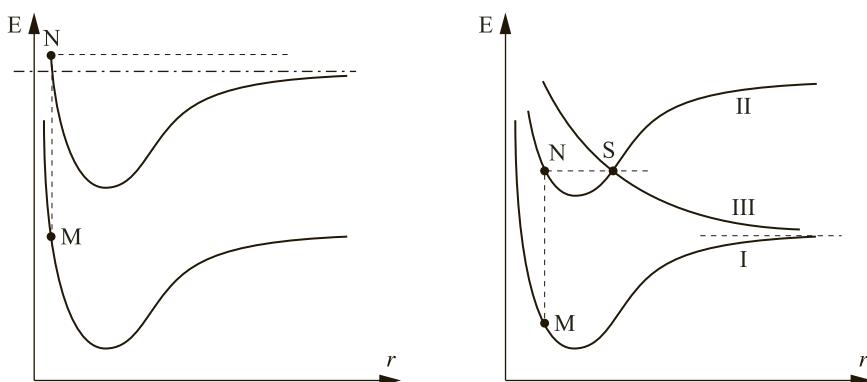
##### 10.4.2.2. Molecule dissociation by electronic transition

Figure 10.10a shows the operation of such a process. The starting point is represented by point M. The molecule receives energy which brings the representative point to N which is located on a new Morse's curve corresponding to a more excited electronic state and at a height greater than the dissociation limit in this state.

##### 10.4.2.3. Molecule dissociation by pre-dissociation

Figure 10.10b represents such a case. The energy input is the representative point in N that lies on a curve of attraction of a higher electronic level S, which is the repulsion curve type II in Figure 10.1, whose point is above the dissociation energy. The molecule is dissociated after returning to its ground state along curve II. Such a pre-dissociation has been suggested in the case of the dissociation of nitric oxide (NO) into atoms.

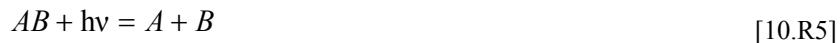
NOTE 10.2.– A molecule entering an electronically excited state becomes highly unstable and the probability that the system will directly return to its normal state following path NM of Figure 10.10b becomes high. This results in transmission factor  $\alpha$  having extremely low values in the order of  $10^{-5}$  to  $10^{-8}$  in the reaction rate equation, in comparison to the value 0.5 that we took for thermal reactions.



**Figure 10.10.** a) Dissociation by passing through the activated state; and b) pre-dissociation via the repulsion curve

#### 10.4.3. Einstein's quantitative law

In a primary photochemical act there are as many broken down molecules as there are absorbed photons, which mean that the primary act can be written as:



*Warning:* this law is only true for the reaction in the direction from left to right. If the reverse reaction is significant or the transmission factor is low there will not be as many molecules of  $AB$  broken down as there will be photons absorbed. It is said that the quantum yield is less than one because it is the ratio of broken down  $AB$  molecules over the number of photons absorbed.

The fact that the quantum yield is smaller or larger than one provides important information on the mechanism. We have already seen factors that diminish the quantum yield. Other factors promote its increase. Reactions of high quantum yield are always exothermic reactions and are responsible for the discovery of chain reactions. Indeed, if the photochemical act is the initiation step in the chain, as is most often the case, the amount of product that has reacted following the absorption of one photon can be considerable. These reactions can achieve quantum efficiencies

of several orders of magnitude, such as the photochemical action of hydrogen and chlorine in which the quantum yield is about 100,000.

#### **10.4.4. Influence of temperature on photochemical reactions**

The influence of temperature on photochemical reaction rates can be very different depending on the type of reaction, almost always following the same order of magnitude as the quantum yield. The primary act is never affected by temperature and thus the change of reaction rate with temperature is always due to other, thermal, steps of the mechanism.

Consider first a reaction with simple, limited sequences. If the rate-determining step is the primary photochemical act, usually the first step, and conditions are far from equilibrium, we will have a reaction with a quantum yield with units and a reaction rate that is not influenced by temperature.

For the same reaction, if we are close to thermodynamic equilibrium conditions the quantum yield will be less than one and the influence of temperature will be felt by the term of distance from equilibrium (and lead to a negative influence of temperature).

If we now consider the case of a reaction scheme in the pseudo-steady state mode but with no rate-determining step, such as a chain reaction far from equilibrium, the quantum yield will be high and the speed will obey a law given by the complex application of Arrhenius' law at every stage.

NOTE 10.3.— The concentration of the reactants does not affect the rate of the photochemical act, but this concentration is involved in the absorbed light intensity following the Beer–Lambert law. The absorbed intensity is therefore:

$$\Delta I = I_0 - I = I_0 \left[ 1 - \exp(-Kl[A]) \right] \approx K l [A] \quad [10.75]$$

Thus the reaction rate is proportional to the intensity absorbed and almost proportional to the concentration of absorbing species.

The modeling of the elementary act has been developed where gas phase interactions between molecules are practically negligible. The modeling theory of an activated complex, unlike the old theory of collisions, leads to the correct orders of magnitude for pre-exponential factors of the rate coefficient and allows the calculation of activation energy. It is indeed an absolute calculation of the reaction rate in the gas phase.

### 10.5. The theory of activated complexes

The current concept of activated collision was developed in Eyring and Polanyi's (see Figure 10.11) seminal work. Before this time, reaction rate calculations were based on the classical mechanics of the collision of rigid spheres, which produced values that were much higher than experimental measurements.



**Henri Eyring**  
(1901–1981)



**Michael Polanyi**  
(1899–1976)

**Figure 10.11.** Eyring and Polanyi developed the theory of activated complexes

## Chapter 11

# Modeling Elementary Reactions in Condensed Phase

In this chapter, we discuss the modeling of elementary steps in condensed liquids and solids as well as reactions located with the interphases. The aim is always to analyze the elementary step and deduce an expression of the reactivity.

### 11.1. Elementary reaction in the liquid phase

In the liquid phase, species involved in the elementary step can be neutral molecules or other ions. In comparison with reactions occurring in the perfect gas, which we studied in Chapter 10, the fundamental difference is due to the involvement of interaction energy between molecules, molecules and ions and between ions, therefore modifying of the potential energy of every atom (or ion).

For reactions in solution, although we sense the influence of the solvent on the reaction rate, this influence does not appear to be caused by a possible deactivation from collision with solvent molecules because a similar number of collisions are able to activate molecules.

Reaction in solution will actually involve at least three steps that may be elementary:

- the diffusion of reacting molecules (or ions) towards one another;
- the actual chemical reaction between molecules with the formation of the activated complex; and
- diffusion of the molecules produced away from each other.

Diffusion in a liquid can be treated as an elementary process requiring a specific activation energy, but the magnitude of this energy (close to  $20\text{ kJ/mol}^{-1}$ ) is two to five times lower than the level involved in the chemical act and therefore this chemical step is often much slower. Alongside the rate-determining modes of diffusion or interface reaction, in many cases we encounter mixed pseudo-steady modes that are treated classically.

### 11.1.1. Generic expression of an elementary step reaction rate in the liquid phase: the Brønstedt–Bjerrum law

With a bimolecular reaction between molecules  $A$  and  $B$  in the gas phase involving the activated complex  $M^\ddagger$ , we again consider expression [10.43], where  $\Delta V_0^b$  represents the volume associated with the activation reaction. For liquids we have  $P\Delta V^\ddagger = 0$  and so:

$$k = \frac{\alpha k_B T}{h} \exp\left(-\frac{\Delta(G_0^\ddagger)}{RT}\right) = \frac{\alpha k_B T}{h} \frac{[M^\ddagger]}{[A][B]} = \frac{\alpha k_B T}{h} K_c \quad [11.1]$$

The true equilibrium constant is defined from the activities and is linked to the one defined from concentrations ( $K_c^\ddagger$ ) by the ratio of activity coefficients:

$$K^\ddagger = \frac{|M^\ddagger|}{[A][B]} = \frac{[M^\ddagger]}{[A][B]} \frac{\gamma'_M \gamma'_B}{\gamma_A \gamma_B} = K_c^\ddagger \frac{\gamma_M \gamma_B}{\gamma_A \gamma_B} \quad [11.2]$$

In this expression,  $|B|$ , is the activity of  $B$  and  $\gamma_B$  is its activity coefficient, which is defined by:

$$\gamma_B = \frac{\text{Concentration of } B \text{ in the vapor in equilibrium with the solution at 1 atm}}{\text{Concentration of } B \text{ in the solution}} \quad [11.3]$$

By combining [11.1] and [11.2], we get:

$$k = \frac{\alpha k_B T}{h} K^\ddagger \frac{\gamma_A \gamma_B}{\gamma_{M^\ddagger}} = k_0 \frac{\gamma_A \gamma_B}{\gamma_{M^\ddagger}} \quad [11.4]$$

When considering solutions, it is often more convenient to take the pure solvent and an infinitely dilute solute reference since the corresponding activity coefficient  $\gamma'_B$  is defined by:

$$\gamma'_B = \frac{\text{Concentration of } B \text{ in the ideal solution}}{\text{Concentration of } B \text{ in the solution}} \quad [11.5]$$

$\gamma_B$  and  $\gamma'_B$  are linked by the expression:

$$\gamma_B = \beta \gamma'_B \quad [11.6]$$

so equation [11.4] becomes:

$$k = k_0 \frac{\beta_A \beta_B \gamma'_A \gamma'_B}{\beta_{M^\neq} \gamma'_{M^\neq}} \quad [11.7]$$

After review of [11.3] and [11.6], it is clear that  $\beta_i$  must be a constant for each species at a given temperature and thus equation [11.7] can be written:

$$k = k'_0 \frac{\gamma'_A \gamma'_B}{\gamma'_{M^\neq}} \quad [11.8]$$

Since  $k'_0$  does not depend on reactants  $A$  and  $B$  or the activated complex, this is a constant for a given reaction at a given temperature, independent of the nature of the medium in which  $k$  is measured. For two different solvents, labeled  $I$  and  $II$ , we deduce:

$$\frac{k_I}{k_{II}} = \left( \frac{\gamma'_A \gamma'_B}{\gamma'_{M^\neq}} \right)_I \left( \frac{\gamma'_{M^\neq}}{\gamma'_A \gamma'_B} \right)_{II} \quad [11.9]$$

NOTE 11.1.— It is possible to write this relation in another form by noticing the  $\gamma'_B$  ratio between these two solvents, which according to [11.7] is equal to the ratio of partial pressures of solute  $B$  in the vapors in equilibrium with the solutions. We denote this ratio  $\pi_B$  and have:

$$\frac{k_I}{k_{II}} = \frac{\pi_A \pi_B}{\pi_M \neq} \quad [11.10]$$

If we introduce the activity coefficient  $f_B$  defined by choosing the infinitively diluted solution as a reference, in the same way as above we can write:

$$k = k_0^s \frac{f_A f_B}{f_M \neq} \quad [11.11]$$

$k_0^s$  is therefore the rate coefficient in the chosen solvent and at an infinite dilution when every activity coefficient is in units. Equation [11.11] is known as the Brønstedt–Bjerrum law.

### 11.1.2. Influence of the environment

It is clear that the influence of the species environment, such as the dielectric constant of the medium, solvent used, etc., can be summarized as the influence of all these variables on the activity coefficient. This returns us to the expression of the activity coefficients in various types of solutions. Although the problem is fairly easy with reagents that are relatively stable compounds, it is more challenging with the activated complex for which we do not have any means of measurement.

Activity coefficients are likewise assessed using thermodynamics, either using Margulès or Wagner limited development, or by assessing the free molar enthalpy of the component in excess using the following relation:

$$\overline{G_i^{\text{ex}}} = -RT \ln \gamma_i \quad [11.12]$$

The activated complex is much more dilute than the reactants and products. In many cases, it is therefore possible to have reactions involving only neutral molecules and establish that the activity coefficient of the activated complex within an infinitely dilute reference solution maintains a unit value.

We will illustrate the influence of the environment in both cases. First, we will compare the reaction rate of the same reaction undertaken in the gas phase and in solution. Second, we will look at the case involving reactions in sufficiently diluted ionic solutes, by looking at the influence of both the dielectric constant of the

solvent and the ionic strength of the medium for these diluted solutions. We will then discuss the case of concentrated solutions.

### 11.1.3. Comparison of the reaction rate in solution and gas phases

It is easy to compare the reaction rates obtained in both the gas phase and a given solvent. By taking into account [11.4] and [10.39], the reaction rate factors ratio will be given by:

$$\frac{k_{\text{liq}}}{k_{\text{gas}}} = \frac{k}{k_0} = \frac{\gamma_A \gamma_B}{\gamma_{M^\neq}} \quad [11.13]$$

The solubility  $s_B$  of a solute  $B$  of the gas phase in a solvent can be represented by the relation:

$$\begin{aligned} s_B &= \exp\left(-\frac{\Delta G_B}{RT}\right) = \exp\left(\frac{\Delta S_B}{T}\right) \exp\left(-\frac{\Delta H_B}{RT}\right) \\ &= s_B^0 \exp\left(-\frac{\Delta H_B}{RT}\right) \equiv \frac{1}{\gamma_B} \end{aligned} \quad [11.14]$$

where  $\Delta G_B$ ,  $\Delta S_B$  and  $\Delta H_B$  are the dissolution Gibbs free enthalpy, entropy and enthalpy respectively.

Using [11.13], we have:

$$\frac{k_{\text{liq}}}{k_{\text{gaz}}} = \frac{s_{M^\neq}}{s_A s_B} = \frac{s_{M^\neq}^0}{s_A^0 s_B^0} \exp\left(-\frac{\Delta H^\neq}{RT}\right) \quad [11.15]$$

with:

$$\Delta H^\neq = \Delta H_{M^\neq} - \Delta H_A - \Delta H_B \quad [11.16]$$

If, however, we write the reaction rate coefficients in a classic manner according to Arrhenius, we have:

$$\frac{k_{\text{liq}}}{k_{\text{gas}}} = \frac{A_{\text{liq}}}{A_{\text{gas}}} \exp\left(-\frac{E_{\text{liq}} - E_{\text{gas}}}{RT}\right) \quad [11.17]$$

By comparing [11.15] and [11.17], it appears that the difference in activation energy in the liquid and gas phase is equivalent to  $\Delta H^\ddagger$ .

We frequently notice that  $\Delta H^\ddagger$  is nearly zero. In this case, the activation energies in the gas phase and in solution are identical and the reaction rate coefficient ratio according to [11.15] becomes:

$$\frac{k_{\text{liq}}}{k_{\text{gas}}} = \frac{s_{M^\ddagger}^0}{s_A s_B} \quad [11.18]$$

In most of the gases, the entropic factor is within the order of  $10^2$  and the reaction rate in solution therefore appears 100 times more rapidly than in the gas phase:

$$\frac{k_{\text{liq}}}{k_{\text{gas}}} \approx 10^2$$

If the problem can be approached correctly with the reacting species (stables in some conditions), however, this remains for the activated complex unless we implement the intermediaries' properties between the reactants and products of the reaction. Such an approach allows us to obtain interesting generic solutions. We will now provide an overview of how to deal with dilute ionic solutions.

#### 11.1.4. Reactions between ions in diluted solution

As the activity coefficient of an ion in solution depends primarily on its charge, it is possible to use reasonable assumptions about the shape of the activated complex in order to estimate the activity coefficient more easily than for other types of reactions.

In fact, each reactant is assimilated to a sphere, and two models have been proposed for a bimolecular reaction:

- The bi-spherical model in which the activated complex is a double-sphere, each keeping the same charge as its origin molecule, the total charge of the activated complex remaining the same as those of the ions' reactants.
- The single-sphere model in which there is a fusion between the two spheres corresponding to each reactant to generate one sphere carrying the sum of charges and of radius  $r_M \neq$ .

Curiously, these two models lead to qualitatively similar conclusions. This proves again that the charge of ions is more important than their shape.

We will first express the partial molar Gibbs free energy and use relation [11.12], considering that this is the Gibbs free energy required for transferring an ion from a medium dielectric constant unity (equal to 1) to that of the solution.

Here:

- $z_i$ : the electrovalence of ion,  $i$  (positive or negative); and
- $\epsilon$ : the elementary charge.

We assume that the ion is first released in a vacuum ( $D = 1$ ). After Born, the free energy associated with it is  $\frac{\epsilon^2 z^2}{2r}$ . The radical obtained is transferred into the solution of infinite dilution, thus there is an increase in the free energy  $\Phi'$  due to the Van der Waals forces between the radical and its neighbors. The radical is then recharged in a solution of a dielectric constant,  $D$ , and the associated free energy is  $\frac{\epsilon^2 z_i^2}{2Dr}$ . During this last phase, polarization of the ion by charges would lead to a term  $\Phi''$ .

The total change of free energy for transferring one ion isolated from vacuum (or an infinitely diluted gas) to a solution of infinite dilution is therefore:

$$\Delta F = -\frac{\epsilon^2 z_i^2}{2r} + \frac{\epsilon^2 z_i^2}{2rD} + \Phi' + \Phi'' \quad [11.19]$$

This quantity is clearly related to the activity coefficients  $\beta$ . So, for an ion  $i$ , after [11.12] we shall have:

$$\ln \beta_i = \frac{\varepsilon^2 z_i^5}{2k_B T r_i} \left( \frac{1}{D} - 1 \right) + \frac{\Phi_{\beta'} + \Phi_{\beta''}}{k_B T} \quad [11.20a]$$

Consequently we deduce the term:

$$\ln \frac{\beta_A \beta_B}{\beta_M \neq} = \frac{\varepsilon^2}{2k_B T_i} \left( \frac{1}{D} - 1 \right) \left[ \frac{z_A^2}{r_A} + \frac{z_B^2}{r_B} - \frac{(z_A + z_B)^2}{r_M \neq} \right] + \frac{\Delta \Phi_\beta}{k_B T} \quad [11.20b]$$

In a diluted solution, the coefficient of activity  $f$  (with the infinitely diluted solution as a reference) is given by the Hückel model (by adding the non-electrostatic term  $\Phi_f$ ):

$$\ln f_i = - \frac{B \varepsilon^2 z_i^2}{2D k_B T_i} + \frac{\Phi_f}{k_B T} \quad [11.21]$$

In this expression,  $B$  is given by:

$$B^2 = \frac{8\pi N_a \varepsilon^2}{1000 D k_B T} \mu \quad [11.22]$$

where  $\mu$  is the ionic strength of the medium defined by:

$$\mu = \sum_i [A_i] z_i^2 \quad [11.23]$$

which is the sum including all the ions present in solution. Using [11.21], we can therefore deduce:

$$\ln \frac{f_A f_B}{f_M \neq} = \frac{\varepsilon^2 z_A z_B}{D k_B T} + \frac{\Delta \Phi_f}{k_B T} \quad [11.24]$$

Using relation [11.7], we can write:

$$\ln k = \ln k_0 + \ln \frac{\beta_A \beta_B}{\beta_{M^{\neq}}} + \ln \frac{f_A f_B}{f_{M^{\neq}}} \quad [11.25]$$

from which we introduce [11.20] and [11.24] into [11.25]:

$$\begin{aligned} \ln k &= \ln k_0 + \frac{\varepsilon^2}{2k_B T} \left( \frac{1}{D} - 1 \right) \left[ \frac{z_A^2}{r_A} + \frac{z_B^2}{r_B} - \frac{(z_A + z_B)^2}{r_{M^{\neq}}} \right] \\ &\quad + \frac{B\varepsilon^2 z_A z_B}{D k_B T} + \frac{\Delta\Phi}{k_B T} \end{aligned} \quad [11.26]$$

Moreover, by using relation [11.11], we can also write the Debye–Hückel model:

$$\ln k = \ln k_0^s + \frac{B\varepsilon^2 z_A z_B}{D k_B T} \quad [11.27]$$

By comparing both the two previous equations, we get:

$$\ln k_0^s = \frac{\varepsilon^2}{2k_B T} \left( \frac{1}{D} - 1 \right) \left[ \frac{z_A^2}{r_A} + \frac{z_B^2}{r_B} - \frac{(z_A + z_B)^2}{r_{M^{\neq}}} \right] + \frac{\Delta\Phi}{k_B T} \quad [11.28]$$

By reporting this in [11.27] we get the following for the reaction rate coefficient:

$$\ln k = \ln k_0^s + 2A z_A z_B \sqrt{\mu} \quad [11.29]$$

where  $A$  is a quantity defined by:

$$A = \frac{N_a^2 \varepsilon^2 (2\pi)^{1/2}}{(DRT)^{3/2} \sqrt{1,000}} \quad [11.30]$$

For  $A$  we calculate a value of about 0.51 in aqueous solutions at 25°C, and obtain:

$$\ln k = \ln k_0^s + z_A z_B \sqrt{\mu} \quad [11.31]$$

This relation gives a refined law between the logarithm of the reaction rate factor and the square root of the ionic strength. This law has been experimentally verified for different reactions.

To calculate the influence of the dielectric constant, we use relation [11.26] extrapolated to zero ionic strength (or at  $B$  equal zero):

$$\left( \frac{d \ln k_0}{d(1/D)} \right)_{\mu=0} = \frac{\epsilon^2}{2k_B T} \left[ \frac{z_A^2}{r_A} + \frac{z_B^2}{r_B} - \frac{(z_A + z_B)^2}{r_M \neq} \right] \quad [11.32]$$

From this relationship, we can show that if the initial  $A$  and  $B$  ions are oppositely charged, the curve  $\ln k_0$  versus  $1/D$  (at zero ionic strength) is a straight line with a negative slope; whereas it is positive slope if the ions carry charges of the same sign.

This result is correctly found experimentally for the reaction between thiosulfate-bromoacetate ions in different aqueous solutions containing urea or glucose and covering a range of dielectric constants from 20 to 140. The experimental points towards zero ionic strength are aligned properly as a function of  $1/D$ .

### 11.1.5. Reactions in concentrated solutions: the acidity factor

In solvents with high dielectric constant, such as water, the solution deviates very little from ideal solutions if they are diluted enough (about 0.1 M) and can be treated using the Debye–Hückel model, as described in section 11.4.

With higher concentrations or solvents with lower dielectric constants, the situation is much less clear. The deviation from the ideal can be significant and we no longer have a suitable model with a reasonable number of constants by which to *a priori* calculate the reaction rate coefficient.

As a result of Hammet's work, however, we realized that it was possible to calculate the reaction rate coefficient of a reaction that is structurally similar by

multiplying the latter by a compensation coefficient defined for a family of reactions.

#### 11.1.5.1. Influence of substituents on the reaction rate coefficient

Let us write the reaction rate coefficient as:

$$k = \frac{\alpha k_B T}{h} \exp\left(-\frac{\Delta(G_0^\ddagger)}{RT}\right) \quad [11.33]$$

At constant temperature we can then write:

$$\ln k = \text{const} - \frac{\Delta(G_0^\ddagger)}{RT} \quad [11.34]$$

Where  $\chi$  is an intensive variable such as pressure, electric field, etc., let us define the following:

$$\frac{\partial \Delta(G_0^\ddagger)}{\partial \chi} = g^\ddagger \quad [11.35]$$

In the hypothesis that the derivative [11.35] remains relatively constant over a wide interval of  $\chi$ , we can write:

$$\Delta(G_0^\ddagger)_T = \left[ \frac{\partial \Delta(G_0^\ddagger)}{\partial \chi} \right]_T d\chi \quad [11.36]$$

Equation [11.34] then takes the following form:

$$\ln k = \text{const.} - \frac{g^\ddagger}{RT} d\chi \quad [11.37]$$

We now imagine a group of reactions designated by the index ( $B$ ) in which the steps are basically the same and differ from each other only by the nature of the

group substitution. The measure  $\chi$ , which might be the electric field in the reaction medium, will be a series of particular values:

$$\chi_1^{(B)}, \chi_2^{(B)}, \chi_3^{(B)}, \dots \chi_i^{(B)}$$

Then for each reaction  $i$  of type  $(B)$ , equation [11.37] can be written:

$$\ln k_i^{(B)} = \text{const} - \frac{g^\neq(B)}{RT} d\chi_i^{(B)} \quad [11.38]$$

Now consider a second family of reactions  $(D)$  undertaking the same group substitutions. The relation for this family of reactions corresponding to relation [11.37] will be:

$$\ln k_i^{(D)} = \text{const} - \frac{g^\neq(D)}{RT} d\chi_i^{(D)} \quad [11.39]$$

If the two families of reactions  $(B)$  and  $(D)$  are not of very different types, for example if they all involve the approach of molecules of the same signs, then the ratio  $d\chi_i^{(B)}/d\chi_i^{(D)}$  is likely to be the same for all groups of substitutions. In many cases this ratio is indeed close to one unit.

By replacing this ratio with  $C$  in [11.38] and [11.39], we have:

$$\ln k_i^{(B)} = C \frac{g^\neq(D)}{g^\neq(B)} \ln k_i^{(D)} \quad [11.40]$$

If as we have admitted before, families  $(B)$  and  $(D)$  are fundamentally similar, the influence of variable  $\chi$  on the Gibbs free energy of the reaction activation of type  $(B)$ :  $g^\neq(B)$  is connected to the corresponding term for family  $(D)$ :  $g^\neq(D)$  such that

the ratio of these free enthalpies is nearly constant  $\frac{g^\neq(D)}{g^\neq(B)} = \text{const.}$

In this case, equation [11.40] becomes:

$$\ln k_i^{(B)} = X \ln k_i^{(D)} \quad [11.41]$$

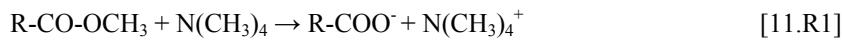
In this expression,  $X$  is a constant between the two types of reactions regardless of the substituent.

For a substitution group, this equation links the influence of the reaction rate for a family of reactions ( $B$ ) to the rate of reactions of another reaction family ( $D$ ) with the same substitution group.

#### 11.1.5.2. Rate coefficients and equilibrium constants

Instead of comparing the influence of substitution groups on the reaction rates of two reactions, we can compare the effect of a group on the equilibrium constant and rate coefficient of the same reaction.

For example, we can compare the effects of modifying different groups,  $R$ , on the rate coefficient of reaction [11.R1], with the influence of the same groups on the equilibrium constant of reaction [11.R2], which is the dissociation constant of acid  $R\text{-COOH}$ :



The variation of the equilibrium constant with the intensive variable  $\chi$  can be represented by an equation similar to [11.39], which is:

$$\ln K_i^{(D)} = \text{const} - \frac{g^\#(D)}{RT} d\chi_i^{(D)} \quad [11.42]$$

In this expression,  $g^\#(D)$  equals the partial derivative of the Gibbs free energy of the equilibrium studied with respect to variable  $\chi_i$  (by analogy with [11.36]). By introducing the same assumptions as before, which is that the ratio  $d\chi_i^{(B)}/d\chi_i^{(D)}$  is a constant for a given group  $i$ , equations [11.38] and [11.42] allow us to write the following:

$$\ln k_i^{(B)} = C \frac{g^\#(D)}{g^\#(B)} \ln K_i^{(D)} \quad [11.43]$$

where  $g^\#(D)/g^\#(B)$  is a constant, the modification of free activation enthalpy by passing from one substituent to another is a defined ratio from the corresponding

Gibbs free energy modification of an equilibrium similar to the reaction. Hence, as before we will have:

$$\ln k_i^{(B)} = X \ln K_i^{(D)} + \text{const} \quad [11.44]$$

It is possible to link the influence of a series of substituted groups on the equilibrium constant of two groups of reactions in a similar way. Here we obtain the following equation:

$$\ln K_i^{(B)} = X \ln K_i^{(D)} + \text{const} \quad [11.45]$$

Experimental confirmations of equations [11.41], [11.44] and [11.45] are easily noticeable in the literature through the numerous examples that are available.

#### 11.1.5.3. Example of the Hammett's activity coefficient

The first to have introduced such a relationship is Hammett, through what is called the Hammett acidity function.

To introduce it, let us consider equilibrium [11.R3] between a neutral base  $B$  and its strong conjugated acid  $BH^+$  in aqueous solution:



The equilibrium constant  $K_B$  of the base is expressed as a function of activities by:

$$K_B = \frac{|BH^+|}{|B||H^+|} = \frac{1}{K_{BH^+}} \quad [11.46]$$

We can express an activity by the product of concentration using corresponding activity coefficient. Here, the constant becomes:

$$K_B = \frac{[BH^+]}{[B]} \frac{\gamma_{BH^+}}{\gamma_B} \cdot \frac{1}{\left[H^+\right] \gamma_{H^+}} \quad [11.47]$$

If the base  $B$  (or its conjugate acid) is a color-indicator solution, the concentration ratio of  $[BH^+]/[B]$  is measured experimentally by the absorption of light.

The value of this ratio is a measure of the tendency of the solution to transfer a proton to the neutral base  $B$ .

From relation [11.47], we can deduce:

$$\log \frac{[BH^+]}{[B]} = \log K_B + \log \frac{\gamma_B}{\gamma_{BH^+}} \cdot |H^+| \quad [11.48]$$

If we choose the infinitely diluted solution as the reference state for the activity coefficients, the activity coefficients tend toward one in diluted solutions and equation [11.48] takes the simplest form:

$$-\log |H^+| = -pK_B - \log \frac{[BH^+]}{[B]} \quad [11.49]$$

Hammett suggests that if the  $[H^+]$  proton concentration measures the power of protonation of the diluted solution, the corresponding term of relation [11.48] can be used in the case of concentrated solutions to measure the same property. Hence, he defines the acidity function  $H_0$  of an acidic solution compared to a neutral base:

$$H_0 = -pK_B - \log \frac{[BH^+]}{[B]} = -\log \frac{\gamma_B}{\gamma_{BH^+}} \cdot |H^+| \quad [11.50]$$

For such a function to be really useful, it must be independent from the base,  $B$ , which is to say that the ratio  $\gamma_B / \gamma_{BH^+}$  should be the same for different bases. This is observed for proximate bases that differ by the nature of the chemical group substituted.

For such a family, we simply measure  $K_B$  in a diluted solution and the concentration ratio  $[BH^+]/[B]$  in the concentrated solution to obtain the function  $H_0$ .

The final model of the activated complex developed for gas phase reactions is perfectly suited to liquids and allows us to find the influence of parameters that characterize the environment, as in the case of reactions between ions, with the ionic strength, dielectric constant and the role of the nature of the substituted groups in more concentrated solutions.

This model can also be used with the process of diffusion, viscosity and conductivity of ionic liquid solution, which requires the correct modeling of the liquid state, built as a group of “holes” moving around the matter in the way that gas molecules do in a vacuum.

## 11.2. Elementary reaction in the solid state

There are relatively few elementary reactions in solid phase. The most common involve point defects whose source is the bulk and they do not require an interface to form, or the reactions of association of these defects. A particular mention should be made of the displacement reaction of a point defect, which is the basis of the diffusion process.

### 11.2.1. Potential energy of a solid

The group of individual atoms, molecules or ions that make up a crystalline solid is arranged in space according to a periodic mesh called the crystallographic structure of the solid. This structure is stabilized with regards to the group of components separated from each other by attraction and repulsion energy terms, functions of the distances between the components. In the case of ionic solids, the attractive part of this energy is due to the electrostatic interaction between positive and negative ions.

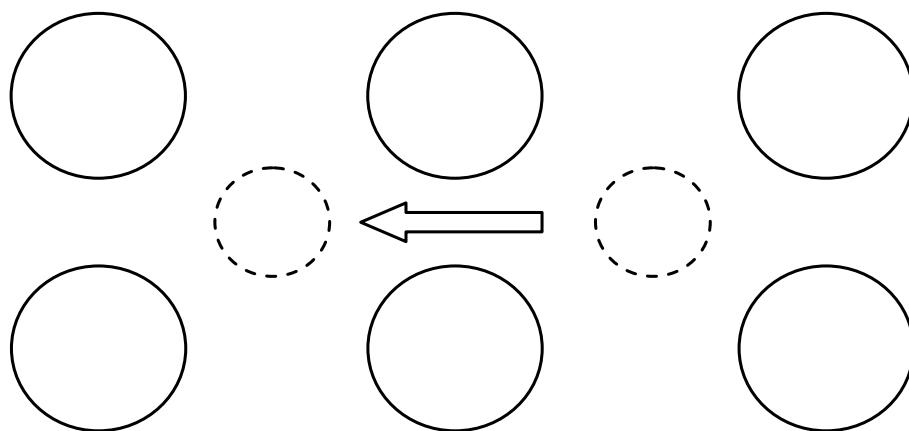
The repulsive part of the lattice energy is due to repulsion between the electron clouds of ions when they come too close to each other. The superposition of both types of energy leads to an equilibrium distance between the ions and to a network potential energy with respect to the energy of the system when all the ions are at an infinite distance from each other. For kinetic studies, it is convenient to take the potential energy of the lattice of an ideal solid as the origin of energies.

### 11.2.2. Reaction pathway

If a point defect (ion or ion vacancy) is introduced into the solid, its potential energy will be changed from the one defining the previous ideal solid and the defect located at infinity. This new potential energy will depend on the position of the defect in the solid. The point defect has a position of equilibrium in the system that will keep the new potential energy at a minimum.

To illustrate this, let us consider a point defect consisting of an additional ion introduced into the solid. As in the case of gas-phase molecules, we can plot a potential energy diagram giving the different levels as a function of, for example, the position defined by the coordinates of the ion relative to a characteristic position of the lattice and forming the equilibrium position of the added ion. The diagram defined therefore requires a 3D space in order to plot the iso-energy curves.

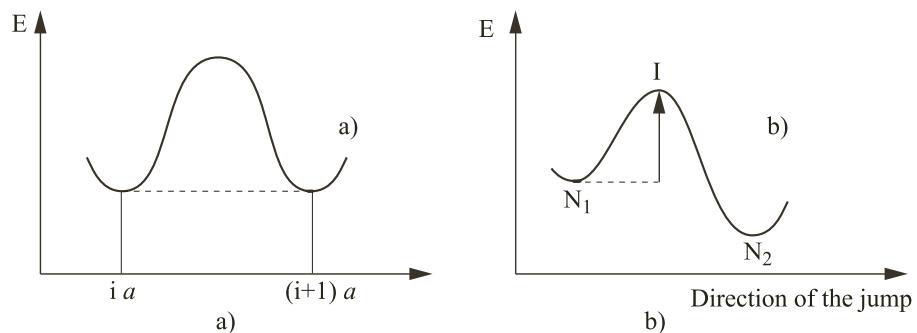
To simplify the plot, we only consider the motion in the plane consisting of equilibrium positions immediately adjacent and one ion between these positions. We then construct a diagram similar to Figure 10.6. If we now consider displacement of the ion in the plane (Figure 11.1), we obtain the potential energy curve as a function of the position of the ion.



**Figure 11.1.** Displacement of an interstitial ion in the lattice

This curve can be represented in two forms, as shown in Figures 11.2a and 11.2b. The first curve is symmetrical with the two successive equilibrium positions that are identical; whereas in the second curve these positions are energetically different. The first curve will be found in the bulk far from the solid walls and for

low defect concentrations. The second curve shows that at least one of these two conditions is not met.



**Figure 11.2.** Variation of the system energy during a jump:  
a) with two identical levels; b) with two different levels

The same results would be obtained if the defect consisted of a missing ion instead of an added ion. This vacancy allows the movement of other ions. We prefer to take into account the displacement of the vacancy rather than the corresponding ion, since the defect will still be considered an often-diluted vacancy solution in many cases.

From the previous energetic configuration (section 11.2.2), we deduced the nature of the elementary step within a solid. The elementary step is the jump of a particle (or vacancy) from one equilibrium location to the nearest equilibrium location. In the case of solid, as with the activated collision of two molecules in a gaseous medium, it is no longer necessary to use the mass point analogy, since the jumping particle analogy perfectly characterizes the process and creates the reaction path.

### 11.2.3. Rate of an elementary jump

To calculate the rate of the jump, we can fully adopt the same logic as in Chapter 10. If we choose to represent the reactivity of the elementary step as a function of the concentration  $[\delta]$  in default at the initial position, we have:

$$\varphi = k[\delta] \quad [11.51]$$

Thus we can use relation [10.39]. The coefficient  $\alpha = \frac{1}{2}$  is justified in the case of energetic equivalence at the starting and arrival points:

$$k = \frac{k_B T}{2h} K_c^\ddagger = \frac{k_B T}{2h} \exp\left(-\frac{(\Delta G_0^\ddagger)}{RT}\right) \quad [11.52]$$

Our defect is considered in the same way in the solid as in the solution, so we can apply the same changes to the model if the solution is not pure. The only difference is that in our case the constant  $k$ , which is related to the concentration, is defined directly from the diluted solution rather than the mixture in the gas.

In the case of solid phases we prefer to use the reactivity per unit of area of the plane perpendicular to the path of reaction instead of the volume reactivity. We easily pass from one to another by multiplying the previous rate coefficient by the distance between the planes, which is of the same order of magnitude as the lattice parameter.

We therefore use relation [10.22] in both area and volume, the rate coefficient being a coefficient as appropriate per unit area and surface reactivity or per unit of volume and volume reactivity.

For the activation energy, we can use relation [10.49] and write:

$$\frac{d \ln k}{T} = \frac{1}{T} + \frac{\Delta(U_0^\ddagger)}{RT^2} = \frac{E_a}{RT^2} \quad [11.53]$$

In the case of a reaction with a solid, the change in volume activation is near zero and [11.53] is written:

$$E_a = RT + \Delta(H_0^\ddagger) \quad [11.54]$$

In general, given the characteristics of the Arrhenius coordinates and the low temperature ranges covered for the same reaction, the temperature dependence of the activation energy is negligible.

#### 11.2.4. Diffusion in solids

Diffusion is often a determining process of a mechanism. It cannot be modeled by a single step but through a succession of jumps from a starting interface or interface “0” to an incoming interface or interface “X”.

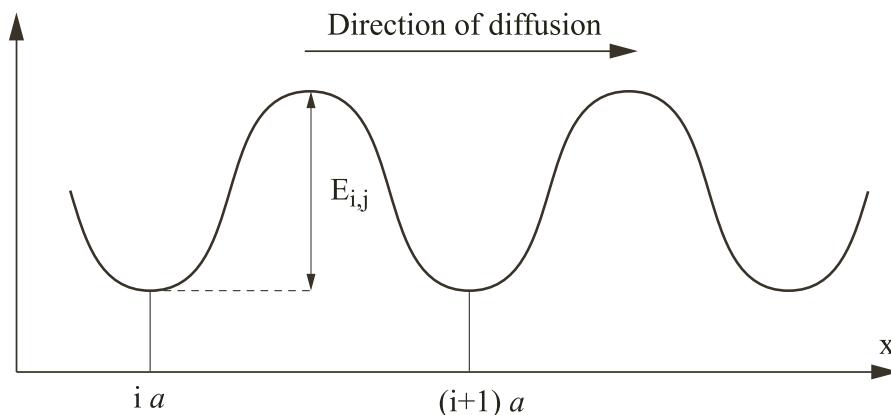
We will determine the diffusion flux of the defect  $M$  in one direction, in the case of diffusion through a thick plate X. The number of jumps is given by the number of planes between the departure and arrival, hence  $n = X/a$ .

Between planes  $i$  and  $i + 1$ , the flux from left to right (see Figure 11.3) is given by applying [11.51] and [11.52]:

$$\vec{J}_i = \frac{ak_B T}{2h} [M]_i \exp\left(-\frac{[\Delta G_0^\neq]_i}{RT}\right) \quad [11.55]$$

In the opposite direction, the flux will be:

$$\overleftarrow{J}_{i+1} = \frac{ak_B T}{2h} [M]_{i+1} \exp\left(-\frac{[\Delta G_0^\neq]_i}{RT}\right) \quad [11.56]$$



**Figure 11.3.** Schematic representation of jumps in a unidirectional diffusion

The resulting flux between planes  $i$  and  $i + 1$  will be given by the difference between the two previous fluxes:

$$J_i = \frac{a k_B T}{2h} \{[M]_i - [M]_{i+1}\} \exp\left(-\frac{[\Delta G_0^\neq]_i}{RT}\right) \quad [11.57]$$

According to the formula of finite increments, the concentration at  $i + 1$  is given according to:

$$[M]_{i+1} = [M]_i + a \left( \frac{\partial [M]}{\partial x} \right)_i \quad [11.58]$$

By incorporating this into [11.57], we get:

$$J_i = -\frac{a^2 k_B T}{2h} \left( \frac{\partial [M]}{\partial x} \right)_i \exp\left(-\frac{[\Delta G_0^\neq]_i}{RT}\right) \quad [11.59]$$

We define a diffusion coefficient of plane  $i$  by:

$$D_i = \frac{a^2 k_B T}{2h} \exp\left(-\frac{[\Delta G_0^\neq]_i}{RT}\right) \quad [11.60]$$

The flux at plane  $i$  will be:

$$J_i = -D_i \left( \frac{\partial [M]}{\partial x} \right)_i \quad [11.61]$$

This last equation is the Fick's first law for unidirectional diffusion.

We will now consider the pseudo-steady state mode for diffusion through a plate of thickness  $Y$  and a constant unit section. To do so, we write that the variation in the amount of diffusing species on plane  $i$  is zero, so:

$$\frac{\partial \{M\}_i}{\partial x} = J_{i-1} - J_i = 0 \quad [11.62]$$

Gradually, as the diffusion section is constant, we deduce that the flux is independent of the plane, so:

$$J_1 = J_2 = \dots = J_{i-1} = J_i = \dots \quad [11.63]$$

This flux is therefore:

$$J = \frac{a k_B T}{2h} \left\{ [M]_i - [M]_{i+1} \right\} \exp \left( - \frac{[\Delta G_0^\neq]_i}{R T} \right) \quad [11.64]$$

The concentrations at the interfaces with borders 0 and  $Y$  are denoted  $[M]_0$  and  $[M]_Y$ . We assume that these concentrations are independent of time. From what precedes, we can write the following group of relations:

$$\begin{aligned} [M]_0 - [M]_1 &= \frac{2h}{ak_B T} \exp \left( \frac{[\Delta G_0^\neq]_1}{RT} \right) \\ &\dots \\ [M]_i - [M]_{i+1} &= \frac{2h}{ak_B T} \exp \left( \frac{[\Delta G_0^\neq]_i}{RT} \right) \\ &\dots \\ [M]_n - [M]_X &= \frac{2h}{ak_B T} \exp \left( \frac{[\Delta G_0^\neq]_n}{RT} \right) \end{aligned}$$

By adding the previous equalities, we obtain:

$$J = \frac{a k_B T}{2h} \frac{\{[M]_0 - [M]_Y\}}{\sum_1^n \exp\left(\frac{[\Delta G_0^*]_i}{RT}\right)} \quad [11.65]$$

The application of this relation requires knowledge of the free activation enthalpies. In the case of Figure 11.3, and in general with diffusion, all the equilibrium positions are equivalent and therefore the activation energy is independent of the x-axis. Moreover, at the solid state the activation entropy can be neglected and so the flux can be written:

$$J = \frac{a^2 k_B T}{2h} \frac{\{[M]_0 - [M]_Y\}}{Y} \exp\left(-\frac{E_D}{RT}\right) \quad [11.66]$$

The new expression of the diffusion coefficient, which is now independent of the x-axis, becomes:

$$D = \frac{a^2 k_B T}{2h} \exp\left(-\frac{E_D}{RT}\right) \quad [11.67]$$

We again find the expression of the flux in the pseudo-steady state mode:

$$J = D \frac{\{[X]_0 - [X]_Y\}}{Y} \quad [11.68]$$

This expression is very important because it allows us to replace a group of elementary diffusion steps by a single step that can be formally considered basic and is written by distinguishing two different components of the same species X:  $X_0$  at the starting point and  $X_Y$  at the diffusion finishing point. This new “elementary step” will be:



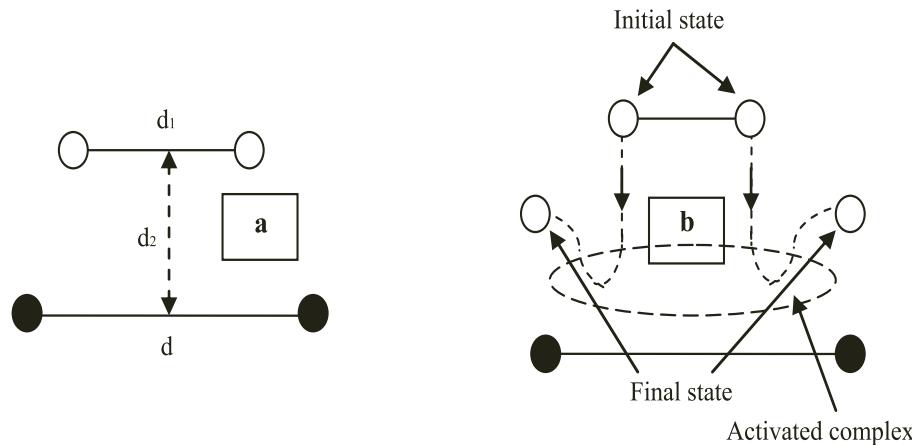
### 11.3. Interphase reactions

Interphase reactions are of great importance in heterogeneous kinetics and include a number of physical processes, such as dissolution. We will classify these reactions based on the type of interphase.

#### 11.3.1. Gas–solid interphases: adsorption, desorption

Adsorption and desorption processes are the reverse of each other and are always considered as occurring, whatever the nature of the solid and gas. During chemical transformations there is chemisorption. When this double process occurs as steps of a reaction mechanism, the Langmuir mechanism is satisfied.

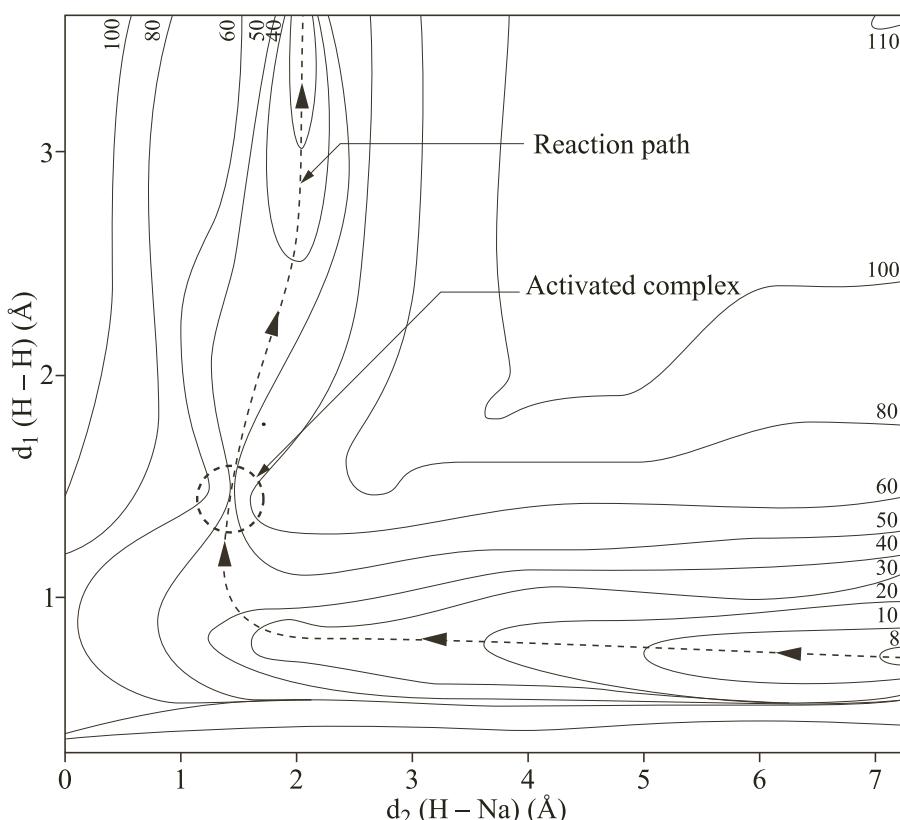
It is possible to plot the equipotential curves of the system and therefore determine the activation energy and activated complex. Let us have a look at the example of hydrogen adsorption on sodium. We consider all four atoms (presumed to be coplanar) of the hydrogen molecule parallel to the metal surface (the position of minimum energy) and the two sodium atoms that face it (see Figure 11.4a). Using methods described in section 10.1, we can calculate the energy of this group for the distance between each hydrogen atom and between the gas molecule and the metal surface, assuming a fixed distance  $d$  between the two sodium atoms.



**Figure 11.4.** Adsorption of dihydrogen on sodium: a) a four-atom system; and b) the approach and dissociation of a dihydrogen molecule

Using the calculated energies, we plot every equipotential curve in the axis system chosen (see Figure 11.5). Starting from the initial state of the gas molecule

(on the right of the diagram) to an infinite distance from the metal surface, we follow the potential valley, cross the pass and reach the final position of the hydrogen adsorbed on metal. This defines the reaction path. If we now represent the dihydrogen molecule approaching the surface, we find that the molecule moves closer to the surface. Two atoms then depart to find their equilibrium position further from the surface than the activated complex (see Figure 11.4b).

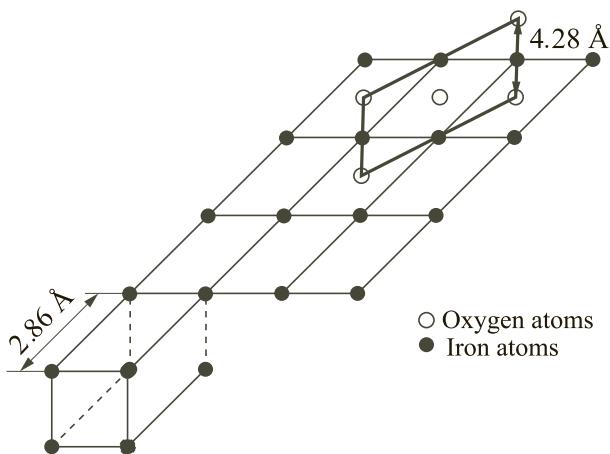


**Figure 11.5.** Equipotential surfaces during dihydrogen adsorption

### 11.3.2. Solid–solid interface: the concept of epitaxy

Interface reactions between two solid transfer reactions are sometimes accompanied by the construction or destruction of a crystal lattice.

It has been known for a long time that two crystalline solids, one which starts at the surface of the other, often show mutual orientation relationships: this is the process of epitaxy. Studies such as thin layers of oxides formed by oxidation of a metal, for example, have shown such a process. Figure 11.6 shows the example of the schematic orientations of cubic iron oxide ( $\text{FeO}$ ) formed on the 001 side of the cubic iron. The side of the iron oxide cube is  $2.86 \text{ \AA}$ . The parameter of  $\text{FeO}$  is  $4.29 \text{ \AA}$ . In the isolated crystal,  $\text{FeO}$  iron atoms are spaced at  $4.29 / \sqrt{2} = 3.89 \text{ \AA}$  intervals, resulting in a slight deformation of the iron oxide crystal. If the layer of  $\text{FeO}$  is thick, the defect fades away from the interface; the oxide has found its own structure.



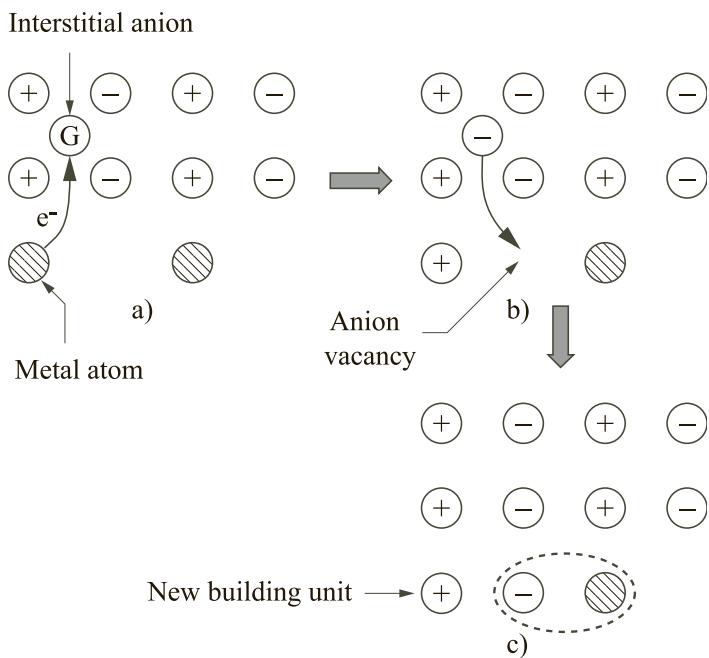
**Figure 11.6.** Epitaxy of the iron oxide onto iron

The process of epitaxy with the constraints it generates in the layers can explain the delamination of some of the layers as well as cracks forming in the layer.

In the same case where an epitaxial layer is not detected, its existence is proposed as the basic hypothesis.

The epitaxial relationship that ensures the continuity of the network will allow particles such as atoms, ions, and electrons to jump from one solid to another. It will likewise lead to a jump within the same solid. Beside this, the energy levels of the start and finish positions of the jump have no reason to be identical. It is the last property that will lead to changing vocabulary following diffusion, which is a succession of elementary steps that are all identical and continue with a jump across the interface. This latter jump will be seen as a reaction but we see that modeling is equivalent to that which we have developed within the solids.

Figure 11.7 shows the pattern of jumps of the interfacial reaction between a metal and an atom of  $G$  in an interstitial position of the compound  $GM$ , which corresponds to the reaction:



**Figure 11.7.** Interface reaction between a metal atom and an interstitial atom  $G$

This reaction takes place in two elementary steps. In the first step, an electron jumps from the metal on the interstitial atom, which creates an interstitial anion as well as an anion vacancy at the interface and a new structure unit of the product  $MG$  (step a→b, Figure 11.7). In second step (b→c) the interstitial ion jumps into the vacancy that completes the structure element:





In a pseudo-steady state mode, we show that the rate of the interface reaction is written formally as if it is elementary:

$$\phi = k' [G_i] - k'' \quad [11.69]$$

where  $k'$  and  $k''$  are rate pseudo-coefficients. We can show that with a pseudo-steady state mode, these coefficients are related to the reaction rate coefficients of the two elementary steps that constitute the interface reaction by the relations:

$$k' = \frac{k'_1 k'_2}{k'_2 + k'_1} \text{ and } k'' = \frac{k''_1 k''_2}{k''_2 + k''_1} \quad [11.70]$$

NOTE 11.2.– A review of relations [11.70] shows that if the rate coefficients of elementary steps follow Arrhenius' law with temperature. The apparent rate coefficient will do unless one of the denominator terms is negligible compared to the other, which is often the case of the jump of the ion compared with the jump of the electron.

## 11.4. Electrochemical reactions

Electrochemical reactions make up a specific family of interface reactions. These are described and analyzed in Chapter 3, section 3.4.

### 11.4.1. Definition

An elementary electrochemical reaction is a redox reaction occurring at the interface between an electron-conducting solid, called the electrode, and a solution of ions, called the bath or electrolyte solution.

Such a reaction can be written in one of the following forms:





or:



The coefficients  $v$  then make sense of algebraic stoichiometric coefficients. This reaction may take place in one direction or another.

NOTE 11.3.– The electrode can be either a metal (or carbon) or a semiconductor. The electrolyte can be either an ionic liquid or an ion-conducting solid.

Thermodynamics tells us that when no current passes through the electrode, there is a potential called the potential drop  $e_{i=0}$ , often given by the Nernst equation:  $e_{th}$ . If a current now passes through the system, an electrochemical reaction takes place at the electrode and it has a potential,  $e$ , that is different from that of the potential drop. The electrode is therefore polarized. The potential difference (positive or negative):

$$E = e - e_{i=0} \quad [11.71]$$

is called the polarization.

If the potential drop is the Nernst thermodynamic potential:

$$\eta = e - e_{th} \quad [11.72]$$

the polarization is called an overpotential.

#### 11.4.2. Reactivity of an electrochemical reaction

The classic definition of reactivity can be applied to an electrochemical reaction and we can therefore write it considering the number of electrons  $dne$  consumed between instants  $t$  and  $t + dt$ . The interface area being bi-dimensional, we often use the surface reactivity. We have:

$$\phi = -\frac{1}{Sv_e} \frac{dn_e}{dt} \quad [11.73]$$

or the number of electrons per unit of time is proportional to the current intensity  $I$ , we call it the current density  $i$ . This is the intensity per unit of surface.

CONVENTION 11.1.– In electrochemistry, intensities corresponding to an oxidation are counted positively, and those corresponding to a reduction are counted negatively.

If  $v_e$  is taken as an absolute value and  $\bar{F}$  denotes the Faraday, the reactivities of oxidation and reduction will be:

$$\phi_{oxy} = \frac{I}{Sv_e \bar{F}} = \frac{i}{v_e \bar{F}} \quad \text{and} \quad \phi_{red} = -\frac{I}{Sv_e \bar{F}} = -\frac{i}{v_e \bar{F}} \quad [11.74]$$

respectively. Thus, the surface reactivity of an electrochemical reaction is the current density (to the nearest coefficient).

#### 11.4.3. *The De Donder–Pourbaix inequality*

According to the De Donder inequality, the product of the affinity of a reaction and its rate is positive or zero. When transposed to electrochemical reactions, the inequality becomes:

$$\eta \cdot i \geq 0 \quad [11.75]$$

Thus, according to the agreement above, an electrochemical reaction can only take place in the direction of oxidation if the overpotential is positive and in the direction of a reduction if the overpotential is negative.

#### 11.4.4. *Polarization curves*

Among the various parameters that may affect the reactivity of an electrochemical reaction (the current density), one of the most important is the potential  $e$  at the electrode, which is ultimately the difference at the equilibrium.

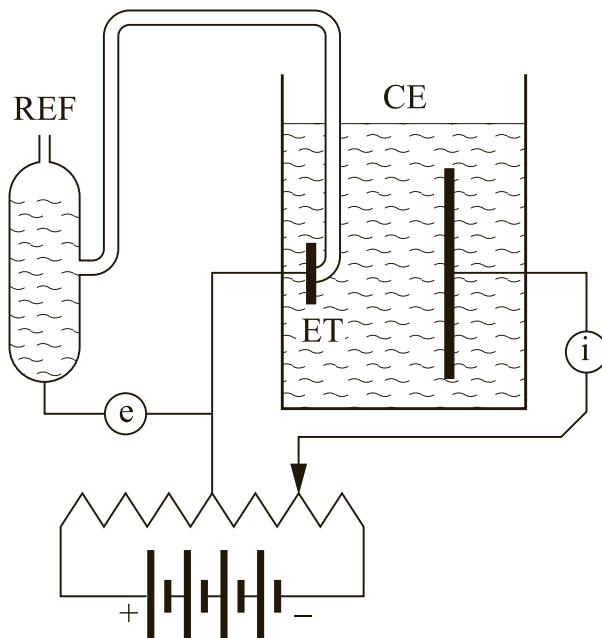
#### 11.4.4.1. Definition

We will be informed about an electrochemical reaction by studying the influence of the potential. To do this, we draw the curves  $e(i)$  that are the polarization curves corresponding to the reaction being considered. Curves  $\eta(i)$  are also called polarization curves. They differ from the previous ones by a translation, and pass through the origin (if  $i = 0$ , the overpotential is zero because the electrode potential is equal to the thermodynamic potential  $e_{th}$ ).

#### 11.4.4.2. Obtaining polarization curves

It is always difficult to obtain a polarization curve because we must avoid potential parasites that can appear in different parts of the circuit, particularly in the vicinity of the electrode.

The schematic diagram is given in Figure 11.8. A potential difference is established between the electrode studied (ET), also known as the working electrode, and the counter-electrode (CE), which is arranged so that the current density on the working electrode is as uniform as possible.



**Figure 11.8.** Potentiometric set-up to plot a polarization curve

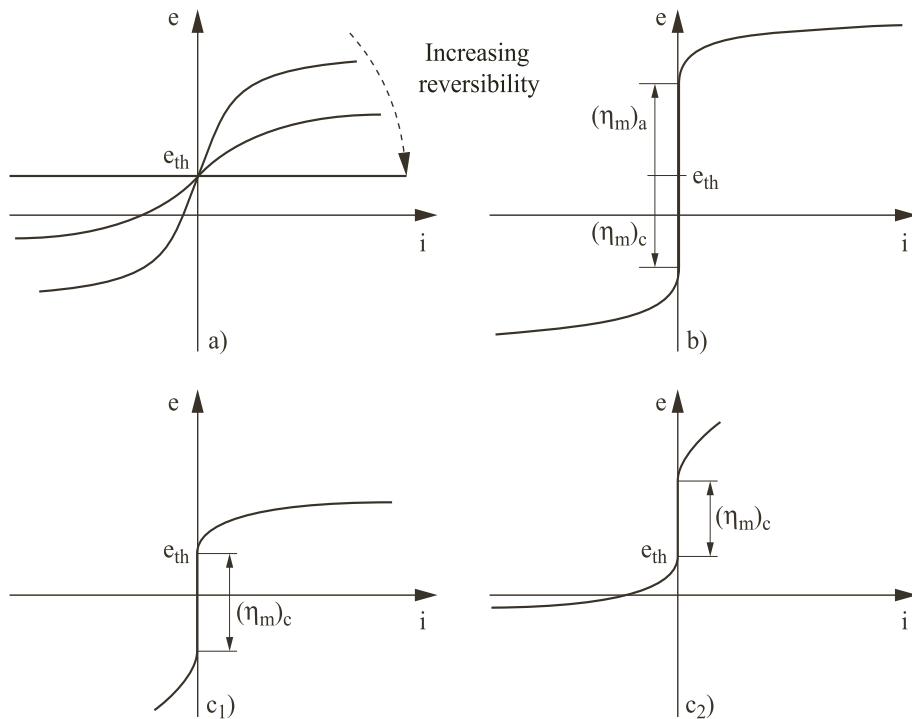
The electrode potential is measured relative to a reference electrode (REF) using an electronic voltmeter with very high impedance, which is working with a current close to zero. Measurement of the potential in the vicinity of the electrode is performed by a capillary tube extending from a siphon of the reference electrode.

Polarization of the electrode can be achieved using three different set-ups:

- the potentiometric set-up as shown in Figure 11.10;
- the intensiostatic set-up, where the intensity  $I$  passing through the electrode is imposed; and
- the potentiostat set-up, in which the voltage of the electrode is at a fixed value.

#### 11.4.4.3. The shapes of polarization curves

The polarization curves resulting from inequality [11.75] and at coordinates  $(\eta, i)$  are located entirely in the first and third quadrants of the plane. The gradient  $(de/di)_{i=0}$  is always positive at equilibrium.



**Figure 11.9.** Different types of polarization curves

On the other hand, as the curve actually represents the reactivity of the electrochemical reaction, its pace will depend on the reactivity. We therefore distinguish three cases:

- The reaction is fast in both directions: the system is often called quasi-reversible. With a low voltage positive or negative enough to cause the passage of a large current, the gradient of the curve at the origin  $(de/di)_{i=0}$  is low. Where the reaction is infinitely fast, the system is always at equilibrium and the polarization curve is horizontal (see Figure 11.9a).
- The reaction is slow in both directions. On each side of the balance voltage, a minimum overvoltage  $\eta_m$  is required to pass a detectable current (see Figure 11.9b).
- The reaction is slow in one direction or is much slower in one direction than another. Here there is a minimum cathodic (see Figure 11.9c1) or anodic (see Figure 11.9c2) potential and the polarization curve is very asymmetrical.

#### 11.4.5. *Polarization curve equation*

Consider an electrochemical equation written:



This represents two opposite elementary reactions: a reduction toward the left, and an oxidation toward the right.

The total current density will therefore be the algebraic sum of two oxidation and reduction current densities:

$$i = i_{oxy} + i_{red} \quad [11.76]$$

We can apply the activated complex model to each of the elementary steps. We must first define an activated complex of oxidation ( $Red^\ddagger$ ) and the activated complex of reduction ( $Oxy^\ddagger$ ). These two complexes are not identical since, as we will see in Figure 11.10, the energetic pathways of these two opposing steps are not the reverse of each other. The reactivities are written:

$$\varphi_{oxy} = \frac{i_{ox}}{v_e F} = \frac{k_B T}{h} [Red^\neq] \quad [11.77]$$

$$\varphi_{red} = -\frac{i_{red}}{v_e F} = \frac{k_B T}{h} [Oxy^\neq] \quad [11.78]$$

By proceeding as we did and introducing the activation equilibrium constants, we obtain:

$$i = \frac{v_e F k_B T}{h} \left\{ K_{oxy}^\neq [Red^\neq] - K_{red}^\neq [Oxy^\neq] \right\} \quad [11.79]$$

We now consider the energy paths of these two opposing steps. In each of these reactions, the electron crosses a potential barrier  $\Delta\Phi$ , which is the absolute potential of the electrode. We can therefore calculate the Gibbs free energy of activation:

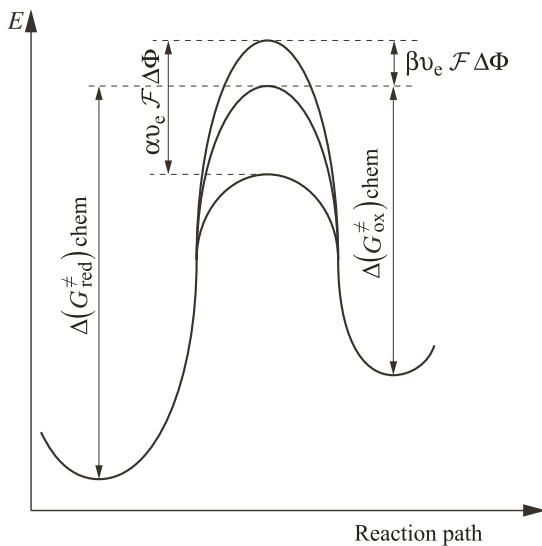
$$\Delta G_{ox}^\neq = (\Delta G_{ox}^\neq)_{chem} - \alpha v_e F \Delta\Phi \quad [11.80]$$

$$\Delta G_{red}^\neq = (\Delta G_{red}^\neq)_{chem} + \beta v_e F \Delta\Phi \quad [11.81]$$

Figure 11.10 shows the shape of the energy of the system as a function of the reaction path of each step. Coefficients  $\alpha$  and  $\beta$  are the transfer coefficients. These would be equal if the chemical barrier was symmetrical. According to these patterns, the Gibbs free energies of activation are:

$$K_{oxy}^\neq = \exp \left( -\frac{(\Delta G_{oxy}^\neq)_{chem}}{RT} \right) \exp \left( \frac{\alpha v_e F \Delta\Phi}{RT} \right) \quad [11.82]$$

$$K_{red}^\neq = \exp \left( -\frac{(\Delta G_{red}^\neq)_{chem}}{RT} \right) \exp \left( -\frac{\beta v_e F \Delta\Phi}{RT} \right) \quad [11.83]$$



**Figure 11.10.** Schematic representation of the potential energy of an electrochemical reaction

Substituting these expressions into equation [11.79], the current density will be:

$$i = \frac{v_e F k_B T}{h} \left\{ [Red] \exp - \frac{(\Delta G_{oxy}^{\ddagger})_{chem}}{RT} \exp \frac{\alpha v_e F \Delta \Phi}{RT} - [Oxy] \exp - \frac{(\Delta G_{red}^{\ddagger})_{chem}}{RT} \exp - \frac{\beta v_e F \Delta \Phi}{RT} \right\} \quad [11.84]$$

However, the absolute potential of the electrode is not measurable, but it is equal to the relative potential for the nearest additive constant. We write relation [11.84] by grouping the constants in the following form:

$$i = v_e F \left\{ k_{oxy} [Red] \exp \frac{\alpha v_e F \Delta \Phi}{RT} - k_{red} [Oxy] \exp - \frac{\beta v_e F \Delta \Phi}{RT} \right\} \quad [11.85]$$

At thermodynamic equilibrium, the overall reaction rate and therefore the current density are zero, therefore:

$$e_{th} = \frac{RT}{v_e F (\alpha + \beta)} \left\{ \ln \frac{[Oxy]}{[Red]} + \ln \frac{k_{red}}{k_{oxy}} \right\} \quad [11.86]$$

but at equilibrium we know that the system obeys Nernst's law, which is written:

$$e_{\text{th}} = e_0 + RT \ln \frac{[Oxy]}{[Red]} \quad [11.87]$$

Relations [11.86] and [11.87] only match if:

$$\alpha + \beta = 1 \text{ and } e_0 = \frac{RT}{v_e F} \ln \frac{k_{red}}{k_{oxy}} \quad [11.88]$$

To simplify things, let us write down:

$$\begin{aligned} i_0 &= v_e F k_{ox} [Red] \exp \frac{\alpha v_e F e_{\text{th}}}{RT} \\ &= v_e F k_{red} [Oxy] \exp - \frac{\beta v_e F e_{\text{th}}}{RT} \end{aligned} \quad [11.89]$$

Expression [11.66] becomes:

$$i = i_0 \left[ \exp \frac{\alpha v_e F (e - e_{th})}{RT} - \exp - \frac{\alpha v_e F (e - e_{th})}{RT} \right] \quad [11.90]$$

This is the expression of the electrode reaction rate. If we introduce an overpotential defined by [11.72], the current density becomes:

$$i = i_0 \left[ \exp \frac{\alpha v_e F \eta}{RT} - \exp - \frac{\alpha v_e F \eta}{RT} \right] \quad [11.91]$$

Function [11.91] is the polarization curve equation. This curve admits one inflection point defined by:

$$\frac{d^2 i}{d\eta^2} = 0 \quad [11.92]$$

which leads to the coordinates for this inflection point:

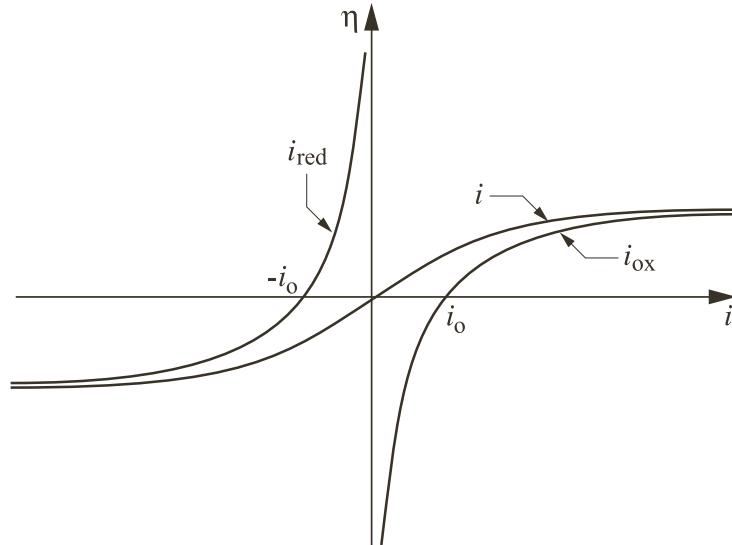
$$\eta_{\text{infl}} = -\frac{2RT}{v_e F} \ln \frac{\alpha}{\beta} \quad \text{and} \quad i_{\text{infl}} = i_0 \left( \frac{\beta}{\alpha} \right)^{2\alpha} \left( 1 - \frac{\alpha^2}{\beta^2} \right) \quad [11.93]$$

The position of this point does not necessarily coincide with the origin; this confusion only occurs when:

$$\alpha = \beta = 1/2 \quad [11.94]$$

In this case, the polarization curve equation becomes:

$$i = 2i_0 \sinh \frac{v_e F \eta}{2RT} \quad [11.95]$$



**Figure 11.11.** Partial and total currents for  $\alpha = \beta = 1/2$

Figure 11.11 shows the curves of the partial currents  $i_{\text{red}}$  and  $i_{\text{ox}}$  as well as the total current  $i$  in the latter case. The inflection point of the polarization curve then coincides with the origin.

The results related to the reaction rates of the elementary steps can be introduced into more complex systems, including one or more rate-determining electrochemical steps as is the case for other types of elementary steps. Elementary electrochemical steps can also be combined with thermal steps.

### 11.5. Conclusion

The steps occurring in solid interface phases ultimately result from the same modeling for the activated complex as with the reactions in homogeneous phases. In this case, these steps are not activated collisions, however, but particle jumps. The useful reactivities are therefore the surface reactivities written in  $\text{mol}/\text{m}^2\text{s}^{-1}$ .

# Chapter 12

## The Kinetics of Chain Reactions

In this chapter, we will expand on the modeling of chain reactions, which are of considerable practical importance in the fields of polymer chemistry and combustion, of molecules such as hydrocarbons for example, and explosions. Our study will examine the chain reactions that can lead to pseudo-steady state modes. The extension to non-pseudo-steady state modes will be discussed in Chapter 15.

### 12.1. Definition of a chain reaction

A chain reaction is a reaction in which a small number of elementary steps are repeated numerous times with the help of a small number of intermediate species that are constantly formed and destroyed. The repetitive sequence is called a link in the chain. The best known example is the reaction of hydrogen bromide synthesis, according to reaction [12.R1], whose mechanism may be represented by steps [12.R1a] to [12.R1d]:



By extension, a chain reaction is also called a linear reaction, which consists of a large number of very similar steps. Thus, the polymerization and polycondensation reactions are also considered chain reactions, each step being very close to the previous since it corresponds to the addition of a small entity to the molecular chain. Another example of such a chain reaction consists of all the steps of solid nucleus formation from a liquid solution or a solid (see Chapter 14).

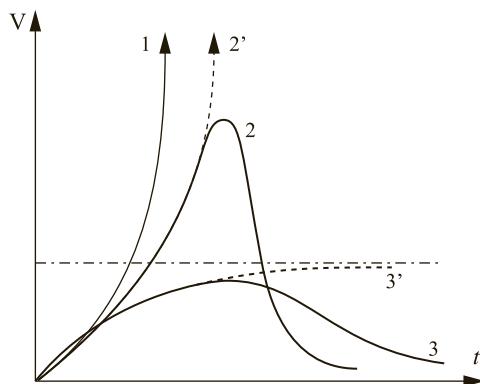
In homogeneous kinetics, chain reactions can be arranged into three large groups:

- reactions involving halogens or derivatives;
- reactions of oxidation and combustion (hydrogen, hydrocarbons); and
- reactions involving the formation of macromolecules (polymerizations and polycondensations).

## 12.2. The kinetic characteristics of chain reactions

Chain reactions have characteristic rate–time curves (see Figure 12.1):

- the initial rate is zero;
- rates (see Figure 12.1) may lead to high values showing a maximum (curve 2) or to ignition or explosion in some areas of the pressure–temperature plane (curve 1 and see sections 15.3 and 15.4); we frequently notice the important role of inhibitors and promoters;
- we often notice the influence of the reactor surface–volume ratio on the reaction rate.



**Figure 12.1.** The shape of the rate–time curves of a chain reaction

### 12.3. Classification of chain reactions

We can distinguish three classes of chain reactions:

- linear, straight chain or non-branch chain reactions;
- reactions with direct branching; and
- reactions with indirect branching.

#### 12.3.1. Straight or non-branched chain reactions

In such a reaction, the intermediate is called the active center and reacts with a reactant to give another active center having the same properties and final products as the previous one. The initial active center is formed by initiation and disappears with the breaking reaction. From the perspective of an active center, the Semenov diagram is linear (see Figure 12.2).



**Figure 12.2.** Schematic representation of a linear chain reaction with only one active center

With most generic cases, there are two alternating reactants and active centers,  $X$  and  $Y$ , as illustrated in Figure 12.3.



**Figure 12.3.** Schematic representation of a linear chain with two active centers

We define the number of chain links as follows. If an initial active center is responsible for the formation of  $n$  active centers of the same type, the chain will have  $n$  links. For example, Figure 12.4 shows the example of a chain with three links.



**Figure 12.4.** Example of a linear chain with three links

The length of a chain is its number of links. In theory, in the reaction medium the length of the chain varies from zero to infinity. In practice, short chains are predominant. The mean chain length will be the mean number of links susceptible to formation by only one active center. This is a statistical measure.

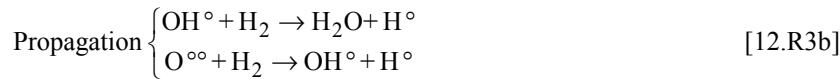
### 12.3.2. Reactions with direct branching

In any step of the mechanism, if an active center gives rise to several active centers, each giving rise to a chain, the reaction is said to have direct branching. The branching process may be represented by:



where  $\mu$  is an integer greater than 1 (otherwise the reaction would be linear) and is called the chain multiplying factor.

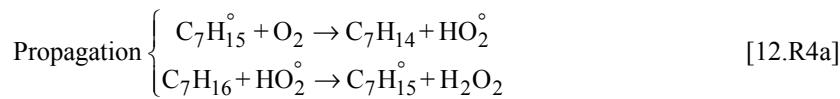
In the example of hydrogen combustion, the branching diagram is:

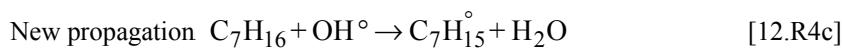


We see that each propagation link gives rise to two active centers –  $OH^\circ$  and  $H^\circ$  – hence the branching.

### 12.3.3. Reactions with indirect branching

With these reactions, a chain is forming and gives rise not to the final reaction products but to intermediate products  $I$ , which are fairly stable and are at the origin of new active centers leading to the development of secondary chains. Such a chain type has been suggested for heptane oxidation.





We see that the chain grows because of  $\text{HO}_2$  and that the formation of  $\text{H}_2\text{O}_2$ , which is relatively more stable than  $\text{HO}_2$ , is at the origin of a new reaction.

## 12.4. Chain reaction sequences

In a chain reaction, we are led to distinguish four types of sequences:

- chain initiation;
- chain propagation;
- chain breaking; and
- chain branching.

The first three phases are necessary.

### 12.4.1. Initiation of a chain reaction

Initiation aims to form active centers that are called initiation centers. These will often be different from the propagation centers. Initiation centers are often radicals, atoms, or ions.

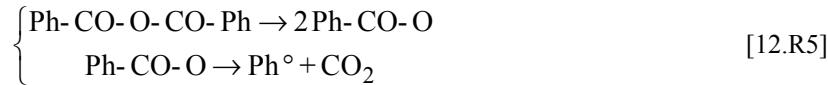
The initiation reaction can be triggered by several factors:

- heat (thermal initiation);
- catalysis (catalytic initiation); and
- light (photochemical initiation).

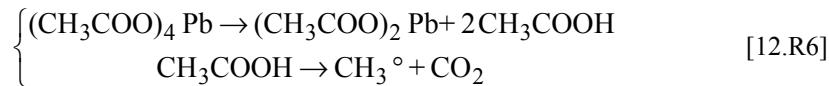
#### 12.4.1.1. Thermal initiation

An unstable substance under the control of heat is added to the reaction, which will dissociate and produce free radicals. These are often molecules with weak bonds: peroxide compounds or di-nitrogen derivatives.

For example, benzoyl peroxide is a source of free radicals that work according to the following:



Similarly, with lead tetraacetate:



It seems in fact that the frequency of these reactions is rather low in the bulk of the reaction but frequent at the surface of the reactor walls.

The rate of an initiation sequence in volume units can have variable forms but is often proportional to the initiator concentration [*In*]:

$$v = k_i [In] \quad [12.1]$$

#### 12.4.1.2. Catalytic initiation

Although thermal initiation often leads to the formation of radicals and atoms, catalytic initiation leads to the formation of ionic initiation centers. These centers are formed by the reaction of the reactant with the catalyst.

For example, Friedel–Crafts reactions are catalyzed by Lewis acids ( $\text{AlCl}_3$ ,  $\text{BF}_3$ , etc.). The catalysis only acts during the initiation stage:



This reaction is elementary.

#### 12.4.1.3. Photochemical initiation

In this case, the initiation center is produced by the action of light at a suitable wavelength on an appropriate molecule (halogens, halides, ketones, etc.). The reaction is written:



The rate per volume unit of such a reaction is generally proportional to the light intensity and rarely directly depends on the concentration of reactant *A*:

$$v = kI \quad [12.2]$$

Photochemical initiation generally produces excited atoms or free radicals.

If the initiation stage includes several steps, the rate of initiation will be from the last step, strictly speaking, but in the case of a pseudo-steady state initiation mode the initiation rate can be the rate of any of the steps divided by its multiplying coefficient.

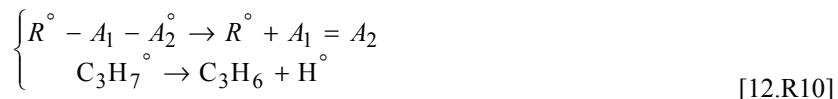
#### **12.4.2. Propagation of a chain reaction**

The propagation reaction often has the function of producing the products of the reaction, or at least to regeneration of the active centers. This is the most frequently repeated stage during the reaction. Propagation reactions are classified in four categories:

– addition reactions:



– decomposition reactions:



– isomerization reactions:



– transfer or substitution reactions:



If the synthesis of the reaction product requires several steps, the propagation rate will be the rate of the last step. If the propagation sequence is in a pseudo-steady state mode, the propagation rate is the rate from any step divided by its multiplying coefficient.

The rate of disappearance of the reactants is the sum of the initiation and propagation rates. This is the propagation phase consuming the vast majority of the reactants (and that also synthesizes the majority of the products). The rate of initiation will therefore be much lower than the rate of propagation, so that

eventually the rate of reactants' disappearance (or product synthesis) is almost equal to the rate of propagation:

$$-\frac{d[A]}{dt} = v_i + v_p \cong v_p \quad [12.3]$$

#### 12.4.3. *Chain breaking*

Breaking reactions lead to the disappearance of active centers. Breaking can be caused by:

- a quadratic reaction between two identical or different active centers:



– the reaction between an active center and impurities that act as inhibitors of the reaction. For free radicals, inhibitors are often with a free pair of electrons, such as O<sub>2</sub>, NO<sub>2</sub>, CO, etc.

Both quadratic reactions and reactions between active centers and impurities occur in the reactor volume and are called “bulk breakings” as opposed to a type of breaking that frequently occurs at the surface of the reactor walls, which concentrates the active centers by adsorption.

#### 12.4.4. *Branching chain reaction*

The branching process is an essential step corresponding to the multiplication of active centers. There are a huge number of branching reactions, such as simple linear branching, for example:



or indirect crossed reactions like:



## 12.5. Kinetic study of straight chain or non-branch chain reactions

The modeling of straight chain reactions aims to determine the influence of the different variables on the average length of the chains and the reaction rate. This type of modeling was developed by Semenov.

### 12.5.1. Mean length of the chains

In the reaction medium and at a given time, chains of variable length coexist. These chains theoretically vary from one to an infinite number of links (even if the number of short chains is by far the largest, as we will see later). The mean length of the chain will be the mean number of links able to generate an initial active center. This is a statistical quantity.

There is no generic way to calculate of the mean length of a chain and therefore no general relation is applicable for any sort of straight chain reaction, whichever structure this has. To calculate the mean length, we will study two specific cases that will allow us to develop the Sochet's method, which is a very generic application.

#### 12.5.1.1. Decomposition reaction by a single active center

Let us first consider the chain reaction of the decomposition of reactant  $A$ . The initiation step generates the active center  $X$  that will be reproduced at every link (even if the link can include several successive intermediate steps).  $\alpha$  is the probability an active center  $X$  will generate another active center by reaction with reactant  $A$ . The probability of this active center disappearing without expanding the chain will therefore be  $\beta$ :

$$\beta = 1 - \alpha \quad [12.4]$$

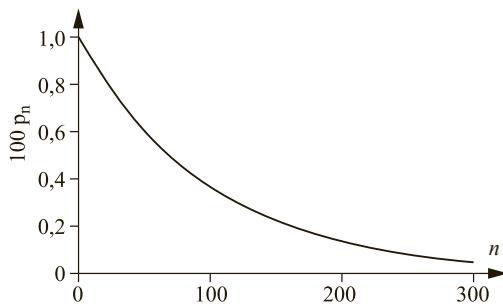
With the help of Table 12.1, let us summarize the active centers generated by the initiating step.

	Formed chains	Number of links $n$	Probability $p$
Initiation	Breaking (term)	0	$(1 - \alpha)$
	$X \rightarrow$ Breaking	1	$\alpha(1 - \alpha)$
	$X \rightarrow X \rightarrow$ term	2	$\alpha^2(1 - \alpha)$
	$X \rightarrow X \rightarrow X \rightarrow$ term	3	$\alpha^3(1 - \alpha)$

**Table 12.1.** Calculation of the mean length of a chain involving only one reactant and one active center

Multiplying each probability by the number of corresponding links and adding the terms obtained, we obtain the total number of links, which is the mean length of the chain:

$$\bar{v} = 1\alpha(1-\alpha) + 2\alpha^2(1-\alpha) + 3\alpha^3(1-\alpha) + \dots + n\alpha^n(1-\alpha) \quad [12.5]$$



**Figure 12.5.** Probability of having chains including  $n$  links with  $\alpha = 0.99$  and  $\bar{v} = 100$

$$\bar{v} = (1-\alpha) \sum_{n=1}^{\infty} (n\alpha^n) = \frac{\alpha}{1-\alpha} = \frac{1}{\beta} - 1 \quad [12.6]$$

In the case of long chains with low  $\beta$ , we have Semenov's relation:

$$\bar{v} \approx \frac{1}{\beta} \quad [12.7]$$

We can therefore see that one active center can lead to the formation of chains with  $\bar{v}$  molecules of product and the disappearance of  $\bar{v}$  molecules of reactant  $A$ . If we plot the curve giving the probability  $p_n = \alpha^n(1-\alpha)$  of forming chains with  $n$  links for a given value  $\alpha$  versus  $n$ , we obtain the curve in Figure 12.5 with  $\bar{v} = 100$  (or  $\alpha = 0.99$ ), which shows that short chains are by far the most probable.

#### 12.5.1.2. Reaction between two reactants with two alternated active centers

We now choose the case where we have two reactants,  $A$  and  $B$ , and two alternate active centers,  $X$  and  $Y$ . The two active centers are called alternates if the one ( $X$ ) results from the reaction of the other ( $Y$ ) with one of the reactants ( $A$  or  $B$ ) and vice versa.  $F$  and  $G$  are the final products obtained according to:



Chain formed	<i>n</i>	No. of <i>F</i>	No. of <i>G</i>	<i>p</i>
Initiation <i>X</i>	Breaking	0	0	$(1 - \alpha_1)$
	$Y \rightarrow$ breaking	0	1	$\alpha_1 (1 - \alpha_2)$
	$Y \rightarrow X \rightarrow$ breaking	1	1	$\alpha_1 \alpha_2 (1 - \alpha_1)$
	$Y \rightarrow X \rightarrow Y \rightarrow$ breaking	1	2	$\alpha_1^2 \alpha_2 (1 - \alpha_2)$
	$Y \rightarrow X \rightarrow Y \rightarrow X \rightarrow$ breaking	2	2	$\alpha_1^2 \alpha_2^2 (1 - \alpha_1)$
	$Y \rightarrow X \rightarrow Y \rightarrow X \rightarrow Y \rightarrow$ breaking	2	3	$\alpha_1^3 \alpha_2^2 (1 - \alpha_2)$

**Table 12.2.** Calculation of the mean chain length with two reagents and two active centers

We see that the example of hydrogen bromide synthesis (see section 12.1) corresponds to the case of *F* and *G* identical to two HBr.

We denote that  $\alpha_1$  is the probability centre *X* will generate active center *Y* by reaction [12.R16] and  $\alpha_2$  is the probability center *Y* will generate active center *X* by reaction [12.R17]. The opposite probabilities are therefore  $1 - \alpha_1 = \beta_1$ ,  $1 - \alpha_2 = \beta_2$ , ... We assume that the initiation reaction results in the formation of active center *X*. As with the previous example, we build up the repertory of the different chains that may form (see Table 12.2).

The formation of a link is obtained when the same active center is regenerated (e.g. between two *X* centers in our example) requiring two elementary steps. The average length of a chain is then:

$$\bar{v} = 1 \cdot [\alpha_1 \alpha_2 (1 - \alpha_1) + \alpha_1^2 \alpha_2 (1 - \alpha_2)] + 2 \cdot [\alpha_1^2 \alpha_2^2 (1 - \alpha_1) + \alpha_1^3 \alpha_2^2 (1 - \alpha_2)] + \dots \quad [12.8]$$

which can be written:

$$\bar{v} = \alpha_1 \alpha_2 [1 - \alpha_1 \alpha_2] + 2\alpha_1^2 \alpha_2^2 [1 - \alpha_1 \alpha_2] + \dots + n\alpha_1^n \alpha_2^n [1 - \alpha_1 \alpha_2] \quad [12.9]$$

or finally:

$$\bar{v} = [1 - \alpha_1 \alpha_2] \sum_{n=1}^{\infty} (n \alpha_1^n \alpha_2^n) = \frac{\alpha_1 \alpha_2}{1 - \alpha_1 \alpha_2} \quad [12.10]$$

We note that this result could have been deduced directly from Table 12.1 by remembering that the probability of passing from  $X$  to the next  $X$  is the product of  $\alpha_1 \alpha_2$ . We can generalize relation [12.7], which gives the mean length of a chain as the reverse of the breaking probability.

The development of Table 12.2 is justified if we want to study the formation of products  $F$  and  $G$  or the disappearance of reagents  $A$  and  $B$ .

In order to count the number of products formed, we have added the number of molecules of  $F$  and  $G$  formed for each chain from an initial center (see Table 12.2). We see that the number of  $G$  molecules formed is equal to the number of links or  $\bar{v}$ . The number of  $F$  molecules formed will be given by:

$$\{F\} = [1 - \alpha_1 \alpha_2] \sum_{n=1}^{\infty} n \alpha_1^n \alpha_2^{n-1} = \frac{\alpha_1}{1 - \alpha_1 \alpha_2} = \frac{\bar{v}}{\alpha_2} \quad [12.11]$$

In the specific case where  $F$  and  $G$  are identical (e.g. in the case of HBr synthesis), there is formation of  $\bar{v} + \frac{\bar{v}}{\alpha_2}$  (HBr) molecules.

### 12.5.2. Expression of the reaction rate

We have seen that the reaction rate could almost be expressed as the propagation rate of the reaction (see relation [12.3]).

We can also express this rate in a pseudo-steady state mode, by writing that whenever the active center is formed by initiation,  $\bar{v}$  numbers of active centers disappear.

We consider the case of a single reactant  $A$  and product  $B$ , and only one active center (as in Table 12.1). Each active center disappears during a reaction and has

destroyed  $\bar{v}$  moles (or  $\bar{v} + 1$  or  $\bar{v} + 2$  moles, depending on the reactions of initiation and breaking or the absence of reactant  $A$ ) of the reactant and produced  $\bar{v}$  moles of the final product. If the chains are long enough we will therefore have:

$$v = \bar{v} \cdot v_i \quad [12.12]$$

In the case of two reactants,  $A$  and  $B$ , two products,  $F$  and  $G$ , and two alternating active centers (as in Table 12.2), an active center formed by initiation involves the destruction of  $\bar{v}$  molecules of  $B$  and  $\bar{v}/\alpha_2$  molecules of  $A$ . These active centers lead to the production of  $\bar{v}$  molecules of  $G$  and  $\bar{v}/\alpha_2$  molecules of  $F$ . The rate of appearance or disappearance of these compounds is expressed with one of the two following relations:

$$v = \bar{v} \cdot v_i \quad [12.13]$$

$$v = \frac{\bar{v}}{\alpha_2} v_i \quad [12.14]$$

These expressions imply that the breaking reactions do not involve reactants and the initiation reaction does not involve a reactant or, if any of these conditions is not met, that the chains are long enough.

We thus have two ways to calculate the reaction rate, either by using relation [12.3] or by using any of the relationships [12.12] [12.13] or [12.14], as appropriate.

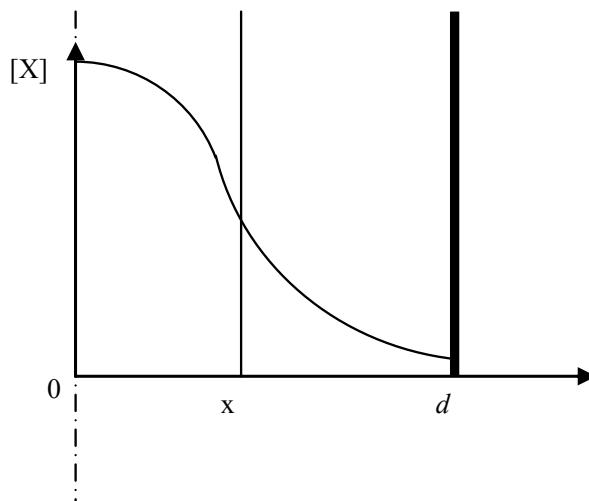
NOTE 12.1.— In all our calculations, we have assumed that the stoichiometric coefficients of the reactants and products were equal in the overall reaction. A basic correction is required if this was not the case.

### 12.5.3. Calculation of the rate and mean length of chains in the reactor

We will now apply expressions [12.12], [12.13] and [12.14] to practical cases.

#### 12.5.3.1. Equation of the rate in a reactor

We will consider a linear chain reaction with a single active center, presenting an even initiation rate  $v_i$  in the volume of the reactor, first order breaking in the volume in relation to the active centers, and breaking on the external walls.



**Figure 12.6.** Semi-reactors between two planes

We choose a very simple closed reactor made of two plane walls of area  $S$  that are  $2d$  apart (see Figure 12.6) and we assume that the breaking reaction is occurring on the walls alone. We can apply the intermediate  $X$  balance in a constant volume for the point  $x$  of the  $x$ -axis, to express the variation in the active center concentration at the  $x$ -axis point  $x$  between times  $t$  and  $t+dt$ , with  $f_r$  being the breaking reaction rate factor assumed to be first order with respect to the active center:

$$\frac{\partial[X]}{\partial t} = v_i + f_r [X] + D \frac{\partial^2[X]}{\partial x^2} \quad [12.15]$$

Integrating this equation would result in determining the concentration of active centers at point  $x$  of the reactor for a time  $t$ . Integrating this concentration in the whole reactor would lead to the total quantity of active centers  $\{X\}$  in the reactor as well as their average concentration  $\overline{[X]}$ , given by:

$$\overline{[X]} = \frac{\{X\}}{d} \quad [12.16]$$

We define the lifetime of an intermediate involved as a reactant in a reaction as the ratio of the concentration of this intermediate over the reactivity of the step,  $\rho$ :

$$\Delta\tau_p = \frac{[X]}{\varphi_p} = \frac{[X]}{f_p[X]^{\beta_p}} \quad [12.17]$$

This latter relative quantity for the propagation step  $p$  therefore allows us to calculate the reaction rate by:

$$v = \frac{\overline{[X]}}{\Delta\tau_p} \quad [12.18]$$

The mean length of the chains is calculated using equation [12.12].

#### 12.5.3.2. Chains breaking on the reactor walls

Equation [12.15] is defined by:

$$\frac{\partial[X]}{\partial t} = v_i + D \frac{\partial^2[X]}{\partial x^2} \quad [12.19]$$

We first look at the pseudo-steady state mode. In our case, the reaction happens within a constant volume. The pseudo-steady state mode becomes a quasi-steady state mode. This quasi-steadiness is translated using [12.19] by:

$$v_i = -D \frac{d^2[X]}{dx^2} \quad [12.20]$$

By integrating between  $x = 0$  with  $(dX/dx)_0 = 0$  and  $x = \pm d/2$  with  $[X]_{\pm d/2} = 0$ , we have:

$$[X] = \frac{v_i}{2D} \left( \frac{d^2}{4} - x^2 \right) \quad [12.21]$$

This means that we have a parabolic distribution of the active centers in the reactor, perpendicularly to its symmetric plane. The total number  $\{X\}$  of active centers is therefore:

$$\{X\} = \int_{-d/2}^{+d/2} [X] dx = \frac{v_i d^3}{12D} \quad [12.22]$$

The average concentration of an active center will be given using equation [12.16]:

$$\overline{[X]} = \frac{v_i d^2}{12D} \quad [12.23]$$

After [12.17], the rate for a pseudo-steady state mode is:

$$v = \frac{v_i d^2}{12D\Delta\tau_p} \quad [12.24]$$

The diffusion coefficient of gas as a function of the pressure, the average speed of particles and the free mean path under atmospheric pressure are related by:

$$D = \frac{\lambda_0 \bar{c}}{3P} \quad [12.25]$$

Otherwise, the lifetime  $\Delta\tau_p$  of an active center is about the time interval between two collisions (ratio of the average free path  $\lambda$  at the average speed of displacement  $\bar{c}$ ) multiplied by the average number of collisions  $q$  that are required for an active center to react, so:

$$\Delta\tau_p = \frac{q\lambda}{\bar{c}} = \frac{q\lambda_0}{P\bar{c}} \quad [12.26]$$

The reaction rate therefore becomes:

$$v = \frac{v_i d^2 P^2}{4q\lambda_0^2} \quad [12.27]$$

and the mean chain length according to [12.12] is:

$$\bar{v} = \frac{d^2}{12D\Delta\tau_p} = \frac{d^2 P^2}{4q\lambda_0^2} \quad [12.28]$$

The reaction rate and the mean chain length are therefore both proportional to the square of the pressure and the width  $d$  of the reactor.

### 12.5.3.3. Chains breaking in the bulk and the walls

We must now resolve equation [12.15]. At this point, we will consider the pseudo-steady state mode, which is defined by:

$$v_i = -f_r [X] - D \frac{d^2[X]}{dt^2} \quad [12.29]$$

The integration of this expression, if considering the same limiting conditions as in section 12.5.3.2, gives:

$$[X] = \frac{v_i}{f_r} \left[ 1 - \frac{\cosh\left(x\sqrt{\frac{f_r}{D}}\right)}{\cosh\left(\frac{d}{2}\sqrt{\frac{f_r}{D}}\right)} \right] \quad [12.30]$$

After this integration over the width of the reactor, relation [12.16] leads to the average concentration of active centers:

$$\overline{[X]} = \frac{v_i}{f_r} \left[ 1 - \frac{\tanh\left(\frac{d}{2}\sqrt{\frac{f_r}{D}}\right)}{\frac{d}{2}\sqrt{\frac{f_r}{D}}} \right] \quad [12.31]$$

Equation [12.18] allows us to calculate the volumic rate:

$$v = \frac{v_i}{f_r \Delta \tau_p} \left[ 1 - \frac{\tanh\left(\frac{d}{2}\sqrt{\frac{f_r}{D}}\right)}{\frac{d}{2}\sqrt{\frac{f_r}{D}}} \right] \quad [12.32]$$

Equation [12.12] gives the mean length of the chains:

$$\bar{v} = \frac{1}{f_r \Delta \tau_p} \left[ 1 - \frac{\tanh\left(\frac{d}{2}\sqrt{\frac{f_r}{D}}\right)}{\frac{d}{2}\sqrt{\frac{f_r}{D}}} \right] \quad [12.33]$$

We can simplify the above equations by taking the limited development of the hyperbolic tangent and using the first three terms of the development:

$$1 - \frac{\tanh(u)}{u} = \frac{u^2}{3} - \frac{2u^4}{15} \quad [12.34]$$

Therefore [12.31] becomes:

$$\overline{[X]} = \frac{v_i d^2}{12D} \left[ 1 - \frac{f_r d^2}{10D} \right] \quad [12.35]$$

According to [12.32], the rate becomes:

$$v = \frac{v_i d^2}{12D\Delta\tau_p} \left[ 1 - \frac{f_r d^2}{10D} \right] \quad [12.36]$$

If  $\beta$  is the breaking probability, using [12.17] we have:

$$f_r \Delta\tau_p = \frac{v_r}{v_r + v_p} = \beta \quad [12.37]$$

Using [12.24], [12.26], [12.34] and [12.37], the rate becomes:

$$v = \frac{v_i d^2 P^2}{4\lambda_0^2 q} \left[ 1 - \frac{3\beta P^2 d^2}{10\lambda_0^2 q} \right] \quad [12.38]$$

According to [12.33], the mean chain length is:

$$\bar{v} = \frac{d^2}{12D\Delta\tau_p} \left[ 1 - \frac{f_r d^2}{10D} \right] \quad [12.39]$$

which, using [12.28] and [12.29], we can transform into:

$$\bar{v} = \frac{d^2 P^2}{4\lambda_0^2 q} \left[ 1 - \frac{3\beta P^2 d^2}{10\lambda_0^2 q} \right] \quad [12.40]$$

Hence the reaction rate and the average length of the chains are complex functions of the pressure within the reaction medium and the dimensions of the reactor.

NOTE 12.2.– Two limited cases can be deduced from these expressions. If the breaking of chains at the wall is negligible, this is the same as having  $D = 0$  in expression [12.29] and the rate is therefore:

$$v = \frac{v_i}{f_r \Delta \tau_p} = \frac{v_i}{\beta} \quad [12.41]$$

On the other hand, if it is breaking within the mass that is negligible, we have  $f_r = 0$  in expression [12.29] and the rate becomes:

$$v = \frac{v_i d^2}{12 D \Delta \tau_p} = \frac{v_i d^2 P^2}{4 \lambda_0^2 q} \quad [12.42]$$

Type of diffusion	Laplacian operator
In the direction of Ox	$\frac{d^2[A]}{dx^2}$
Radial in a sphere	$\frac{d^2[A]}{dr^2} + \frac{2}{r} \frac{d[A]}{dr}$
Radial in a cylinder	$\frac{d^2[A]}{dr^2} + \frac{1}{r} \frac{d[A]}{dr}$

**Table 12.3.** Expression of the Laplacian operator according to the coordinates chosen

NOTE 12.3.– We assumed that the reactor was limited to two planes, but calculations can be done as easily for a cylindrical or spherical reactor by using equations [12.20] and [12.29] and adapting the Laplacian to the shape of the reactor (see Table 12.3). The expressions obtained have the same form with different numerical coefficients, especially the variations of rate or length of chains as a function of the pressure when the reactor's dimensions (radius) remain the same.

#### 12.5.4. Variation of reaction rate with temperature

Using expression [12.42] again, we can admit that the initiation step is often an elementary step and therefore obeys Arrhenius' law with the temperature and activation energy  $E_a$ , therefore:

$$v_i = v_i^0 \exp\left(-\frac{E_a}{RT}\right) \quad [12.43]$$

With regards to the average number  $q$  of collisions required for an active center to react, its reverse  $1/q$  measures the probability that a reaction will occur at one center for each collision. The kinetic theory of gases shows that this probability must increase with temperature following Arrhenius' law with an activation energy  $B$ , which is nearly the activation energy of the propagation reaction, and therefore:

$$\frac{1}{q} = a \exp\left(-\frac{B}{RT}\right) \quad [12.44]$$

According to the kinetic theory of gases, the average free distribution  $\lambda_0$  varies proportionally to  $T^{3/2}$  and therefore this variation is negligible in comparison to the exponentials.

By incorporating [12.43] and [12.44] into [12.41], we get:

$$v = \frac{v_i^0 ad^2 P^2}{4\lambda_0^2} \exp\left(-\frac{E + B}{RT}\right) \quad [12.45]$$

The reaction rate of non-branching-chain reactions therefore follows Arrhenius' law; the activation energy is the sum of the activation energies of the initiation and propagation steps.

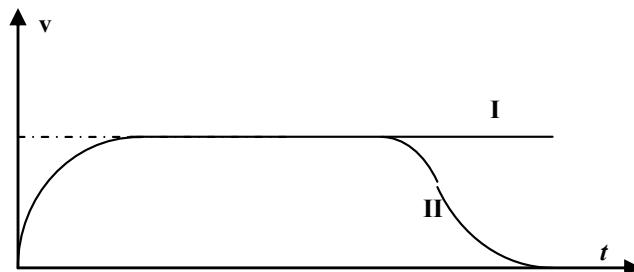
#### 12.5.5. Permanency of the pseudo-steady state mode and reactant consumption

We have admitted that everything preceding the pseudo-steady state mode was permanently established. It is obvious that at the start of the reaction, there are no reactive centers and therefore the reaction occurs in a transient manner. This is

obtained for the solutions to equation [12.15] or its specific cases. In practice, we can see that the pseudo-steady state is quickly reached. We can experimentally determine at which instant the rate is independent of time and therefore see the appearance of the pseudo-steady state mode.

All the previous expressions were established by keeping the initiation rate independent of time (by integration of equations [12.20], [12.22] and [12.29]). This is a correct approximation for the first instance of the reaction and before reaching 10% of its full extent. We have also worked with constant reactant concentrations, as shown in the integration of equation [12.22] that was done by keeping the breaking rate factor constant. The decreasing level of reactants is translated by a decrease in the concentration of active centers, which is also the breaking of the pseudo-steady state mode. This leads to the breaking rate decreasing rather than remaining independent of time, hence replacing curve I by curve II in Figure 12.7.

Moreover, if we examine the rate in expression [12.42], we can see that the rate varies with the squared value of the pressure. In the gas phase of a sealed reactor, this pressure can be a function of the reaction extent, which does not remain constant with time.

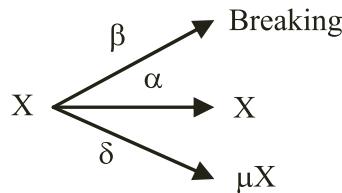


**Figure 12.7.** Rate–time curve: I) without consumption of reactants; and II) with consumption of reactants

## 12.6. Kinetic study of chain reactions with direct branching

Branching chain reactions are distinct from linear chain reactions because of the presence of another type of reaction step: the branching step. Hence, for an active center  $X$  there are three reaction possibilities, which are illustrated in Figure 12.8 with their corresponding  $\alpha$ ,  $\beta$  and  $\delta$  probabilities for the propagation, breaking, and branching steps respectively:

$$\alpha + \beta + \delta = 1 \quad [12.46]$$



**Figure 12.8.** Reaction possibilities of an active center in a chain reaction with direct branching

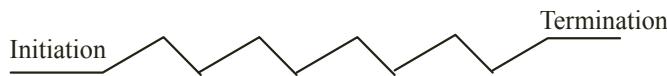
The probability a chain will not break is  $(1 - \beta)$ . The branching probability can be expressed as:

$$\delta = (1 - \beta) \delta^* \quad [4.47]$$

Relation [12.45] expresses the branching probability, which is the product of the probability the chain will not break and the probability branching will occur preferentially instead of propagation. In other words,  $\delta^*$  is the probability of branching for a breaking probability equal to zero ( $\beta = 0$ ).  $\delta^*$  is called the probability of branching with a chain link since if  $\delta^* = 1$  we have continuous branching occurring on every link.

#### 12.6.1. Simplified representation of reactions with direct branching

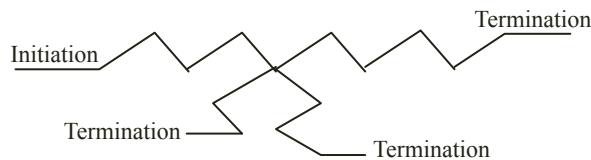
If we represent a link in the chain by a dash, a linear chain reaction would be represented by broken line including as many dashes as links, hence  $\bar{v}$  is the number of lines as shown in Figure 12.9.



**Figure 12.9.** Diagram of a linear chain reaction

With the same symbols, a branch chain reaction will then present several broken lines, as from time to time an active center can give rise to another chain, as shown in Figure 12.10.

If the branching occurs on every link, the reaction is called continued branching, as happens with hydrogen combustion, for example.



**Figure 12.10.** Example of a chain reaction with branching

The general diagram can be simplified if we notice that one active center can disappear by a chain breaking reaction or by giving rise to an average number  $\mu_m$  of active centers. Here, we have the diagram in Figure 12.11.



**Figure 12.11.** Simplified diagram of a chain reaction with direct branching

Every branch chain reaction is therefore a continuous branching ( $\delta^* = 1$ ) for which the number of active centers is multiplied at every link by  $\mu_m$ . The probability of branching is therefore written by taking [12.47] into account:

$$\delta = (1 - \beta) \quad [12.48]$$

The mean number of active centers formed from a single active center is calculated from the probabilities of other, different elements. For example, if we consider the reaction as in Figure 12.5, we have:

$$\mu_m = 1 \cdot p_{X \rightarrow X} + \mu \cdot p_{X \rightarrow \mu X} \quad [12.49]$$

In fact, this result assumes that the branching  $X \rightarrow \mu X$  is done in one elementary step. Generally, branching results from several elementary steps, as in the example of hydrogen combustion, so that it is possible to obtain 1, 2...  $\mu - 1$ , or  $\mu$  numbers of active centers. For chemical reactions,  $\mu$  is lower than or equal to three. Generally, we have:

$$\mu_m = 1 \cdot p_{X \rightarrow X} + 2 \cdot p_{X \rightarrow 2X} + \dots + \mu \cdot p_{X \rightarrow \mu X} = \sum_1^{\infty} i p_{X \rightarrow iX} \quad [12.50]$$

A more concise form of the branching chain reaction is obtained by gathering the branching and breaking steps:



where  $\alpha'$  is the global multiplication factor of active centers. This is the average number of active centers formed by one active center.

This global factor is given by:

$$\alpha' = \mu_m (1 - \beta) \quad [12.51]$$

If the branching is continuous, we get:

$$\mu_m = \mu \quad [12.52]$$

and so:

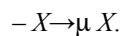
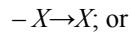
$$\alpha' = \mu (1 - \beta) \quad [12.53]$$

If the branching is both continuous and permanent ( $\mu_m = \mu$  and  $\beta = 0$ ), we have:

$$\alpha' = \mu \quad [12.54]$$

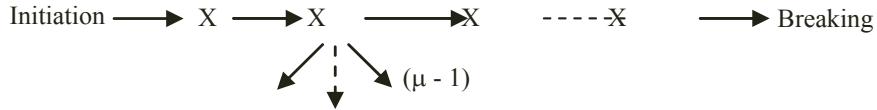
### 12.6.2. Mean chain lengths: condition of the appearance of a pseudo-steady state

Here, we can consider the reaction in Figure 12.12. In the primary chain (horizontal), between the initiation and breaking of the active center, two events can occur:



given a probability equal to  $1 - \beta$ . This defines the length of the primary chain:

$$\bar{v} = \frac{(1 - \beta)}{\beta} \quad [12.55]$$



**Figure 12.12.** Generic diagram of a chain reaction with direct branching

For each active center  $X$ , except the one that breaks  $(\mu - 1)$ , the number of secondary chains can develop with a probability  $\delta^*$ . Since we have  $\bar{v}$  active centers of this type,  $(\mu - 1) \delta^* \bar{v}$  secondary chains can be formed.

Each secondary chain that is  $\bar{v}$  long leads to the formation of  $(\mu - 1) \delta^* \bar{v}$  other chains that are  $\bar{v}$  long. The process can be repeated for all these chains. The average length is therefore:

$$\begin{aligned} \bar{v}' = & \bar{v} + \left[ (\mu - 1) \bar{v} \delta^* \right] \bar{v} + \left[ (\mu - 1) \bar{v} \delta^* \right]^2 \bar{v} + \dots \\ & + \left[ (\mu - 1) \bar{v} \delta^* \right]^n \bar{v} + \dots \end{aligned} \quad [12.56]$$

or:

$$\bar{v}' = \frac{\bar{v}}{1 - (\mu - 1) \bar{v} \delta^*} \quad [12.57]$$

For the series defined by the convergence of relation [12.57] we need to have:

$$(\mu - 1) \bar{v} \delta^* < 1 \quad [12.58]$$

We notice that the mean length of the main chain is  $(1 - \beta)/\beta$  and not  $1/\beta$ , since this primary chain is made of links originating from the simple propagation and branching. Thus by using [12.47] and [12.55], the convergence condition is expressed by:

$$(\mu - 1) \delta < \beta \quad [12.59]$$

This limit will set the threshold at which the pseudo-steady state mode is reachable (see section 15.4).

The mean length of the chain,  $\bar{v}'$ , is therefore meaningful if condition [12.59] is met.

### 12.6.3. Example of a chain reaction with both linear branching and breaking in the bulk

Here, we consider the example of a branching chain reaction with an initiation rate  $v_i$ , a linear branching rate  $(\mu_m - 1)f_{ra}[X]$  and a linear breaking in the bulk of speed  $f_r[X]$ .

The kinetic mechanism with reactant  $A$  and product  $P$  is the following:



The change in the concentration of active centers is written:

$$\frac{d[X]}{dt} = v_i + \{(\mu_m - 1)f_{ra} - f_r\}[X] \quad [12.60]$$

If we notice that  $f_r\Delta\tau = \delta$  and  $f_{ra}\Delta\tau = \beta$ , this equation becomes:

$$\frac{d[X]}{dt} = v_i + \left\{ \frac{(\mu_m - 1)\delta - \beta}{\Delta\tau} \right\} [X] \quad [12.61]$$

Using [12.51] and considering [12.53], we obtain:

$$\frac{d[X]}{dt} = v_i + \left\{ \frac{\alpha' - 1}{\Delta\tau} \right\} [X] \quad [12.62]$$

The corresponding equations for [12.60], [12.61] and [12.62] can be written as:

$$\frac{d[X]}{dt} = v_i + \varphi[X] \quad [12.63]$$

where  $\varphi$  is the branching factor. The term  $\varphi$  is the difference between two positive terms, hence it may have a positive or negative value. Depending on the case, it may or may not be possible to consider a pseudo-steady state mode, hence the critical value is  $\varphi = 0$ .

We will now examine the solution obtained when  $\varphi$  is negative. The solution for a positive branching factor related to non-pseudo-steady state modes will be described in Chapter 15, which is dedicated to such modes.

The solution of equation [12.63] is:

$$[X] = \frac{v_i}{|\varphi|} \left\{ 1 - \exp(-|\varphi|t) \right\} \quad [12.64]$$

The concentration of active centers  $X$  reaches a pseudo-steady state mode obtained using [12.64] with the time tending toward infinity:

$$[X]_{st} = \frac{v_i}{|\varphi|} \quad [12.65]$$

Using equation [12.18], for the volumic rate of the reaction we calculate:

$$v = \frac{[X]}{\Delta\tau_p} = \frac{v_i}{|\varphi|\Delta\tau_p} \left\{ 1 - \exp(-|\varphi|t) \right\} \quad [12.66]$$

thereby the concentration of product  $P$  formed by the branching step is:

$$[P] = \frac{v_i}{|\varphi|\Delta\tau_p} \left\{ t + \frac{\exp(-|\varphi|t)}{|\varphi|} - \frac{1}{|\varphi|} \right\} \quad [12.67]$$

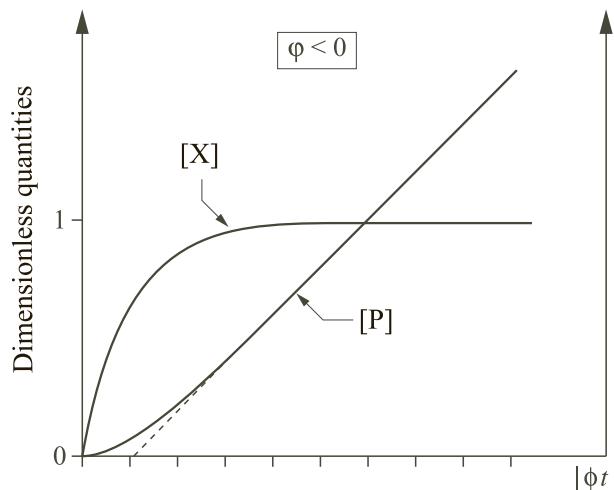
To obtain a suitable graphic representation, we use dimensionless measures denoted  $X$  and  $P$ . The dimensionless concentration of the active centers will be:

$$[X] = \frac{[X]}{v_i / |\varphi|} = \left\{ 1 - \exp(-|\varphi|t) \right\} \quad [12.68]$$

Figure 12.13 gives a representation of dimensionless time,  $|\phi| t$ , as a function of the dimensionless concentrations of the active centers and the product formed. We notice that the pseudo-steady status of the active center (horizontal asymptote) and that the dimensionless rate does not depend on the time (oblique asymptote of the production curve  $P$ ). This result is achieved by using a constant concentration of reactants. In a closed medium, the consumption of reactants limits the production of  $P$ .

The dimensionless concentration of the product formed will be:

$$[P] = \frac{|\phi|^2 [F] \tau_p}{v_i} = |\phi| t + \exp(-|\phi| t) - 1 \quad [12.69]$$

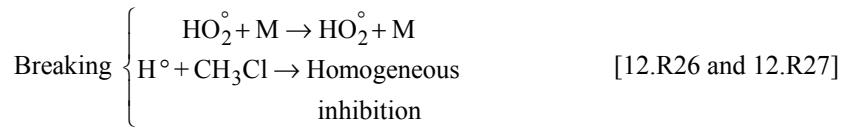
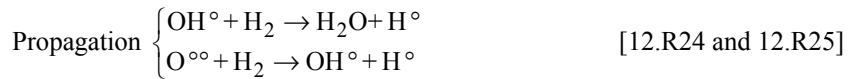


**Figure 12.13.** Solution with a negative branch factor

#### 12.6.4. Example of the calculation of the measures related to a branching chain reaction

To set an example, we will calculate the value of the different measures related to a branching chain reaction during hydrogen combustion. To do so, we will consider a simplified diagram inspired by James *et al.* for the inhibition of hydrogen combustion by methyl-chloride (reaction steps [12.R21] to [12.R27]):





We write the balance of the different intermediate species, ignoring the hydrogen atoms' intermediates for which the pseudo-steadiness is *a priori* not admitted (those resulting from the initiation step):

$$\frac{d[\text{H}]}{dt} = 2k_{18}[\text{H}_2] - k_{19}[\text{O}_2][\text{H}] + k_{21}[\text{OH}][\text{H}_2] + k_{22}[\text{O}^\circ][\text{H}_2] - k_{24}[\text{CH}_3\text{Cl}][\text{H}] \quad [12.70]$$

$$\frac{d[\text{O}^{\circ\circ}]}{dt} = k_{20}[\text{HO}_2^\circ] - k_{22}[\text{O}^\circ][\text{H}_2] = 0 \quad [12.71]$$

$$\frac{d[\text{HO}_2^\circ]}{dt} = k_{19}[\text{O}_2][\text{H}^\circ] - k_{20}[\text{HO}_2^\circ] - k_{23}[\text{M}][\text{HO}_2^\circ] = 0 \quad [12.72]$$

$$\frac{d[\text{OH}^\circ]}{dt} = k_{20}[\text{HO}_2^\circ] - k_{21}[\text{H}_2][\text{OH}^\circ] + k_{22}[\text{H}_2][\text{O}^{\circ\circ}] = 0 \quad [12.73]$$

From equations [12.70] to [12.73], we calculate:

$$\begin{aligned} \frac{d[\text{H}]}{dt} &= 2k_{18}[\text{H}_2] \\ &+ \left\{ k_{19}[\text{O}_2] \left( \frac{3k_{20}}{k_{20} + k_{23}[\text{M}]} - 1 \right) - k_{24}[\text{CH}_3\text{Cl}] \right\} [\text{H}] \end{aligned} \quad [12.74]$$

By comparing with the relation defining the branching factor [12.63], we get:

$$\varphi = 2 \left\{ k_{19} [\text{O}_2] \left( \frac{3k_{20}}{k_{20} + k_{23}[M]} - 1 \right) - k_{24} [\text{CH}_3\text{Cl}] \right\} \quad [12.75]$$

The average number of active centers formed from one active center is calculated using [12.50]:

$$\mu_m = \frac{3k_{20}}{k_{20} + k_{23}[M]} \quad [12.76]$$

The probability of the chain reaction not terminating is  $(1 - \beta)$ , as:

$$1 - \beta = \frac{k_{19} [\text{O}_2]}{k_{19} [\text{O}_2] + k_{24} [\text{CH}_3\text{Cl}]} \quad [12.77]$$

According to definition [12.17], the lifetime of the propagation of an active center is:

$$\Delta\tau_p = \frac{1}{k_{19} [\text{O}_2] + k_{24} [\text{CH}_3\text{Cl}]} \quad [12.78]$$

It is possible that the branching is continuous ( $\delta^* = 1$ ). According to [12.51], the global multiplication factor of the active centers is:

$$\alpha' = (1 - \beta)\mu_m = \frac{3k_{20}k_{19} [\text{O}_2]}{\left( k_{19} [\text{O}_2] + k_{24} [\text{CH}_3\text{Cl}] \right) \left( k_{20} + k_{23}[M] \right)} \quad [12.79]$$

The mean length of a chain is calculated from [12.57], as:

$$\bar{v}' = \frac{\bar{v}}{1 - (\mu_m - 1)\bar{v}} \quad [12.80]$$

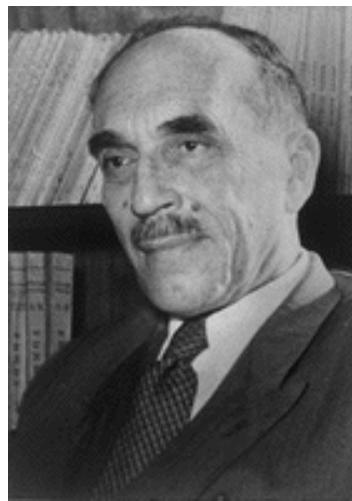
The length of the corresponding linear chain is given by [12.7]; hence the mean chain length is

$$\bar{v}' = \frac{\{k_{19}[O_2] + k_{24}[CH_3Cl]\}\{k_{20} + k_{23}[M]\}}{\{k_{20} + k_{23}[M]\} - \{k_{19}[O_2] + k_{24}[CH_3Cl]\}\{2k_{20} - k_{23}[M]\}} \quad [12.81]$$

We will return to branching chain reactions in a non-pseudo-steady state mode with  $\varphi > 0$ , in Chapter 15, in order to explain explosions of gaseous media.

### 12.7. Semenov and the kinetics of chain reactions

Semenov (see Figure 12.14) carried out an exhaustive analysis of the application of chain theory to various reactions, especially combustion processes. He proposed the theory of branching, discussed in this chapter, which led to an improved understanding of the phenomena associated with the induction periods of oxidation processes.



**Figure 12.14.** Nikolai Semenov (1896-1986) won the Nobel Prize for chemistry in 1956



## Chapter 13

# Catalysis and Catalyzed Reactions

Catalysis is the acceleration of a reaction by the addition of a component: the catalyst.

To catalyze a reaction is to change its mechanism in order reduce its energy requirements. In the simplest case of a reaction with a single rate-determining step, to catalyze is to replace this potentially slow step with another with a lower activation energy that is therefore potentially faster.

There are two areas of catalysis based on whether the catalyst belongs to the same phase as the main constituents or a separate phase (usually a solid). The first case is essentially homogeneous catalysis in the liquid phase; the second is heterogeneous catalysis between gas reactions catalyzed by a solid.

At the end of a reaction, the catalyst is chemically reconstituted so it is the same as it was at the beginning of the reaction. This property implies that catalysis does not change the thermodynamic state functions, such as enthalpy, entropy and Gibbs free energy of the reaction, as well as the equilibrium constant.

NOTE 13.1.– At the end of a reaction, in the case of heterogeneous catalysis the catalyst may have significant textural differences with its initial state.

Even though the catalyst is not consumed in the reaction, its quantity often plays an important role in the rate of the catalyzed reaction.

### 13.1. Homogenous catalysis

The most common homogeneous catalysis reactions involve catalysis in solution. A very generic mechanism of homogeneous catalysis has been proposed by Herzfeld.

Consider a reaction of the following form:



Catalyzed by a substance  $C$ , Herzfeld has proposed the following mechanism:



We see that the sum of the three steps [13.R1a], [13.R1b] and [13.R1c] gives the overall reaction.

If the reaction state is determined by step [13.R1c], the first two steps are in equilibrium and therefore:

$$[X_2] = \frac{K_1[A][C]}{[X_1]} \text{ and } [X_3] = \frac{K_2[X_1][B]}{[E]} \quad [13.1]$$

Hence the speed is:

$$\frac{d[F]}{dt} = k_3[X_2][X_3] = k_3 \frac{K_1 K_2 [B][C]}{[E]} \quad [13.2]$$

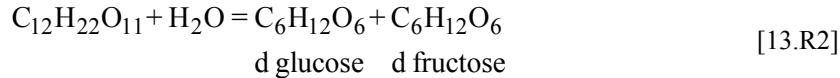
The rate is first order with respect to a reactant and the catalyst. We notice an order that is  $-1$  with respect to a product.

With a pseudo-steady state in general it is easy to show that the three steps have the same reactivity and the volumic rate of disappearance of reactant  $A$ , which is given by  $\phi_1$  is far from the equilibrium:

$$-\frac{d[A]}{dt} = k_1[A][C] \quad [13.3]$$

### 13.1.1. Specific acid–base catalysis by $H^+$ and $OH^-$ ions

An entire family of reactions is catalyzed by water ions. We will explore the catalysis of  $H^+$  and  $OH^-$  in the case of the hydrolysis of sucrose into *d*-glucose and *d*-fructose, which is written:



It was found that the rate of this reaction was proportional to the concentration of protons and sucrose as:

$$v = k_H |H_3O^+| [\text{sucrose}] \quad [13.4]$$

Comparing this with [13.3], we see that Herzfeld's mechanism may be used.

We define an apparent rate coefficient  $k$ , so that the rate is written:

$$v = k \cdot [\text{sucrose}] \quad [13.5]$$

In most cases, the reaction can be catalyzed by both protons and  $OH^-$  ions. In many cases, the reaction also occurs with an appreciable rate in the absence of the catalyst so that the apparent rate coefficient is the sum of three terms, as defined in:

$$k = k_0 + k_H |H_3O^+| + k_{OH} |OH^-| \quad [13.6]$$

With protonic solvents, the concentrations of protons and hydroxide ions are not independent. If occurring in water solution, for example, we must respect the ionic product of water:

$$|H_3O^+| |OH^-| = K_e \quad [13.7]$$

so that the apparent rate coefficient takes the form:

$$k = k_0 + k_H \left|H_3O^+\right| + k_{OH} \frac{K_e}{\left|H_3O^+\right|} \quad [13.8]$$

If from [13.8] we plot the logarithm of the apparent rate coefficient as a function of pH, we obtain the curve in Figure 13.1.

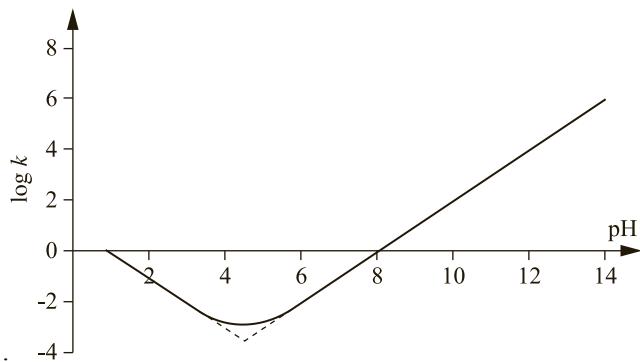


Figure 13.1. Variation of the reaction rate coefficient with pH

Both slightly linear parts of the curve cross each other at a point on the x-axis:

$$\left|H_3O^+\right|_{min} = \sqrt{\frac{K_e k_{OH}}{k_H}} \quad [13.9]$$

or:

$$pH_{min} = \frac{1}{2} \left( pK_e - \log \frac{k_{OH}}{k_H} \right) \quad [13.10]$$

These two parts form straight lines with slopes of +1 and -1.

If  $k_{OH}$  is very low, we have a specific catalysis  $H^+$ , and the left arm of the curve is absent. On the other hand, if  $k_H$  is low, we have a specific catalysis  $OH^-$  and the right arm of the curve is absent.

In any case, we always try to be as far as possible from the lowest point of the curve, which may require us to displace the minimum by changing the protonic

solvent. This is because it is shown from expressions [13.9] and [13.10] that the ionic product of the solvent ( $K_e$ ) is involved with the position of this minimum.

### 13.1.2. Generic acid–base catalysis

If we consider the more generic Bronstedt's definition of a base and acid, protons and hydroxide ions do not have specific properties in comparison to other bases. For example, with an acid  $AH$  and its conjugated base  $A^-$ , with generic acid–base catalysis, the apparent rate coefficient will have the form:

$$k = k_0 + k_H \left| H_3O^+ \right| + k_{AH} \left| AH \right| + k_{OH} \left| OH^- \right| + k_A \left| A^- \right| \quad [13.11]$$

acid form	base form
-----------	-----------

On the other hand, if we use base  $B$  so that:



the reaction rate coefficient will be written:

$$k = k_0 + k_H \left| H_3O^+ \right| + k_{BH} \left| BH \right| + k_{OH} \left| OH^- \right| + k_B \left| B \right| \quad [13.12]$$

acid form	base form
-----------	-----------

To determine whether catalysis is specific or generic, we undertake catalysis in the presence of a buffer solution, adjusting the pH of the solution according to the Henderson's equation:

$$\left| H_3O^+ \right| = K_a \frac{\left| AH \right|}{\left| A^- \right|} \quad [13.13]$$

The pH is fixed and the experiment is carried out using different concentrations of  $AH$  and  $A^-$  respecting the ratio in [13.13]. We then have two cases:

- if the reaction rate does not vary, this means that  $A^-$  and  $AH$  concentrations do not influence the reaction and the catalysis is specific to the protons and hydroxide ions;
- if the rate varies, this means that all the species influence the rate and that we are dealing with generic acid–base catalysis.

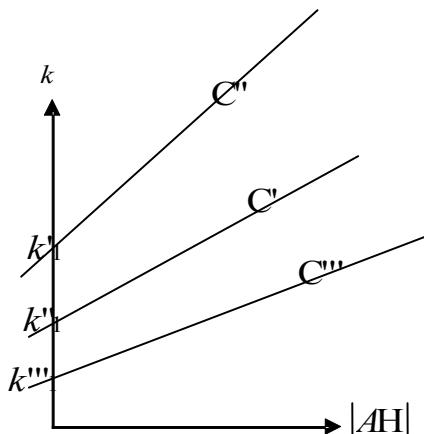
In the latter case, we wish to determine the different rate coefficients  $k_0$ ,  $k_{AH}$ ,  $k_H$ ,  $k_{OH}$  and  $k_A$ .

To do this, we can write equation [13.11] so that:

$$k = k_1 + |AH| (k_{AH} + k_A q') \quad [13.14]$$

and having:

$$k_1 = k_0 + k_H |H_3O^+| + k_{OH} |OH^-| \text{ and } q' = \frac{|A^-|}{|AH|} \quad [13.15]$$



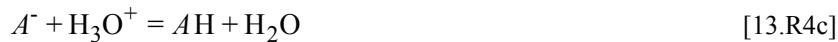
**Figure 13.2.** Determination of the different rate coefficients

We carry out three experiments using the three values  $q'$ ,  $q''$  and  $q'''$  of the concentrations ratio and report the value of the constant  $k$  calculated as a function of the activity of  $AH$ . The three straight lines (see Figure 13.2)  $C'$ ,  $C''$  and  $C'''$  allow us to calculate three different values for  $k'_1$ ,  $k''_1$  and  $k'''_1$  of  $k_1$ , which are the intercept values, and the slope of the curves are the constants  $k_{AH}$  and  $k_A$ .

Mechanisms like the Herzfeld type can account for the different types of generic acid-base catalysis that are possible. For example, in the case of acid catalysis by an acid  $AH$  during the hydrolysis product  $SH$  leading to an isomer  $P$ :



Herzfeld's mechanism can be written using the following three steps:



NOTE 13.2.— In all the experiments involving ions in solution, it is recommended keeping a ionic strength of the medium constant between the different experiments. To do this, we systematically add a large amount of strong acid salt and strong base in the medium (potassium chloride, for example) so that the total ion concentration remains almost unchanged between experiments.

### 13.1.3. Catalysis by Lewis acids

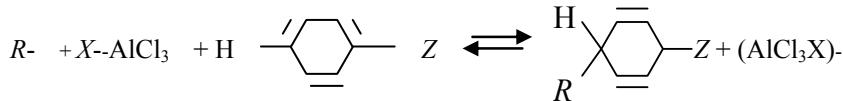
As we did by generalizing the specific acid–base catalysis specific to Bronstedt's generic acid–base catalysis, we also have generic Lewis acid–base catalysis involving electron pairs. We are reminded that Lewis has generalized the acid–base concept by noticing that a Bronstedt base was fixing a hydrogen ion through a pair of available electrons. For Lewis, a base is a molecule able to accept an electron pair and an acid has an electron pair available. This new definition allows us to consider generic catalytic acid–base reactions in a non-protonic medium.

As an example involving Lewis acid–base catalysis, we can cite the case of Friedel–Crafts alkylation of benzene hydrocarbons catalyzed by aluminum chloride, which is a Lewis acid. A four-step mechanism reports the results:

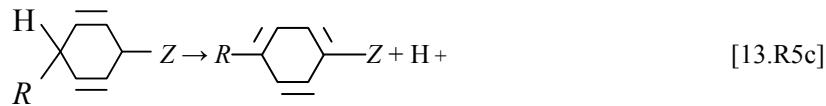
— The first step involves the addition of alkyl halide to aluminum chloride, which is a Lewis acid. Giving the complex polarized addition, this step can be written:



— Electrophilic attack of the benzene ring causes alkylation:



– This is followed by a deprotonation:



– Finally there is regeneration of the catalyst:



The global reaction is:



We adopt the pseudo-steady state mode with infinite rate coefficients for the two reverse reactions of the first step, which is therefore constantly at equilibrium, the other three steps being determining.

According to the equilibrium of the first step, we have:

$$K_1 = \frac{[RX \text{ AlCl}_3]}{[RX][\text{AlCl}_3]} \quad [13.16]$$

The three other steps having the same rate, we can write:

$$r = \frac{\phi_2 E_2}{1} = k_2 [RX \text{ AlCl}_3] [\text{C}_6\text{H}_5Z] \frac{V}{n_0} \quad [13.17]$$

According to [13.16], this leads us to:

$$r = \frac{k_2 K_2 V}{n_0} [RX] [\text{C}_6\text{H}_5Z] [\text{AlCl}_3] \quad [13.18]$$

The rate is therefore of the first order with respect to each of the reactants and also proportional to the concentration of the catalyst. This result is confirmed experimentally.

### 13.1.4. Redox catalysis

Many redox reactions require the hypothesis that intermediate oxidation states are needed to meet kinetic laws, which is made possible by the presence of the catalyst.

Hence the reduction reaction [13.R6] of ferric ion by tin (II), which is extremely slow without a catalyst, is strongly catalyzed by chloride ions that are assumed to permit the presence of oxidation state III for tin:



With a high iron (III) over tin (II) concentration ratio, the rate law is:

$$-\frac{d[\text{Fe}^{3+}]}{dt} = k[\text{Fe}^{3+}][\text{Sn}^{2+}] \quad [13.\text{R19}]$$

In this expression, the constant  $k$  depends on the chloride ion concentration.

The following mechanism was first proposed by Weiss. It occurs according to the steps [13.R6a] and [13.R6b]:



With the pseudo-steady state mode, it is easy to show that the rate becomes:

$$-\frac{d[\text{Fe}^{3+}]}{dt} = \frac{2k'_1 k''_1 [\text{Fe}^{3+}][\text{SnCl}_3^-]}{k''_1 [\text{Fe}^{2+}] + k_2 [\text{Fe}^{3+}]} \quad [13.\text{R20}]$$

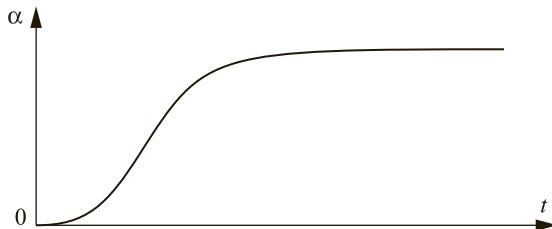
### 13.1.5. Autocatalytic reactions

An autocatalytic reaction is so called if any of the products catalyze this reaction. This includes, for example, the acid hydrolysis of esters catalyzed by protons:



In general, an autocatalytic reaction is characterized by a curve of extent (or concentration of a product formed in a closed environment) versus time that shows the so-called "S" shape, as shown in Figure 13.3.

NOTE 13.3.— Such “S” kinetic curves are also commonly obtained without any autocatalytic effect being required to explain them. Hence, remember that a “S” curve in is not necessarily due to autocatalysis.



**Figure 13.3.** “S” shape of an autocatalytic curve

### 13.1.6. Enzymatic catalysis

Enzymes are substances found in living organisms that catalyze most biochemical reactions. These catalysts have four important properties:

- an enzyme is specific in its reaction, and may even be stereochemistry specific;
- enzymes are water soluble substances;
- enzymes are catalysts that have an optimum temperature of action. This is because enzymes are not stable with temperature and thus counteract the kinetic effect of temperature, thus the existence of an optimum temperature;
- enzymatic reactions have a particularly low temperature coefficient in the order of tens kilojoules per mole – 10 times less than a conventional chemical reaction. This allows these reactions to achieve significant rates at relatively low temperatures *in vivo*.

The catalytic power of an enzyme is called its activity. The enzyme activity is the amount of enzyme that produces the transformation of 1  $\mu\text{mol}$  of reactant, which is called the substrate, per minute at 25C.

The specific activity of an enzyme is its activity per milligram of enzyme. There is also a molar specific activity, which is the amount of substrate transformed per unit time per mole of enzyme.

#### 13.1.6.1. Enzymatic catalysis in solution

The simplest calculation of enzymatic reaction was encompassed in a mechanism determined by Michaelis and Menten. It is especially well suited for

enzymatic reactions involving a single substrate  $S$  (reactant) and a single enzyme  $E$ . This mechanism accounts for the most common experimental results:

- the reaction rate is proportional to the enzyme concentration;
- the reaction rate is proportional to very high substrate concentrations but is no longer dependent of this concentration if very low.

The mechanism is proposed in two stages:

- During the first step a complex between the enzyme  $E$  and substrate  $S$  is formed:



– This complex is broken down during the second step, giving the product  $P$  and regenerating the enzyme:



We solve this system in the pseudo-steady state mode, neglecting the reverse reaction of step [13.R8b] and remembering that the sum of the amounts of free and bound enzyme are constant:

$$[E - S] + [E] = [E]_0 \quad [13.21]$$

From pseudo-steadiness, we deduce:

$$[E - S] = \frac{k'_1 [E]_0 [S]}{k'_1 [S] + k''_1 + k'_2} \quad [13.22]$$

The reaction rate becomes:

$$v = k'_2 [E - S] = \frac{k'_1 k'_2 [E]_0 [S]}{k'_1 [S] + k''_1 + k'_2} = \frac{k'_2 [E]_0 [S]}{(k'_2 + k''_1)/k'_1 + [S]} \quad [13.23]$$

The constant  $(k'_2 + k''_1)/k'_1$  is often called the Michaelis constant and denoted  $K_m$ , which leads to:

$$v = \frac{k'_2 [E]_0 [S]}{K_m + [S]} \quad [13.24]$$

Two constants are determined from the experiment:  $k'_2$  and  $K_m$ . To determine them, we plot the inverse of the reaction rate versus the reciprocal of substrate concentration (see expression [13.25]). If the model is acceptable, we obtain a straight line. The slope and intercept are used to calculate the two constants, knowing the initial concentration of the enzyme.

This law reflects the experimental results cited above. Indeed, at low substrate concentrations that are negligible in comparison to the Michaelis constant, the reaction rate is proportional to the substrate concentration. With high substrate concentrations, however, the Michaelis constant is negligible and the rate is independent of the substrate concentration and proportional to the initial concentration of the enzyme.

NOTE 13.4.– Relation [13.24] can also be written:

$$\frac{[E]_0}{v} = \frac{1}{k'_2} + \frac{K_m}{k'_2 [S]} \quad [13.25]$$

This expression is the direct application of the law of the slowness to the case of catalytic steps and written as:

$$\frac{I_0}{v} = \sum_i \left( \frac{1}{v_i} \right) \quad [13.26]$$

where  $I_0$  is the sum of the concentrations of free and bound catalytic sites, or  $[E]_0$  in our example.

### 13.1.6.2. Catalysis by immobilized enzymes

In the previous section, we dealt with homogeneous enzymatic catalysis using enzyme solutions. Enzymes can be used in another way by immobilizing them on membranes. Substrate and product species are adsorbed at the adsorption sites, which are formed by the bound enzyme molecules. The kinetic study is then completely identical to that of kinetics with heterogeneous catalysis and is

analogous to the treatment presented in section 13.2. The Michaelis constant is an adsorption constant.

### 13.2. Heterogeneous catalysis reactions

A heterogeneous catalysis reaction is a reaction between reactants leading to products generally belonging to the same phase (liquid or gas) that uses the surface of a solid phase as its mechanism. There are two possible cases where this happens:

- chain reactions in a homogeneous phase for which the reactor walls play a role, usually by causing a breaking reaction of recombination in the active centers, which we have already discussed in Chapter 12, section 12.4.5.6;
- heterogeneous catalysis itself, in which the solid phase is the catalyst (and sometimes makes it more selective) chosen to accelerate the reaction.

We will now examine the mechanisms and kinetics of the catalytic action of a solid onto a reaction between gases.

#### 13.2.1. Experimental laws in heterogeneous catalysis

The kinetic experimental laws of heterogeneous catalysis express the reaction rate as a function of three main parameters: the concentrations or partial pressure of reactants and products; temperature; and surface area of the catalyst.

##### 13.2.1.1. Concentrations (or partial pressures) of reactants and products

There are several types of laws ranging, from simple laws such as rate per unit area that admit a single order with respect to reactants, to negative orders compared to the reaction products, such as the following (for a reaction with two gas reactants, *A* and *B*, for example):

$$v_a = \frac{kP_A P_B}{1 + \sum K_i P_i} \quad [13.27]$$

or:

$$v_a = \frac{kP_A P_B}{(1 + \sum K_i P_i)^2} \quad [13.28]$$

The amounts shown in the denominator may involve all the gases involved in the reaction (reactants, products and inert gases may be present) or only some of them.

### 13.2.1.2. *The temperature*

The reaction rate often seems to obey Arrhenius' law, although this property is sometimes controversial. Sometimes the rate is not influenced by temperature.

### 13.2.1.3. *Surface area of the catalyst*

In general, the absolute rates are proportional to the area of the catalyst. This is obviously true of the area including the pore walls and not the outer area of the solid.

The concept of specific area (measured in  $\text{m}^2$  per gram of catalyst) is of the utmost importance.

This proportionality of the reaction rate with the specific area of the catalyst often disappears with time and part of the area appears to be inactive during the reaction.

### 13.2.2. *Structure of the mechanism of heterogeneous catalysis*

It is commonly accepted that a catalytic reaction involves two reaction zones in which five steps occur:

- *interdiffusion of reacting gases* within the product gases toward the surface area of the catalyst;
- *adsorption of reactants* on the surface area of the catalyst;
- *the catalytic act*, which is the chemical reaction itself, also on the surface area of the catalyst;
- *desorption of gases produced* from the surface area of the catalyst;
- *interdiffusion of gases produced* from the surface area of the catalyst toward the gas volume, far away from the solid.

Interdiffusion phenomena are governed by Fick's law but gas interdiffusion is not activated – the interdiffusion coefficients (variation of  $\lambda_0$  in [12.25]) vary as a power of temperature. We will now focus on the catalytic act and more generally on the phenomena occurring at the catalyst's surface area. Gas pressures that will take part in the specified expressions are the pressures in close proximity to the surface. They become the partial pressures in the volume of the gas phase only in the case of very fast interdiffusions.

In most cases, the steps of adsorption and desorption – when required – are considered to occur very quickly and the whole adsorption–desorption process is

considered to be in equilibrium. The expressions deduced from the models use the [9.R14] or [9.R15] equilibrium depending on whether the gas molecule is dissociated or not during adsorption. The law of mass action applied to these equilibria leads to two written forms: pressure or the square root of pressure of the Langmuir isotherm.

### 13.2.3. Kinetics of the catalytic act

We will now successively consider the reactions of decomposition or isomerization, which involve a single reactant and reactions involving two reactants. The surface reaction is assumed to be elementary.

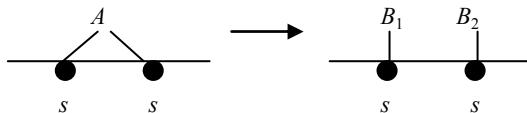
#### 13.2.3.1. Kinetic study of reactions with a single reactant

This reaction is schematically represented by:



##### 13.2.3.1.1. Establishing the generic rate law

We assume that the chemical reaction occurs from the adsorbed reactant and that the products are formed in the adsorbed state (see Figure 13.4), so that step [13.R10] is considered elementary:



**Figure 13.4.** Catalytic reaction with a single reactant

The elementarity of reaction [13.R10] allows the concentration of  $A$  adsorbed ( $A-s_2$ ) to be written:

$$-\frac{d[A-s_2]}{dt} = k [A s_2] \quad [13.\text{R9}]$$

where  $k$  is a rate coefficient that, as a consequence, follows Arrhenius' law with an activation energy  $E_a$ :

$$k = k^0 \exp\left(-\frac{E_a}{RT}\right) \quad [13.30]$$

The concentration per surface unit of  $A$  absorbed is linked to the ratio of the surface  $\theta_A$  covered by  $A$  over the area  $s_0$  of the adsorption site by the following relation:

$$[As_2] = \frac{2\theta_A}{s_0} \quad [13.31]$$

The variation in the amount of  $A$  absorbed in the gas phase is related to its concentration in the absorbed phase (the adsorption equilibrium being always achieved) by:

$$d\{A\} = S \cdot d[As_2] \quad [13.32]$$

and its partial pressure (in the vicinity of the catalyst) is related to the amount of  $A$  by:

$$dP_A = \frac{RT}{V} d\{A\} \quad [13.33]$$

By combining [13.31], [13.32] and [13.33], we have:

$$-\frac{dP_A}{dt} = 2k \frac{RTS}{Vs_0} \theta_A \quad [13.34]$$

The adsorption isotherm of  $A$  follows Langmuir law in the presence of gas  $i$ , which includes all gases present in the medium:  $A$ , the reaction products and inert gases:

$$\theta_A = \frac{K_A P_A}{2 \left( 1 + \sum_i K_i P_i \right)} \quad [13.35]$$

By incorporating this into [13.26], we obtain the rate equation:

$$-\frac{dP_A}{dt} = \frac{kRTS}{Vs_0} \frac{K_A P_A}{1 + \sum_i K_i P_i} \quad [13.36]$$

We can denote the temperature by using [13.30] and the van 't Hoff isochors [9.13] for the adsorption constants, and obtain:

$$-\frac{dP_A}{dt} = \frac{k^0 RTS}{Vs_0} \frac{K_A^0 P_A \exp\left(-\frac{(E_a)_A}{RT}\right) \exp\left(-\frac{(\Delta H)_A}{RT}\right)}{1 + \sum_i \left[ K_i^0 P_i \exp\left(-\frac{(\Delta H)_i}{RT}\right) \right]} \quad [13.37]$$

This generic law is complicated by both the influence of partial pressures of various gases and the temperature. We note in particular that in this very generic case, Arrhenius' law is not followed for rates at constant partial pressures.

Conditions	Rate	Influence of T
$A$ is strongly adsorbed $K_A P_A \gg 1 \gg K_i P_i$	$-\frac{dP_A}{dt} = \frac{kRTS}{Vs_0}$	Arrhenius $\Xi = E_a$
All gases are weakly adsorbed $K_i P_i \ll 1$	$-\frac{dP_A}{dt} = \frac{kRTSK_A P_A}{Vs_0}$	Arrhenius $\Xi = E_a + \Delta H_A$
$A$ is moderately adsorbed $K_A P_A \approx 1 \gg K_i P_i$	$-\frac{dP_A}{dt} = \frac{kRTS}{Vs_0} \frac{K_A P_A}{1 + K_A P_A}$ $1/v = f(1/P_A)$ : straight line	Not Arrhenius
Species $j$ (product or inert) is moderately adsorbed $K_j P_j \approx 1 \gg K_i P_i$	$-\frac{dP_A}{dt} = \frac{kRTS}{Vs_0} \frac{K_A P_A}{1 + K_j P_j}$	Not Arrhenius
Species $j$ (product or inert) is strongly adsorbed $K_j P_j \gg 1 \gg K_i P_i$	$-\frac{dP_A}{dt} = \frac{kRTS}{Vs_0} \frac{K_A P_A}{K_j P_j}$ $v = f(P_j/P_A)$ : straight line	Arrhenius $\Xi = E_a + \Delta H_A$ $-\Delta H_j$
$A$ and $j$ are strongly adsorbed $K_A P_A \approx K_j P_j \gg 1 \gg K_i P_i$	$-\frac{dP_A}{dt} = \frac{kRTS}{Vs_0} \frac{K_A P_A}{K_A P_A + K_j P_j}$ $1/v = f(P_j/P_A)$ : straight line	Not Arrhenius

**Table 13.1.** Specific solutions for reactions involving a single reactant

### 13.2.3.1.2. Obtaining specific forms of the generic law

A number of simple laws can be obtained from [13.37] depending on the importance of different  $K_i P_i$  terms compared to 1 and between each other. Table 13.1 lists some of these particular solutions, indicating the influence of temperature for each.

### 13.2.3.2. Kinetic study of reactions with two reactants

These reactions will be of the form:



With the special case of the reaction between two identical molecules of gas being:



The reaction occurring at the catalyst's surface leads to two interesting hypotheses that need to be considered:

Langmuir and Hinshelwood assume that the surface reaction occurs between adsorbed gases in the following form:



Elsey and Rideal assume that the reaction occurs between a molecule and a gas molecule adsorbed at the interface – a step in the following form:



We will successively consider these two models.

#### 13.2.3.2.1. The Langmuir–Hinshelwood model

This time the reaction rate of the elementary step [13.R13] allows us to write:

$$-\frac{d[A\text{-s}]}{dt} = k [A\text{s}] [B\text{-s}] \quad [13.38]$$

As previously, the concentrations of absorbed *A* and *B* are connected to corresponding degrees of recovery, and applying the Langmuir isotherm, we get:

$$[\theta_A] = \frac{\theta_A}{s_A} = \frac{K_A P_A}{s_A \left( 1 + \sum_i K_i P_i \right)} \quad [13.39]$$

$$[\theta_B] = \frac{\theta_B}{s_B} = \frac{K_B P_B}{s_B \left( 1 + \sum_i K_i P_i \right)} \quad [13.40]$$

Sites *A* and *B* presumably being common, we have:

$$s_A = s_B = s_0 \quad [13.41]$$

We can use [13.32], [13.33] and [13.34], hence we get the rate:

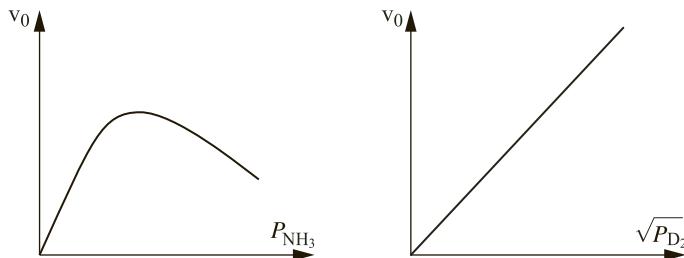
$$-\frac{dP_A}{dt} = \frac{kRTS}{Vs_0^2} \frac{K_A K_B P_A P_B}{\left( 1 + \sum_i K_i P_i \right)^2} \quad [13.42]$$

This expression also shows the complex influence of partial pressures from both gases and that temperature does not follow Arrhenius' law. As before, simpler expressions can be established with some approximations. The second column in Table 13.2 shows such solutions.

We notice that by increasing the pressure  $P_A$  while keeping  $P_B$  constant we should see a succession in the first three cases. This is what is observed in the reaction between ammonia and deuterium (heavy hydrogen) on iron, as shown by the rate variation curves in Figure 13.5 with the partial pressures of ammonia and deuterium.

Conditions	Langmuir–Hinshelwood	Rideal–Elsey
$1 \gg K_i P_i$	$\frac{kRTS}{Vs_0^2} K_A K_B P_A P_B$	$\frac{kRTS}{Vs_0} K_A P_A P_B$
$K_A P_A \approx 1 \gg K_i P_i$	$\frac{kRTS}{Vs_0^2} \frac{K_A K_B P_A P_B}{(1 + K_A P_A)^2}$	$\frac{kRTS}{Vs_0} \frac{K_A P_A P_B}{1 + K_A P_A}$
$K_A P_A \gg 1 \gg K_i P_i$	$\frac{kRTS}{Vs^2} \frac{K_B P_B}{K_B P_B}$	$\frac{kRTS}{Vs_0} P_B$
$K_A P_A \approx K_B P_B$ $K_B P_B \gg 1$ $1 \gg K_i P_i$	$\frac{kRTS}{Vs_0^2} \frac{K_A K_B P_A P_B}{(K_A P_A + K_B P_B)^2}$	Not applicable: B is not absorbed in this model
$K_j P_j \gg 1 \gg K_i P_i$	$\frac{kRTS}{Vs_0^2} \frac{K_A K_B P_A P_B}{(K_i P_i)^2}$	$\frac{kRTS}{Vs_0} \frac{K_A P_A P_B}{K_j P_j}$

**Table 13.2.** Approximate solutions to the reaction rates of two gases for the Langmuir–Hinshelwood and Rideal–Elsey models



**Figure 13.5.** Influence of the pressure of gases on the initial reaction rate of deuterium and ammonia on iron

### 13.2.3.2.2. The Rideal–Elsey model

Considering reaction [13.R14], the rate is written:

$$-\frac{d[A-s]}{dt} = k [As] [B] \quad [13.43]$$

The amount of  $B$  in the gas is linked to its partial pressure by:

$$\{B\} = \frac{P_B}{RT} \quad [13.44]$$

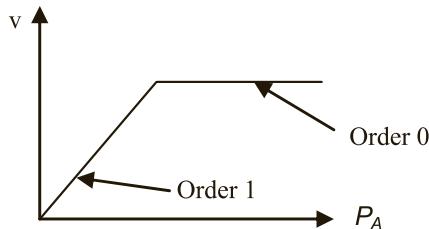
By proceeding as before, the rate becomes:

$$-\frac{dP_A}{dt} = \frac{kRTS}{Vs_0} \frac{K_A P_A P_B}{1 + \sum_i K_i P_i} \quad [13.45]$$

As in the previous cases, the influence of the different gases and the temperature are complex.

Table 13.2 (right column) summarizes some approximate specific solutions.

As with the previous mechanism, by increasing the pressure of  $A$ , we successively go through cases 1, 2 and 3.



**Figure 13.6.** Variation of the rate as a function of the pressure of the adsorbed gas in the Rideal–Elsey mechanism

We notice a different result from the Langmuir–Hinshelwood mechanism. As shown in Figure 13.6, the rate shifts from first order to zero with respect to  $A$ .

NOTE 13.5.— Only the Rideal–Elsey model leads to power units for the sums at the denominators. This result is at the origin of this model.

#### 13.2.4. Example of the kinetics of catalysis on a porous support

To increase the reaction rates, we ideally increase the catalyst's surface area. For this we either use porous catalysts or catalysts deposited on a thin layer at the surface of a porous support. In section 13.2.4.1 we will consider catalysis in porous

media in the case of a first order reaction with respect to a reactant gas. This can be either a reaction with a single gas or a reaction with two gases of zero order with respect to the second gas (such cases are not always listed in Table 13.2, but are possible in special cases). The model we develop comes from Thiele and Wheeler.

#### 13.2.4.1. Wheeler model in a porous medium

$S_{\text{BET}}$  and  $V_p$  are the specific area (area per gram) and the pore volume per gram of solid catalyst, respectively. We will calculate the average radius and length of pores that are assumed to be cylindrical (see Figure 13.7), each having an elliptical opening.

Here,  $p$  the porosity of the solid, defined as the ratio of total pore volume over the apparent volume of the solid  $V_a$ :

$$p = \frac{mV_p}{V_a} \quad [13.46]$$

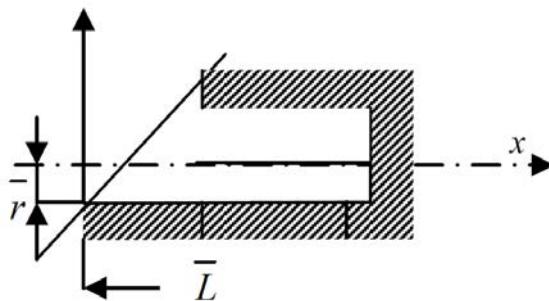


Figure 13.7. Diagram of a cylindrical pore

We assume that the ratio of the area of the pore openings,  $S_O$ , over the total external area of the solid,  $S_e$ , is equal to the porosity:

$$p = \frac{S_O}{S_e} \quad [13.47]$$

With the area of the pore opening, if  $\bar{r}$  is the average radius of the pores, we have:

$$S_O = \pi n_p \bar{r}^2 \sqrt{2} \quad [13.48]$$

The term  $\sqrt{2}$  comes from the fact that we assume the pore axis has an average angle of  $45^\circ$  against the surface (tortuosity coefficient), so:

$$n_p = \frac{pS_e}{\pi r^2 \sqrt{2}} \quad [13.49]$$

The pore volume per particle is therefore:

$$mV_p = n_p \pi r^2 \bar{L} = \frac{S_e p \bar{L}}{\sqrt{2}} \quad [13.50]$$

and the pore area per particles is:

$$mS_{BET} = 2n_p \pi r \bar{L} \quad [13.51]$$

By taking the ratio of expressions [13.50] and [13.51], we obtain a classic relation:

$$\bar{r} = \frac{2V_p}{S_{BET}} \quad [13.52]$$

To determine the average length of a pore, we write:

$$\bar{L} = \frac{mV_p}{S_e p} \sqrt{2} \quad [13.53]$$

and using relation [13.46], we have:

$$\bar{L} = \frac{V_a}{S_e} \sqrt{2} \quad [13.54]$$

For example, if we apply the relation to spherical particles such as:

$$V_a = \frac{4\pi r^3}{3} \quad \text{and} \quad S_e = 4\pi r^2$$

we obtain:

$$\bar{L} = \frac{r}{3} \sqrt{2} \quad [13.55]$$

### 13.2.4.2. Thiele's catalytic model

We take the hypothesis that the absolute rate of a reaction can be written as in [13.56], with  $k$  being the pseudo-rate coefficient per area unit, assumed to obey Arrhenius' law with activation energy  $E_a$ :

$$v_a = k[A] S \quad [13.56]$$

This reaction occurs in the cylindrical pores defined above (in section 13.2.4.2).

We can establish the model for gas  $A$  by ignoring the surface at the bottom of the cylinder (hypothesis:  $\bar{r} \ll \bar{L}$ ), which gives:

$$\frac{\partial \{A\}}{\partial t} = k[A] + \pi r^2 D \frac{\partial^2 [A]}{\partial x^2} dx \quad [13.57]$$

We are considering a pseudo-steady state mode so:

$$2k[A] = Dr \frac{d^2 [A]}{dx^2} \quad [13.58]$$

To resolve differential equation [13.58], we adopt the following limits:

– If  $x = 0$ , therefore  $[A] = [A]_\infty$ : concentration of the gas volume far away from the solid.

– If  $x = \bar{L}$ , therefore  $\left( \frac{\partial [A]}{\partial x} \right)_{\bar{L}} = 0$ : this assumes that all the gas is consumed in the pore, since the flow at the bottom of the pore is zero.

The solution is written:

$$[A] = [A]_\infty \frac{\cosh \left[ h \left( 1 - \frac{x}{\bar{L}} \right) \right]}{\cosh(h)} \quad [13.59]$$

By introducing the measure  $h$ , called Thiele's modulus and defined by:

$$h = \bar{L} \sqrt{\frac{2k}{Dr}} \quad [13.60]$$

using [13.56], the absolute rate of the reaction is therefore written:

$$v_a = 2\pi \bar{k} r \int_0^{\bar{L}} [A] dx \quad [13.61]$$

But by using [13.58], this rate can also be written:

$$v_a = \pi D r^{-2} \int_0^{\bar{L}} \frac{d^2[A]}{dx^2} dx \quad [13.62]$$

The integration leads to:

$$v_a = \pi D r^{-2} \left[ \frac{d[A]}{dx} \right]_0^{\bar{L}} \quad [13.63]$$

We take into account that the flow is zero at the bottom of the pore, thus the rate the gas is consumed in a pore becomes:

$$v_a = -\pi D r^{-2} \left( \frac{d[A]}{dx} \right)_0^- \quad [13.64]$$

Hence by using [13.59]:

$$v_a = \frac{\pi D r^{-2} [A]_\infty}{\bar{L}} h \tanh(h) \quad [13.65]$$

For the group of pores of a grain, the absolute rate is written:

$$v_a = \frac{\pi n_p D r^{-2} [A]_\infty}{\bar{L}} h \tanh(h) \quad [13.66]$$

We obtain the solution to our problem in the pseudo-steady state mode with a constant partial pressure of  $A$  in the gas volume and a constant flow of a gas containing  $A$ .

Two limiting cases are interesting, depending of the range of Thiele's modulus value.

If  $h < 0.2$ , then we can admit that  $\tanh(h) \approx h$  and the rate becomes:

$$v_a = \frac{2\pi n_p D r^{-2} [A]_\infty}{L} h^2 = 2n_p \pi r \bar{L} k [A]_\infty = kS [A]_\infty \quad [13.67]$$

We obtain a rate proportional to the concentration of  $A$  (first order) in the gas volume. In this expression, only constant  $k$  varies with temperature and therefore taking the logarithm of rate and expressing the temperature, we notice that Arrhenius' law is followed and the temperature coefficient is equal to the activation energy (true or measured) of the reaction interface:

$$\Xi = E_a \quad [13.68]$$

NOTE 13.6.– We notice that expression [13.67] is obtained for a pseudo-steady state mode with the interface reaction as the rate-determining step.

If, on the contrary,  $h > 2$  we can admit that  $\tanh(h) \approx 1$  and the rate becomes:

$$v_a = \frac{\pi n_p D r^{-2} [A]_\infty}{L} h = \pi n_p r^{-2} [A]_\infty \sqrt{\frac{2D}{r}} \sqrt{k} \quad [13.69]$$

In the resulting expression, only constant  $k$  varies significantly with temperature, since the diffusion of gas in a pore varies little with temperature. Passing to the logarithm of the rate and expressing the temperature, we notice that Arrhenius' law is still followed but the temperature coefficient is half the activation energy of the reaction interface:

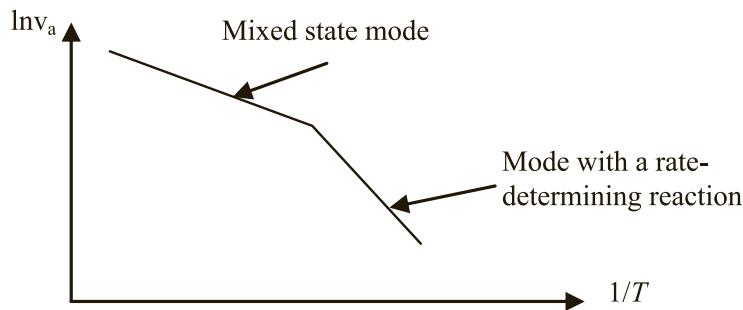
$$\Xi = \frac{E_a}{2} \quad [13.70]$$

Note that the result obtained is a particular solution of the pseudo-steady state mode determined by both the reaction and diffusion steps. It is not the diffusion rate-determining mode since constant  $k$  would be infinite. As it occurs frequently, we

cannot say that we have a diffusion mode: the mode is a mixture of diffusion and reaction.

If we plot the Arrhenius graph (see Figure 13.8) from the two relations [13.67] and [13.69], we obtain two straight lines corresponding to each of the two specific modes. The slopes of both segments are in a ratio of 2:1. It is assumed that the transition between the two fields is obtained for  $h = 1$ :

$$\frac{2\bar{L}^2 k_c}{D\bar{r}} \equiv 1 \text{ or } \bar{L} \sqrt{\frac{2k_c}{D\bar{r}}} = 1 \quad [13.71]$$



**Figure 13.8.** Arrhenius graph for catalysis in a porous medium

If the rate given by [13.45] is denoted  $(v_a)_0$  in the absence of diffusion and we calculate the ratio of the general pseudo-steady solution rate [13.66] over the rate obtained in the absence of diffusion resistance, we have:

$$\frac{(v_a)}{(v_a)_0} = \frac{\frac{n_p \pi r^2 D [A]_\infty h \tanh(h)}{\bar{L}}}{2n_p \pi k [A]_\infty \bar{r} \bar{L}} \quad [13.72]$$

therefore the ratio  $E$  is:

$$\frac{v_a}{(v_a)_0} = \frac{\tan(h)}{h} = E \quad [13.73]$$

This ratio is called the *catalyst efficiency factor*. The rate is therefore:

$$(v_a) = 2\pi \bar{r} n_p k \bar{L} [A]_\infty E \quad [13.74]$$

The same two catalysts efficiency factors,  $E$ , operate in similar conditions. Their Thiele modulus is also the same. If the average lengths of the pores of these catalysts are  $\bar{L}_1$  and  $\bar{L}_2$ , respectively, we immediately have the ratio of the pseudo-rate coefficients (if the radii are the same):

$$\left(\frac{\bar{L}_1}{\bar{L}_2}\right)^2 = \frac{k_2}{k_1} \quad [13.75]$$

NOTE 13.7.— When integrating equation [13.57], we assumed that the concentration of  $A$  in the middle, away from the catalyst, was constant. In practical terms, this means that the experiments meet this condition. For this, three ways of proceeding can be used:

- We can work in a closed medium and only look at the beginning of the reaction, as for example with a consumption of less than 5% of  $A$ , but then what will happen to the time needed to establish pseudo-steady state mode before the reaction?
- We can work in a closed medium for a longer period and extrapolate the experiments to a time, zero, but then which extrapolation should we choose?
- We can work in an open medium, fix a consumption rate of  $A$  – let us say 5% – and set the flow based on the difference between the inlet and outlet concentrations  $d[A]$ . The rate is therefore given by the gas flow and we can choose the average concentration of  $A$  between the inlet and outlet values.

### 13.2.5. Influence of the catalyst surface area: poisoning

Poisoning of catalysts is due to the specific action of certain species – poisons – accidentally being present at trace levels in the gas phase. It is assumed that the poisoning is due to adsorption of the poison at the catalyst surface:

- by a very strong adsorption that will greatly increase the denominators of relations [13.28], [13.34] or [13.39]; or
- by adsorption of large molecules that will cover several sites in the catalyst rendering it unusable by decreasing the sites' surface density.

These adsorptions cause “aging” of the catalyst. A poison is characterized by its toxicity coefficient, which is the strongly negative slope of the line of the rate ratio in the presence and absence of poison, depending on its concentration in the inlet gas.

### 13.3. Gas–solid reactions leading to a gas

Here we consider heterogeneous reactions of the type:



Such as, for example, the reaction of fluoridation of uranium tetra fluoride:



From the viewpoint of reaction zones, this type of system is similar in all respects to that of heterogeneous catalysis, with the same phenomena of diffusion and interfacial reaction. The only difference is consumption of the solid. In most cases this consumption will result in a continuous variation of the interface area between gas and solid (except in the case of a solid form of non-porous thin plates).

For example, if we take the case of the porous solid in section 13.2.4, the reaction at the x-axis point will lead to a variation of the average pore radius that can be related to the reaction rate by writing that the variation in volume is equal to the molar volume of the solid via the reaction rate:

$$2\pi\bar{r}.dx.d\bar{r} = 2\pi\bar{r}V_m v.dx.dt \quad [13.76]$$

or:

$$d\bar{r} = V_m v.dt \quad [13.77]$$

The integration of [13.77] quickly becomes complicated, particularly due to the variation of the surface rate with time and the x-axis that converts the cylindrical pore into a cone-shapes pore, for example. A simple case is where, working in an open environment at a constant concentration of gas reactants and a state mode determined by the reaction interface, the rate per unit area  $v$  is constant, the pore remains cylindrical and the integration leads immediately to:

$$\bar{r} = \bar{r}_0 (1 - V_m v.t) \quad [13.78]$$

This expression can then be introduced into equation [13.69].

### 13.4. Conclusion on catalysis

We initially only addressed the kinetic aspect of catalysis, but catalytic science, especially heterogeneous catalysis, deals with many other aspects related to the nature of catalysts, their production and texture in relation to their specificity for a given reaction and its evolution over time with the problems of aging acting on a decreased activity. There are many phenomena that kinetics not only notices but can anticipate.

With heterogeneous reactions, we only discussed the case of reactions of [13.R15] type. The most common are those that produce a new solid phase. The study of these types of reaction will be the topic of Chapter 14.

### 13.5. Langmuir and Hinshelwood

Irving Langmuir was awarded the 1932 Nobel Prize in Chemistry for his work in surface chemistry. He contributed to atomic theory and the understanding of atomic structure by defining the concepts of valence shells and isotopes.

Sir Cyril Norman Hinshelwood's early studies of molecular kinetics led to the publication of *Thermodynamics for Students of Chemistry* and *The Kinetics of Chemical Change* in 1926. He studied the explosive reaction of hydrogen and oxygen and described the phenomenon of chain reactions. Hinshelwood was jointly awarded the Nobel Prize in Chemistry in 1956 for his research into the mechanisms of chemical reactions.



**Sir Cyril Norman Hinshelwood**  
1897-1967



**Irving Langmuir**  
1881-1957

**Figure 13.9.** Hinshelwood won the Nobel Prize for chemistry in 1956 and Langmuir won it in 1932

## Chapter 14

# Kinetics of Heterogeneous Stoichiometric Reactions

A heterogeneous stoichiometric reaction is a reaction in which a condensed substance (solid or liquid) or one of its constituents (in the case of solutions) is consumed in stoichiometric proportions compared to the heterogeneous catalysis, which is also an heterogeneous reaction but not stoichiometric. We have already discussed the heterogeneous stoichiometric reactions which do not produce a condensed phase in section 13.3.

In this chapter, we will discuss the case where the condensed substances are pure solid and the reaction generates a new solid phase. We saw in section 6.2.2 the different families of these reactions, which can be represented by the chemical equation:



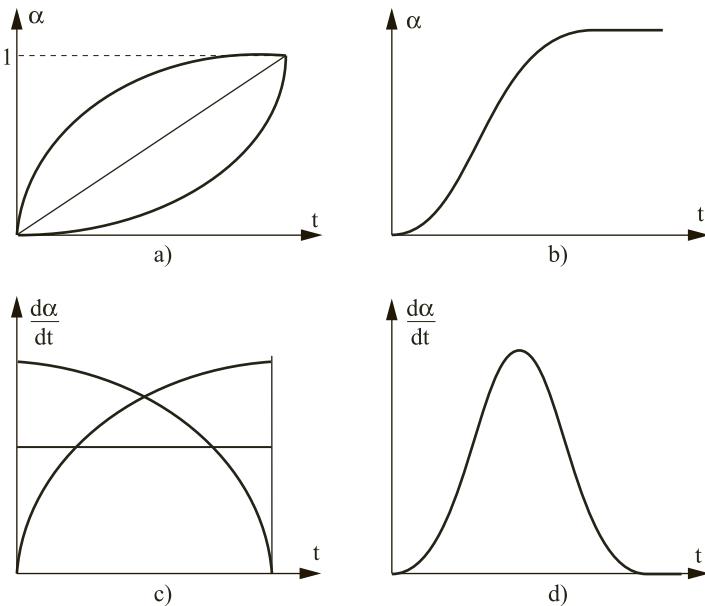
With heterogeneous kinetics of the formation of a new condensed phase, it is usual to present experimental results in various equivalent forms. Thus we find data on the fractional extent (for a solid reactant) versus time and data from rate depending on the fractional extent, as a function of intensive variables such as the partial gas pressures and temperature, and as a function of the size of the grains forming solid reactants. We will now briefly outline the results usually obtained.

### 14.1. Extent versus time and rate versus extent curves

The shapes of kinetic curves obtained for the different types of reactions considered here can be classified into two groups.

We saw in section 6.2.2.2 the first group in which the rate is unchanging (Figure 14.1): continuously growing, continuously decreasing or constant. The corresponding kinetic curves (see Figure 14.1a) therefore curve upwards, downwards or are straight lines. We have given some examples of laws with this behavior, such as the parabolic Wagner law, linear law, etc.

In the second group, the kinetic curves have a so-called “sigmoid” shape (see Figure 14.1b), also called “S-curves”. The reaction rate curve (see Figure 14.1d) has then a maximum corresponding to the inflection point of the kinetic curve. With rate curves presenting a maximum, more complex laws have been proposed, including that by Mampel in 1940. We will see later (in section 14.4.2) that the mathematical forms of such laws are complex.



**Figure 14.1.** Generic shapes of the kinetics curves (fractional extent versus time) and rate curves (rate versus time) for heterogeneous stoichiometric reactions

It is virtually impossible to relate the two sets of kinetic curves to families of specific reactions. For the same reaction, it is possible to move from one family of

curves to another by changing a variable, such as the size of grains of powder. Moreover, we must not overestimate the difference between the two families; a shift of the inflection point in one direction or another would shift sigmoid curves to any of the curves in Figure 14.1a, and this can be done by changing the values of certain variables, such as partial pressures, temperature or the shape and size of grains in the case of solid reactants in powder form.

#### 14.2. The global model with two processes

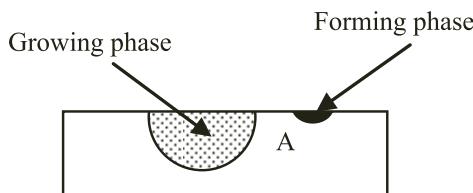
It is commonly accepted that a chemical reaction that leads to the creation of a new phase involves two processes: nucleation and growth. These two processes are actually both identical chemically heterogeneous reactions, as their respective overall balance is the same as the overall reaction balance. Hence, for a reaction that from solid *A* gives solid *B*, the two processes have the same chemical equation [14.R1]. These processes take place in different areas, however, and therefore have different mechanisms.

Indeed, nucleation is the process that allows a small block of solid *B* to be created on the surface of solid *A* (or more rarely within the solid) so that the growth is that of the size of *B* and requires the presence *A* and *B* simultaneously.

Each process operates as a single reaction with its own kinetic properties: rate, fractional extent, surface areas and elementary steps.

It is clear that these two processes are interdependent, however, since they can be considered as:

- two successive reactions, since it is not conceivable to consider growth unless it has been preceded by nucleation;
- two parallel reactions: nucleation reactions may occur at the same time as growth, but in another location, such as on the surface of solid as shown in Figure 6.2.



**Figure 14.2.** Simultaneous nucleation and growth of a phase at two points of a tablet

Regarding reaction zones, nucleation is a single-area reaction: the surface of solid  $A$  is not yet covered by  $B$ ; whereas growth involves several areas, as discussed in section 14.4.1.

As mentioned before, the two processes are intertwined and both are involved in the progress of the reaction. Based on the balanced equation [14.R1], we can write that the rate relative to solid  $A$  is the sum of a contribution of nucleation and growth:

$$\frac{d\alpha}{dt} = \left( \frac{d\alpha}{dt} \right)_{nucl} + \left( \frac{d\alpha}{dt} \right)_{growth} \quad [14.1]$$

Fortunately, in the vast majority of cases, nucleation involves only a small amount of starting material, so its contribution to the total rate can be neglected and equation [14.1] is replaced by:

$$\frac{d\alpha}{dt} \approx \left( \frac{d\alpha}{dt} \right)_{growth} \quad [14.2]$$

*Warning:* this approximation does not mean that all nucleation process effects are neglected. It is clear, for example, in Figure 14.2 that the growth rate at a given time will depend on the number of growing phases that have been created during the previous period.

### 14.3. The $\phi E$ law

Since the growth reaction occurs in several areas, it is not generally possible to define an areal rate. As mentioned in section 14.1.2, however, we will keep to the frequent cases in which we can use the  $\phi E$  law:

$$r = \phi \cdot E \quad [14.3]$$

The growth space function is often complex because it incorporates the process of nucleation.

We assume that every heterogeneous reaction studied here, unless explicitly mentioned, meets conditions set by the  $\phi E$  law and the pseudo-steady state mode.

When these properties are met, we can distinguish the following:

- The study of  $\phi$  properties, which is the rate per unit area and depends on the intensive parameters as any rate does.
- The study of properties of  $E$ , which depends on the morphology and, as we shall see, is often the only measure that varies with time in isothermal and isobaric conditions. Hence the reaction rate variations with time are in fact variations of the space function.

With two physico-chemical processes, it is necessary to model the two reaction mechanisms. Hence the basic steps of nucleation and growth have to be written.

We will initially discuss the modeling of the growth space function that is also called morphological modeling or geometric modeling.

#### **14.4. Morphological modeling of the growing space function**

Morphological modeling is based on the existence of the concept of grains. A grain of reactant  $A$  is defined as the smallest portion of  $A$  that is completely surrounded by other phases. Thus we can measure the total grain surface by measuring the surface area using the BET (Brunnauer, Emmet and Teller) method. This grain is assumed to be non-porous, which can be verified experimentally.

If sample  $A$  is present in the single bulk form, it is said to be made of a single grain only.

NOTE 14.1.– This definition of the grain is different from the one encountered in metallurgy, for which grain is an oriented area in a phase explaining that bulk metals usually contain several grains.

##### **14.4.1. *The hypothesis***

Morphological modeling is based on a number of assumptions, some of which are verifiable experimentally:

- Nucleation of the final solid occurs at the surface of the initial solid whenever the reaction requires an exchange between sample  $A$  and another phase. This means that among the typical reactions, only polymorphic transformations (e.g. transformation of titanium dioxide from anatase form into rutile form) do not meet this criterion and therefore will be the only type of transformation for which the nucleation in bulk  $A$  will be considered (this is not mandatory). In all other cases, we

assume that every spot is formed on the surface of grains of *A*, which can be verified by microscopic examination.

- The surface is homogeneous with regards to the nucleation, which is to say that the probability of seeing a spot is the same at any point located on this surface.

- The nucleation rate (number of spots that have emerged between *t* and *t* dt) is:

$$\Gamma = \gamma S_L \quad [14.4]$$

In this relation, *S<sub>L</sub>* is the surface area of *A* not yet covered by the solid *B* (dimension of the nucleation area).

- The elementary steps of the growth reaction are located in one of the following three areas (see Figure 14.3):

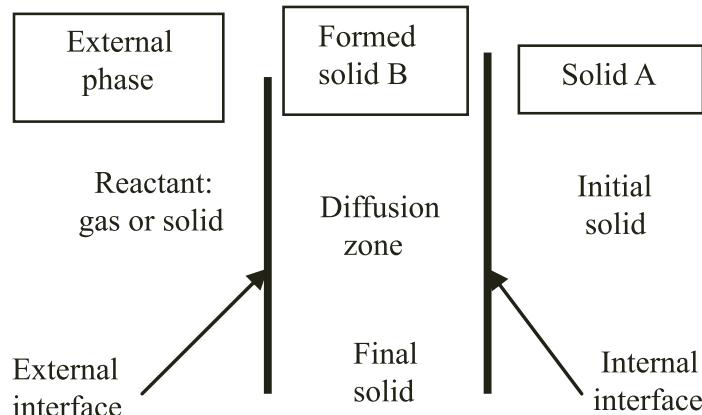
- chemical reactions or adsorptions occurring at the external interface between the initial solid *A* and the external phase;

- chemical reactions taking place at the internal interface between the solid *A* and the solid *B* formed; or

- diffusions through the solid *B* formed.

- Internal and external interfaces are homogeneous, which is to say that the reactions that take place do not depend on the point of these interfaces.

- The rate coefficients of one of the elementary steps of the growth reaction are much lower than the other steps (approximation of a pseudo-steady state mode with a single rate-determining step).



**Figure 14.3. Growth reaction areas**

Reaction area	Reactivity	Factor $G$	Space function
External interface	$\phi_e$	1	$\frac{S_e}{n_0}$
Internal interface	$\phi_i$	1	$\frac{S_i}{n_0}$
Diffusion through the spherical layer	$D  \Delta C $	$\frac{r_e}{r_i (r_e - r_i)}$	$\frac{S_i r_e}{n_0 r_i (r_e - r_i)}$
Diffusion through the cylindrical layer	$D  \Delta C $	$\frac{1}{r_i \ln\left(\frac{r_e}{r_i}\right)}$	$\frac{S_i}{n_0 r_i \ln\left(\frac{r_e}{r_i}\right)}$
Diffusion through a plane layer of thickness $x$	$D  \Delta C $	$\frac{1}{x}$	$\frac{S_i}{n_0 x}$

**Table 14.1.** Reactivities and space functions at the different reaction areas of a grain

We show that the last hypothesis allows us to use relation [14.3] for a growing spot:

– If the rate-determining step is a reaction at the interface,  $\phi$  is its specific rate (rate per surface area units) and  $E$  is the area of this interface ( $Sp$ ) where it is taking place, per unit of initial amount of solid A:

$$E = \frac{S_p}{n_0} \quad [14.5]$$

– If the rate-determining step is the diffusion of species through layer  $B$ , the spatial function will depend on the shape of the diffusion. If  $S_i$  is the area of the internal interface, the spatial function is given by equation [14.6], where  $G$  is the geometric factor given by the second column in Table 14.1:

$$E = \frac{S_i G}{n_0} \quad [14.6]$$

Hence, Table 14.1 summarizes the reactivity and spatial functions of the steps involved in the various areas of Figure 14.3, where  $n_0$  is the initial amount of material in a grain of A.

#### 14.4.2. Types of model involving one or two processes

These models must include the presence of the two processes of nucleation and growth. At the beginning, researchers tried to simplify the problem by analyzing borderline cases in which one of the two processes was taking place very quickly with respect of the other. These are called *borderline cases* or *single process models* since either the single growth or nucleation process evolution over time is taken into account, while the other is considered to have an infinite speed.

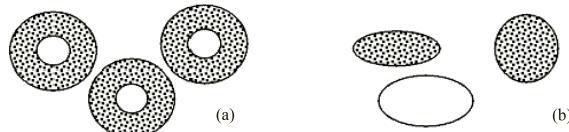
Models in which both processes occur simultaneously have been developed. There are two process models.

##### 14.4.2.1. Single-process models

###### 14.4.2.1.1. Laws issued from the single-process model

With these models, either the nucleation or growth processes occur very rapidly compared to the other. There are two families:

- single-process models with instantaneous nucleation; and
- single-process models with instantaneous growth.



**Figure 14.4.** Appearance of grains of a powder in: a) instantaneous nucleation; and b) instantaneous growth

With instantaneous nucleation models, it is assumed that the entire surface of every grain of A is covered by B from the initial instant, which is then followed by the growth of a layer of B. Looking at the state of the powder during the reaction, we will discover that every grain is in the same state, with a nucleus of A covered by a layer of B (see Figure 14.4a). This layer has the same thickness on every grain, whatever its shape and size.

With instantaneous growth models, each time a growth spot is created over a grain of *A*, it is immediately transformed into *B*. If we look at the state of the powder during the reaction, we have intact grains of *A* and *B* that are fully completed (see Figure 14.4b).

#### 14.4.2.1.2. Principle of the development of instantaneous nucleation models

We will now develop an example of a process that allows instantaneous nucleation in order to approach an easy method that can be extended to other models. In the case of instantaneous nucleation, every grain displays the same behavior over time. It is therefore enough to develop a model for a single grain and apply relation [14.3].

To express the spatial function, we must choose the step that determines the growth. Suppose that this step is diffusion through the solid that is formed: the function space *E* will be given by Table 14.1. We must therefore choose the form of the grains and consider same size of plates (last row in Table 14.1). The kinetic law is written with  $e_0$  being the initial thickness of the plate and  $S_0$  being its initial surface, neglecting the fields:

$$r = \frac{d\alpha}{dt} = \phi \cdot \frac{S_0}{n_0 e} \quad [14.7]$$

If we consider a semi-plate *A* (see Figure 14.5), the initial thickness is  $e_0/2$  and the initial quantity of material is  $n_0 = \frac{S_0 e_0}{2V_{mA}}$ , if  $V_{mA}$  is the molar volume. The internal interface keeps a constant surface area  $S_0$ .

At a time *t* the thickness is *e*, which corresponds to a fractional extent  $\alpha$  for the reaction:

$$\alpha = \frac{2e}{e_0} \quad [14.8]$$

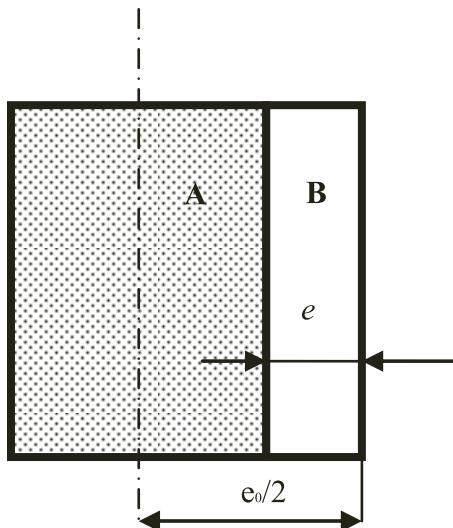
Hence, we get the law:

$$\frac{d\alpha}{dt} = \frac{4\phi V_m A}{e_0^2 \alpha} \quad [14.9]$$

and by integration:

$$\alpha^2 = \frac{8\phi V_M A t}{e_0^2} \quad [14.10]$$

This law is known as Wagner's parabolic law.



**Figure 14.5. Attack of a semi plate**

If the sample is now a powder consisting of the same grains, we can show that with instantaneous nucleation every grain simultaneously has the same behavior and so the law deduced for a single grain can be applied to the whole powder.

#### 14.4.2.1.3. Shapes of curves derived from single-process laws

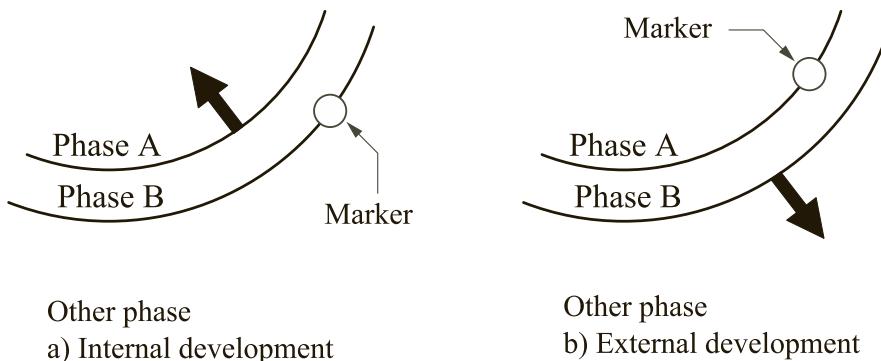
Every law derived from these models involves a process leading to expressions containing only one parameter. This parameter is the reactivity  $\phi$  of the slow

process, even if for nucleation the use of the frequency of surface nucleation  $\gamma$  is preferred, as discussed in section 14.5.5. Graphs of these laws have one of three forms shown in Figure 14.1.a, including constant rates (Figure 14.1.c).

#### 14.4.2.1.4. Data required to define a single-process model

The construction of models has shown that the following data are required to establish the rate law in a single-process model:

- The shape of the grain that defines the shape of the reaction area is required to calculate the space function.
- The direction of growth development. Layer *B* may develop either into *A* (see Figure 14.6.a, internal development) or outward (see Figure 14.7.b, external development). The active surface area will depend on the direction of development. To establish the direction of development a marker is used, such as a thin deposit of gold or wire, placed on a portion of the surface of reactant *A* before the reaction. During the reaction, the microscopic examination of a section allows us to identify the marker position located at interface *A/B* in the case of an external development, or at the external surface of *B* in the case of internal development (see Figure 14.6.b). We can also cut a grain of *A* after a sufficient reaction time if a cavity is found within *A*: this is evidence of external development.



**Figure 14.6.** Development of the new phase: a) internal; and b) external

NOTE 14.2.– Decomposition reactions, such as [14.R2] and polymorphic transformations that involve only a single reactant, always take place with internal development of the new solid phase. Reactions involving two reactants can lead to internal or external development.

Table 14.2, part of which is due to Sharp, summarizes some of the laws involving a single process in the assumption of internal development for powders

made of similar grains. The practice has led each act to be named according to the nomenclature given in the last column. This table is supplemented with models of the determining steps at the external interface. Table 14.3 has been prepared for the case of external developments of the layers formed.

Slow process	Step determining growth	Shape of the grain	Rate law	Name of the Sharp law
Germination	-	Any	$k(1-\alpha)$	F
Growth	Internal interface	Sphere	$k(1-\alpha)^{2/3}$	R3
Growth	Internal interface	Cylindrical rod	$k(1-\alpha)^{1/2}$	R2
Growth	Internal interface	Plane	$k$	R1
Growth	Diffusion	Sphere	$k \frac{(1-\alpha)^{1/3}}{1-(1-\alpha)^{1/3}}$	D4
Growth	Diffusion	Cylindrical string	$k \frac{1}{\ln \frac{1}{1-\alpha}}$	D2
Growth	Diffusion	Plane	$\frac{k}{\alpha}$	D1
Growth	External interface	Sphere	$k$	-
Growth	External interface	Cylindrical string	$k$	-
Growth	External interface	Plane	$k$	-

**Table 14.2.** Morphological laws for a single process for powders with internal development for some types of grains

NOTE 14.3.— We notice the lack of law D3 in Table 14.2. This is in fact law D4, which should have been called D3, but the original table included another law D3 that came from a contracting hypothesis.

Slow process	Step defining growth	Grain shape	Rate law
Growth	Internal interface	Sphere	$k$
Growth	Internal interface	Cylindrical string	$k$
Growth	Internal interface	Plate	$k$
Growth	Diffusion	Sphere	$k \frac{(1+\alpha)^{1/3}}{(1+\alpha)^{1/3} - 1}$
Growth	Diffusion	Cylindrical string	$k \frac{1}{\ln(1+\alpha)}$
Growth	Diffusion	Plate	$\frac{k}{\alpha}$
Growth	External interface	Sphere	$k(1+\alpha)^{2/3}$
Growth	External interface	Cylindrical string	$k(1+\alpha)^{1/2}$
Growth	External interface	Plane	$k$

**Table 14.3.** Morphological laws involving one process for powders with external development and different grain shapes

#### 14.4.2.2. Double-process models

With double-process models, the evolution of both processes over time is taken into account. At time  $t$ , while an existing spot is trying to grow, another spot may be created on an open area of the surface of  $A$  of the same or another grain.

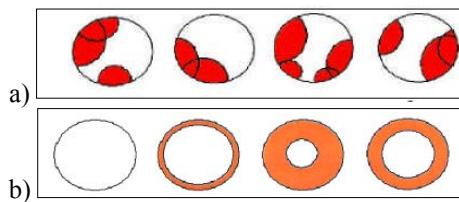
##### 14.4.2.2.1. Two types of growth

With double-process models, two types of growth have been considered and thus two families of models with two processes have been developed, each corresponding to a mode of growth:

- *Anisotropic growth models*: when a spot is formed on a grain, the grain is immediately covered by  $B$ . The tangential growth rate of the new phase is a lot faster than the radial growth rate. If we represent the grains of powder during the reaction, we can simultaneously encounter free and attacked grains of  $A$  at a different level of

growth progression, as well as grains completely transformed into  $B$ , provided the growth reaction time is long enough (see Figure 14.7.a).

– *Isotropic growth models*: for which the growth is the same in all three dimensions so grains of  $B$  are portions of spheres on the surface  $A$  (Figure 14.7b) created from seeds at different times.



**Figure 14.7.** Schematic diagram of a grain: a) isotropic growth; and b) anisotropic growth

#### 14.4.2.2.2. Laws derived from models with two processes

To determine laws derived from these models within the scale of the growing spot, we still use relationship [14.3] expressing  $E$  from Table 14.2. The difficulty is greater, however, because we must estimate the total area of internal interfaces on the set of nucleus being grown on all grains as shown in Figures 14.7a and 14.7b. It is in the calculation of these areas that the second parameter of nucleation appears and therefore the laws obtained are for two parameters whose values are determined by temperature and the partial pressures of gases.

Consider a growing spot created at time  $t$ . At an instant  $t$  subsequent to  $\tau$ , its growth rate will be:  $r_g(\tau, t)$ . Between instants  $\tau$  and  $\tau + d\tau$ , however, new growth spots are born:  $\Gamma(\tau)d\tau$ , if  $\Gamma(\tau)$  is the frequency of nucleation (number of spots produced per time unit). The reaction rate due to the growth at instant  $t$  will be:

$$r(\tau, t) = \Gamma(\tau)r_g(\tau, t) \quad [14.11]$$

New growth spots can be created at any time between 0 and  $t$ , thus in order to express the reactance of the reaction, it is necessary to integrate the previous expression:

$$r(t) = \frac{1}{n_0} \int_0^t \Gamma(\tau) r_g(\tau, t) d\tau \quad [14.12]$$

In this expression,  $r_g(\tau, t)$  is the contribution of a spot created at time  $\tau$  to the growth rate.

We will see later (section 14.6) that if  $\gamma$  and  $S_L(\tau)$  respectively represent the frequency of the surface nucleation (independent of time in a pseudo-steady state mode) and the spatial function of nucleation (which is the area of the free surface of solid  $A$ ), the frequency of nucleation is always:

$$\Gamma(\tau) = \gamma S_L(\tau) \quad [14.13]$$

Expression [14.12] becomes:

$$r(t) = \frac{1}{n_0} \int_0^t \gamma S_L(\tau) r_g(\tau, t) d\tau \quad [14.14]$$

Moreover, if growth is given by [14.3] and  $e_p$  is the growth space function of the spot,  $t$  the time function,  $\tau$  the age of the spot, and  $\phi$  its reactivity that will only be a function of the intensive physico-chemical parameters if the system evolves at constant temperature and partial pressures; the growth rate is:

$$r_g(\tau, t) = \phi(t) e_p(\tau, t) \quad [14.15]$$

$e_p$  is given in the last column of Table 14.1, according to the location of the rate-determining step and the development orientation of the new solid phase. Therefore:

$$r(t) = \frac{\phi}{n_0} \int_0^t \gamma S_L(\tau) e_p(\tau, t) d\tau = \phi E \quad [14.16]$$

Growth has a separable rate, which is also the case of the global reaction so in the generic case the space function is:

$$E = \frac{1}{n_0} \int_0^t \gamma S_L(\tau) e_p(\tau, t) d\tau \quad [14.17]$$

This measure corresponds to the total active area calculated for all the grains of the powder.

The previous development assumes that each powder grain takes part in the reaction, which is true as long as the powder does not contain completely transformed grains. Indeed, grains that are fully transformed at time  $t$  are no longer available to take part in the reaction. A grain that has nucleated at the initial time will be fully transformed at time  $t_f$ , required for the grain transformation. At a time  $t$  larger than  $t_f$ , every grain that has nucleated before time  $t - t_f$  is fully transformed. Hence the previous relations must be divided into two relations:

- if  $t < t_f$ , we can apply [14.16]; and
- if  $t > t_f$ , we will replace it with:

$$r(t) = \frac{\phi}{n_0} \int_{t-t_f}^t \gamma S_L(\tau) e_p(\tau, t) d\tau \quad [14.18]$$

If the physico-chemical variables (temperature and partial pressures of gases) are kept constant throughout the reaction, the frequency of nucleation  $\gamma$  no longer depends on time and the term can be removed from the sum sign.

In the general case of nucleation growth, the rate function [14.16] or [14.18] does not give a general shape to the curves giving fractional extent versus time. We must deal with individual cases to examine the shape of these curves.

In most cases, these laws lead to kinetic curves with an inflection point (S-curves), as shown in Figure 14.2.b. The corresponding rate curve (Figure 14.2.d) will be at a maximum.

The establishment of two-process models requires the same data as for single-process models (grain shape and orientation of the layer development) by adding the chosen mode of growth (isotropic or anisotropic). Note that in models involving an instantaneous nucleation process, the growth is anisotropic by default.

#### 14.4.2.3. Example of a law including two processes

We consider the case of a powder made of wafers with the same surface area  $S_0$ . We assume that the growth is anisotropic and determined by a reaction occurring at the internal interface with a constant area  $S_0$  (neglecting the fields of the wafer). To apply relations [14.16] and [14.18], we must determine functions  $S_L(\tau)$  and  $e_p(t, \tau)$  as well as the limit time  $t_f$ .

Table 14.1 immediately gives us the growth space function in the case of a wafer. This function does not depend on the time or the age of the growing spot:

$$e_p = \frac{S_0}{n_0} \quad [14.19]$$

The growth rate of a grain that has nucleated is:

$$r_g = \phi e_p = \phi \frac{S_0}{n_0} = \phi \frac{V_{mA} S_0}{e_0 S_0} = \phi \frac{V_{mA}}{e_0} \quad [14.20]$$

For a growing spot born at time  $\tau$ , the kinetic law will therefore be:

$$\alpha = \phi \frac{V_{mA}}{e_0} (t - \tau) \quad [14.21]$$

The time taken to consume a grain is the time taken for the fractional extent to reach one unit:

$$t_f = \frac{e_0}{\phi V_{mA}} \quad [14.22]$$

To calculate the area  $S_L$  still available for nucleation at time  $\tau$ , we denote by  $N$  the number of grains not yet attacked at the time  $\tau$ . Since every grain attacked at  $\tau$  is coated with a layer of solid  $B$ , the free surface of nucleation will be given by the product of the area of a grain at the initial time by the number  $N$  free grains.

$$S_L = N S_0 \quad [14.23]$$

Between times  $\tau$  and  $\tau + d\tau$ , however, the decrease in the number of free grains is given by the nucleation frequency:

$$dN = -\gamma N S_0 d\tau \quad [14.24]$$

By integration between times 0 and  $\tau$ , for which the number of free grains are  $N_0$  and  $N$ , respectively, we have:

$$N = N_0 \exp(-\gamma S_0 \tau) \quad [14.25]$$

The available nucleation area is therefore:

$$S_L = N_0 S_0 \exp(-\gamma S_0 \tau) \quad [14.26]$$

The initial number of grains,  $N_0$ , is related to the initial amount of reactant  $A$ , per grain  $n_0$  by the relation:

$$N_0 = \frac{\{A\}_0}{n_0} \quad [14.27]$$

hence the area of the free surface of nucleation is:

$$S_L = \frac{\{A\}_0 S_0}{n_0} \exp(-\gamma S_0 \tau) \quad [14.28]$$

Taking into account [14.20], we express [14.19] and [14.28] in [14.17] and:

- If  $t < \frac{e_0}{\phi V_{mA}}$ :

$$\begin{aligned} r(t) &= \frac{\phi \gamma \{A\}_0 V_{mA}^2}{2e_0^2} \int_0^t \exp(-\gamma S_0 \tau) d\tau \\ &= \frac{\phi \{A\}_0 V_{mA}^2}{2e_0^2 S_0} [1 - \exp(-\gamma S_0 t)] \end{aligned} \quad [14.29]$$

- If  $t > \frac{e_0}{\phi V_{mA}}$ :

$$r(t) = \frac{\phi \{A\}_0 V_{mA}^2}{2e_0^2 S_0} \left[ \exp\left(-\frac{\gamma S_0 e_0}{\phi V_{mA}}\right) - \exp(-\gamma S_0 t) \right] \quad [14.30]$$

Functions [14.29] and [14.30] lead to a curve with a maximum whose position depends on the initial area, the plate thickness and the ratio of  $\phi/\gamma$ .

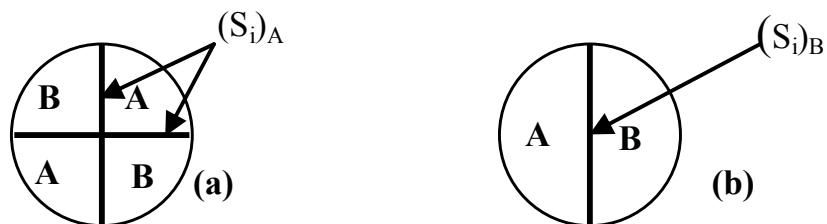
Unlike the case we have just discussed, in most cases the integrals cannot be calculated algebraically and we must be content with rate laws defined by the integrals that are calculated numerically.

In conclusion, we see that many laws are available to account for the function space, which is the rate variation over time in isothermal and isobaric conditions. While it is still difficult to attribute a model to a particular family of reactions, we notice that all the oxidation reactions of a metal (such as [14.R4]) are modeled by single process, which is perfectly logical because it is extremely difficult to carry out experiments in areas that are completely free of metal oxide traces. We also notice that the reactions between solids, such as [14.R5], are also frequently modeled in a single process, since in this case there is fast diffusion on the surface of the grains that are in contact with each other. On the other hand, most decomposition reactions, such as [14.R2], are modeled with two processes; although in some cases the maximum rate of curve 14.2c is quite near to the origin.

#### 14.4.2.4. Influence of sample history on rate

From equations [14.16] and [14.18], we notice that the rate at a given time is not fixed by values of physico-chemical variables, time and extent at this time. As a result of the process of nucleation, the rate depends on the history of the sample, particularly the partial pressures and temperatures that prevailed at the beginning of the reaction that set the surface frequency of nucleation. The reaction extent is no longer a variable of the rate. This phenomenon does not occur in models with one process, for which the fractional extent is enough to fix the rate at given conditions of pressure and temperature, whatever the previous values of these variables.

To illustrate this we will consider the case of a pseudo-steady state mode of growth that is defined, for example, by an elementary step taking place at the internal interface and that develops internally.



**Figure 14.8.** Influence of the sample history on rate for a given state of progress: a) under fixed conditions; and b) under other conditions where the grain's nucleation and growth rate have different values

Figure 14.8a illustrates the configuration of a grain obtained under fixed conditions (in order to visualize the surface areas, plane interphase surfaces are represented). The grain is characterized by certain areas of the interphase surface ( $(Si)_A$ ) coming from the growth of two growing spots of  $B$ .

Figure 14.8b shows a diagram of a grain initially identical to the previous one at the same fractional extent (same volume of the new phase formed), but obtained in other conditions for which the specificity of the grain's nucleation and growth rate had different values. In this figure, we can see only one growing spot of  $B$  instead of two.

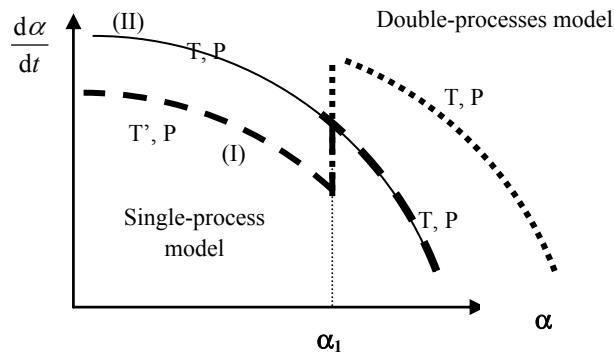
Consequently, the interfacial area ( $Si)_B$  is half the size of the previous case. If this grain was instantly placed in the same development conditions as the grain in Figure 14.8a, the growth reactivity and nucleation frequency of the grain in Figure 14.8b would have had the same values as in a. The space function being half, however, the rate at which the product is formed will be halved compared to the Figure 14.8a. Thus, with nucleation growth it is not possible to characterize the rate in the conditions given by the fractional extent, temperature and partial pressures. The rate depends on the history of the sample.

#### **14.4.3. Experimental research on the type of morphological model**

It is experimentally useful to know whether the search for a morphological model should be directed towards single- or double-process models. We have seen that in the case of a single-process model the rate at a given time depends on the values of variables at that moment, while in a nucleation growth with two processes the previous evolutions of these variables affect the rate, i.e. the rate depends on the history of the system. It is this property that we will use to choose the family of models suitable for the reaction being studied.

A first experiment is carried out under conditions  $T$   $P$  to obtain the rate curve I (see Figure 14.9). A second experiment was started under conditions  $T'$ ,  $P$  with a different temperature from the initial one and gives curve II. The switch method is then applied at a certain stage to restore  $T$  and  $P$  conditions. Two cases may occur:

- after the switch, the rate curve joins the curve obtained with the same initial  $T$  and  $P$  conditions; hence a single-process model will be enough since the speed of conditions ( $T$ ,  $P$ ) does not depend on previous conditions; or
- after the switch, the rate curve deviates from curve I; a double-process model will be necessary here because the rate conditions ( $T$ ,  $P$ ) depend on the previous conditions.



**Figure 14.9.** Test principle for selecting the family of morphological patterns

## 14.5. The nucleation process

### 14.5.1. Description of the nucleation process

Nucleation occurs by agglomeration of point defects on the surface of solid *A*. This nucleation will require two stages: the creation of point defects and their agglomeration.

For example, during the dehydration of a salt to give a solid anhydrous salt, such as:



both processes would lead to the following in the growing spot:

– Formation of water molecule vacancies in the initial hydrate as loss of water in its gaseous state results in non-stoichiometric hydrate, considered a solution of vacancies in the solid and having the structure of the hydrate. This process can be represented by the quasi-chemical equation:

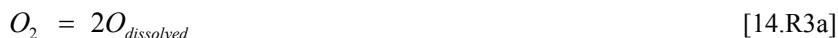


– Precipitation of the second phase by the disappearance of *n* vacancies:



In this quasi-chemical relation, the zero value of the second member represents the presumably perfect new phase.

With the example of a gas–solid reaction, like the formation of an oxide by reaction of gaseous oxygen with a metal, the first stage would be the dissolution of oxygen in the metal:



The second step is the oxide formation:



We see from these examples that the nucleation can always be split into two groups of steps:

- the defect formation in the initial solid, which will be the precursor of the nucleation; and
- the precursor condensation on the surface of the initial solid.

#### 14.5.2. Thermodynamics of nucleation

Here we consider the nucleation model and assume that precursors and their associations are dissolved in solid  $A$  up to a certain level of aggregation that will be the basis of the growing spot, which we assume to be a pure solid in its phase. These aggregates are so small and contain so few atoms, however, that we must take the surface factor into account in the Gibbs free energy function as the product of the variation of the area by its associated measure, which is the surface tension  $\gamma_i$ .

Where  $S$  is the oversaturation of defects in  $A$ , we obtain the following ratio for global reactions such as [14.R1]:

$$S = \frac{\prod_G P_G^{V_G}}{K} = \frac{\prod_G P_G^{V_G}}{\exp\left(-\frac{\Delta G^\circ}{RT}\right)} \quad [14.31]$$

NOTE 14.4.– The definition of  $S$  allows us to link oversaturation to the distance from equilibrium  $\varepsilon$ :

$$1 - \frac{1}{S} = \varepsilon \quad [14.32]$$

Where  $\Delta_{X,i}(G)$  is the condensation free enthalpy linked to the formation reaction of one mole of aggregate each containing  $i$  building units of  $A$ , this is the free enthalpy change associated with reaction:



We can write:

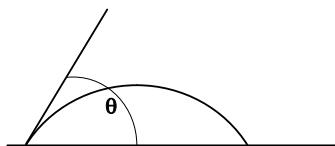
$$\Delta_{X,i}(G) = \Delta_{X,i}(G)_{chem} + \gamma_s \cdot \Delta_{X,i}(\sigma) \quad [14.33]$$

From [14.29], if  $N_a$  is Avogadro's number, we have:

$$\Delta_{X,i}(G)_{chem} = -i \frac{RT}{N_a} \ln(S) \quad [14.34]$$

If the growing spot was a sphere, its surface would be  $4\pi r^2$  and its volume  $4\pi r^3/3$ . If  $V_m$  is the molar volume of  $B$ , the radius of a spot containing  $i$  molecules would be:

$$r = \left( \frac{3V_m i}{4\pi N_a} \right)^{1/3} \quad [14.35]$$



**Figure 14.10.** Nucleation of a drop at the surface

If the spot was a drop shaped as a spherical cap as shown in Figure 14.10, the meniscus would show an angle  $\theta$  with the plane, and the radius would be:

$$r = \left( \frac{3V_m i}{4\pi N_a} f_{het} \right)^{1/3} \quad [14.36]$$

where  $f_{het}$  is a measure related to the cosines of the angle  $\theta$  by:

$$f_{het} = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} = \frac{(2 + p)(1 - p)^2}{4} \quad [14.37]$$

and  $p$  is the spreading parameter between  $-1$  and  $+1$ .

In the case of a solid spot, we can still define a spreading coefficient  $f_{het}$  linked to a spreading parameter  $p$  as a function of interfacial tension, always between  $-1$  and  $+1$ .

The area of the spot will be:

$$\sigma = 4\pi \left( \frac{3V_m i}{4\pi N_a} f_{het} \right)^{2/3} \quad [14.38]$$

Incorporating [14.32] and [14.33] in [14.31], for the free enthalpy per mole we have:

$$\begin{aligned} \Delta_{A,i}(G) &= -iRT \ln(S) + \left( 36\pi\gamma_s V_m^2 N_a f_{het} \right)^{1/3} i^{2/3} \\ &= -ai + bi^{2/3} \end{aligned} \quad [14.39]$$

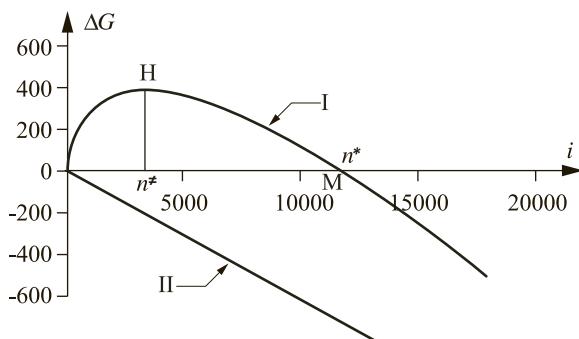
By canceling the derivation, we see that function  $\Delta_{A,i}(G) = f(i)$  admits a maximum value at the coordinates:

$$\left\{ \begin{array}{l} n^* = \frac{32\pi N_a}{3} \frac{\gamma_s^3 V_m^2}{(RT \ln S)^3} \end{array} \right. \quad [14.40]$$

$$\left\{ \begin{array}{l} \Delta_{A,n^*}(G) = \frac{16\pi N_a}{3} \frac{\gamma_s^3 V_m^2}{(RT \ln S)^2} = \frac{n^*}{2} RT \ln(S) \end{array} \right. \quad [14.41]$$

Curve I in Figure 14.11, which gives the representation of [14.38], is called the Volmer curve.

According to [14.41], the maximum ordinate is even smaller when the equilibrium conditions (excluding superficial phenomena) are exceeded (when  $S$  or  $\epsilon$  are large), and this ordinate is cancelled at conditions far from equilibrium ( $S$  infinite), i.e. never.



**Figure 14.11.** Nucleation free enthalpy as a function of the size of the growing spot

As well as the maximum H, point M is also noticeable on this curve and corresponds to an aggregate of size  $n^*$  so that the free enthalpy associated with the condensation reaction of one mole of aggregate is zero and becomes negative:

$$i = n^* = 36\pi N_a \frac{\gamma_s^3 V_m^2}{(RT \ln(S))^3} \quad [14.42]$$

Before M, the associated free enthalpy is positive; whereas it is negative for large sizes.

When the size of the spot grows, curve I tends toward curve II, which represents function [14.46] when the surface parameters are neglected.

The size of the spot will be the size at which we switch from the nucleation process, which considers surface parameters, to the growth process that neglects them (following curve II in Figure 14.11) but considers both interfaces.

Curve I shows that a new growth spot cannot be formed before point M as the free enthalpy value is positive.

It is accepted that the nucleation process ends at point M and that the size of the growth spot is  $n^*$ . We will see that we are not allowed to choose point H in the mechanism, since positive free enthalpy has to be chemically driven by other negative free enthalpies so that the overall reaction free enthalpy is negative. Point M is the first point at which these conditions are required.

#### 14.5.3. *The nucleation mechanism*

In section 14.6.1, we saw that the nucleation process involves two stages, each of them including elementary steps occurring on the whole surface of the solid *A*. The respective rate will therefore have the same space function. We will examine the type of elementary steps that could describe these two stages.

##### 14.5.3.1. *Formation of one or several precursors*

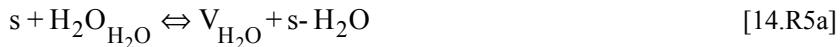
The formation of precursors, which are point defects, will take place during various elementary steps occurring at the interface between the initial solid and a surrounding phase. If gases are involved, chemisorption or desorption processes are also occurring at the surface of the solid.

The formation of an anhydrous salt from its hydrated form will pass via the formation of water vacancies, for example, according to the following process:



This reaction can be split into two steps equivalent to elementary steps:

– the vacancy formation with the chemisorbed water at the gas–solid interface area:



– desorption of water at the solid surface:



We see that the two areas where the two steps take place will always be the same size during the system evolution, even if these areas vary over time. This is valid for any precursor formation at the surface.

#### 14.5.3.2. Precursor condensation

Condensation is the increase of the aggregates' dimensions by the addition of precursors. This reaction occurs on the homogeneous phase of the solid and is comparable to a polymerization reaction.

The condensation of precursors (defects previously created) will happen in the region where they are present at their highest amount, which is at the area of formation. With defects created at the surface, condensation will occur inside the initial solid close to the interface. Thus, condensation only occurs in one area and in the case where the dimensions remain the same as those involved in the precursor formation. The nucleation process occurs in several areas, but the dimensions of these areas always remain equal to each other over the time during which the system evolves. Everything that occurs is the same as if a single area was involved.

It is accepted that condensation is a succession of elementary steps, each of them adding a building unit to the aggregate that follows the addition of a precursor.

There are two types of condensation:

- simple condensation with precursors; and

- condensation of precursors at specific points located within the solid (or at the surface), which are called potential growth spots. These potential spots are limited in number. They are progressively consumed by the nucleation and no new ones are generated. The solid is closed in relation to these potential spots, whereas it is often open in relation to other precursors. These potential sites can often be of a different nature: they can be specific energy points of the solid, dislocations, grain boundaries or foreign species (impurities) dissolved in the solid.

##### 14.5.3.2.1. Simple condensation

We consider the following reaction:



Precursor  $X$  is in a sequence of steps from [14.R6b] to [14.R6n\*]. Entities of the precursor will attach to each other (excluding reactions between two aggregates of dimensions greater than one).

To highlight the fact that the last step results in a new phase, we add the term  $B$  (unit activity). The mechanism is represented by the following:





#### 14.5.3.2.2. Condensation of potential growth spots

Entity  $X_1$  is the potential growth spot that is used as the groundwork to attach the second entity, which is the precursor  $X$  (step [14.R6a]). Molecules of precursor  $X$  successively attach to each other to increase the dimensions of the growing spot (steps [14.R6b] to [14.R6*n*<sup>\*</sup>]) until the production of  $B$ , when the spot enters the growth stage after reaching size  $n^*$ .

Precursor  $X$  is formed from the production stage as with simple condensation; hence the solid is closed in relation to  $X_1$  and open in relation to  $X$ :



#### 14.5.4. The nucleation rate

Only the mechanism of simple condensation will be presented here. This will introduce a method that is also applicable to the potential mechanism of spot growth.

First, looking at steps of the mechanism we see that in order to obtain the overall reaction and form  $v_B$  moles of  $B$ , all the steps must be multiplied by the common multiplying coefficient:

$$\lambda = \frac{v_B}{n^*} \quad [14.43]$$

The nucleation reaction [14.R1] has the same global equation as the transformation reaction. We define the rate of nucleation as the rate in relation to the newly-formed solid  $B$ .

The rate coefficients of step  $i$ :  $k'_i$  and  $k''_i$  are such that their ratio is the equilibrium constant of step  $i$  and we can write:

$$\begin{aligned} K_i &= \frac{k'_i}{k''_i} = \exp\left(-\frac{\Delta_{i-1,i}(G^0)}{RT}\right) \\ &= \exp\left(-\frac{\Delta_{X,i}(G^0) - \Delta_{X,i-1}(G^0)}{RT}\right) \end{aligned} \quad [14.44]$$

The overall equilibrium constant of the condensation is given by:

$$K = \prod_{i=2}^{n^*} \left( K_i \right)^{v_B/n^*} \quad [14.45]$$

The reactivity of step  $i$  is:

$$\phi_i = k'_i x_i x_{i-1} - k''_i x_i \quad [14.46]$$

By applying relations [14.3] and [14.42], the superficial rate of condensation will be:

$$\phi_{nucl} = \frac{\phi_{n^*}}{\lambda} = \frac{\phi_{n^*} n^*}{v_B} \quad [14.47]$$

To reach this rate, we must calculate the reactivity of the last step. Using [14.44], we can write the reactivity of the current step:

$$\phi_i = k''_i (K_i x_i x_{i-1} - x_i) \quad [14.48]$$

or if expressing the Gibbs free energy:

$$\phi_i = \frac{n^*}{v_B} k''_i \left[ \exp\left(-\frac{\Delta_{X,i}(G)}{RT}\right) \right] \left(1 - \frac{1}{S}\right) \quad [14.49]$$

We will assume that the activation energy of the reverse of a reaction step does not depend on the rank of this step, but it is in fact the bond breakage between a promoter and agglomerate, which is more likely with increasing  $i$ . If  $a$  is the length of the order of magnitude of the network of initial solid  $A$ , the surface rate coefficient of the reverse reaction can be written:

$$k''_i = \frac{kTa}{h} \exp - \frac{E_i}{RT} = \frac{kTa}{h} \exp - \frac{E^\neq}{RT} \quad [14.50]$$

If we consider a pseudo-steady state mode and we chose a step resulting in the maximum of the Volmer curve as the determining step, the surface rate of the last step is:

$$\begin{aligned} \phi_{n^*} &= \phi_{[n^*]} \\ &= \frac{n^* a}{v_B} \frac{RT}{N_a h} \exp\left(-\frac{E^\neq}{RT}\right) \left[ \exp\left(-\frac{16\pi f_{het} N_a \gamma_s V_m^2}{3(RT)^3 [\ln(S)]^2}\right) \right] \left(1 - \frac{1}{S}\right) \end{aligned} \quad [14.51]$$

Incorporating [14.51] into [14.47], the rate of nucleation can be expressed knowing that nucleation occurs on the free surface of solid  $A$  of area  $S_L$  at moment  $t$ :

$$r_{nucl} = \phi_{nucl} E_{nucl} = \phi_{nucl} \frac{S_L}{n_0} \quad [14.52]$$

NOTE 14.5.– Some authors calculate the nucleation rate using the Volmer curve as the energy curve of an elementary step (see Figure 14.2.b) with the activation energy of the ordinate maximum. This approach is incorrect, as we cannot accept that a process that involves a large number of chemical bonds can be considered elementary.

In the previous calculation, we assumed the existence of a rate-determining step. Considering the close proximity of each step, it is difficult to believe that one of the steps will have a rate coefficient well below those of all the others. Hence the pseudo-steady state mode is often accepted as a mode in which all stages of the agglomeration are rate-determining. The rate of such a mode can be calculated using the law of slowness using the same space function for all steps because these steps have the same multiplying coefficient given by [14.43] and belong to the same linear sequence.

With this model, the steps of the first stage of the promoter formation are always in equilibrium; their rate coefficients are taken to be infinitely larger than those of the stages of agglomeration. Using [14.51], we can therefore write:

$$\begin{aligned} \frac{1}{\phi_{n^*}} &= \sum_{i=2}^{n^*} \frac{1}{\Phi_{[i]}} \\ &= \frac{v_B h}{n^* a k T \left(1 - \frac{1}{S}\right)} \exp\left(+\frac{E^\neq}{RT}\right) \sum_{i=2}^{n^*} \left[ \exp\left(+\frac{\Delta_{X,i}(G)}{RT}\right) \right] \end{aligned} \quad [14.53]$$

A laborious calculation that is not reproduced here leads to:

$$\phi_{n^*} = \frac{n^* a (RT)^{5/2}}{8\pi v_B N_a^{3/2} h} \cdot \frac{[\ln(S)]^2}{\gamma_s^{3/2} V_m} \cdot \left[1 - \frac{1}{S}\right] f_{het}^{-1/2} \exp\left(-\frac{16\pi N_a \gamma_s^3 V_m^2 f_{het}}{3(RT)^3 [\ln S]^2}\right) \exp\left(-\frac{E^\neq}{RT}\right) \quad [14.54]$$

Hence, with the pseudo-steady state mode, the surface rate is a complex expression as a function of intensive variables. In this expression, we see the term of the distance from actual conditions to the equilibrium emerging as in [14.32]. The temperature appears in both the activation exponential and the standard Gibbs free energy of the reaction in oversaturation (see expression [14.31]). The partial pressures of reactant gases or reaction products appear as one power law in the expression of oversaturation (see expression [14.31]). The control experiments are done keeping  $S$  as a variable. We notice that the variable gas pressures and temperatures are not separated.

With the pseudo-steady state mode, when experiments are performed at constant temperatures and partial pressures of various gases, the areal rate of nucleation is independent of time and only the variations in surface area  $S_L$  (see relation [14.52]) will vary with time due to nucleation, and also growth.

More complex models for non-pseudo-steady state modes have been proposed, but there are no experimental means specific enough to determine the nucleation rate that would decide between such complex expressions.

#### 14.5.5. Surface and nucleation frequencies

Since the amounts of materials involved with nucleation are often very low, we prefer to use the nucleation frequency  $\Gamma$  instead of the rate, which is the number of

growing spots created per time unit as well as the surface nucleation frequency  $\gamma$ . If  $n_0$  is the amount of reference material and  $n^*$  the dimension of the stable growth spot (in numbers of elementary units), we have:

$$\Gamma = \frac{v_B r_{nucl} \cdot n_0 \cdot N_a}{n^*} = \frac{v_B \phi_{nucl} \cdot S_L \cdot N_a}{n^*} \quad [14.55]$$

and the surface frequency of nucleation becomes:

$$\gamma = \frac{\Gamma}{S_L} = \frac{v_B N_a \phi_{nucl}}{n^*} \quad [14.56]$$

Thus, the specific frequency has the same variables as the surface rate of nucleation, which are the temperature and partial pressure via oversaturation. The pseudo-steady state modes leads to surface frequencies of nucleation independent of time with isothermal and isobaric conditions.

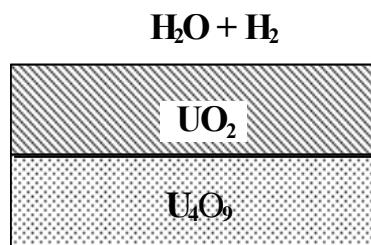
#### 14.6. Physico-chemical growth models

As part of the separable rate and therefore the application of relation [14.3], physico-chemical modeling can be applied to growth. As with homogeneous kinetics, it is the establishment of a mechanism that defines the reaction steps and areas where they occur. Intermediate compounds are formed and consumed during these intermediate steps. Since Wagner's work on the oxidation of metals by gaseous oxygen, it has been assumed that these heterogeneous kinetic intermediates are usually both adsorbed species and point defects in the solid phases, so the basic steps are those of adsorption, desorption, chemical reactions near interfaces and diffusion in solids. From this, we calculate the areal rate of growth versus partial pressures and temperature. Since we have separated the morphological models, we can consider plane interfaces of constant area units for physico-chemical models. This defines equation  $\phi$  of the reactivity as a function of the partial pressure of gases, concentrations in the solid phases with several components and the temperature. We have seen the example of the magnesium oxidation reaction involving oxygen vacancies in Chapter 8, section 8.1.5.2.

We will now examine the case of the growth mechanism of uranium reduction reaction by hydrogen [14.R7], which involves interstitial oxygen as a point defect. The physico-chemical modeling of  $\phi$  does not depend on the morphological model as long as both approaches are addressed with the same direction of development of the formed solid and the same location of the determining step:



Figure 14.12 gives the location of the various phases during growth.



**Figure 14.12.** Relative positions of the phases during the reduction of  $\text{U}_4\text{O}_9$  by hydrogen

The reaction takes place in five steps. Three of these steps [14.R7a], [14.R7b] and [14.R7c] occur at the external interface (between hydrogen and uranium dioxide). The fourth step is diffusion [14.R4d] and the last and fifth step is [14.R7e].

The first step is the dissociative adsorption of hydrogen on a surface site of the dioxide formed:



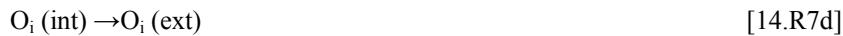
The second step is the use of interstitial oxygen coming from the internal interface (see steps [14.R7d] and [14.R7e]) to form hydroxides:



The third step is desorption of water:



The fourth step is the diffusion of interstitial oxygen ion from the internal interface to the external interface (step [14.R4d]):



The last step involves the oxygen ion passing from the oxide network to the dioxide, which leaves an oxygen vacancy, destabilizes the network and causes the phase change:



The dioxide network is built at the internal interface with inside development.

With this model, as we done in section 8.1.5, we could deduct five of pseudo-steady state solutions with a single rate-determining step.

#### 14.7. Conclusion on heterogeneous reactions

The kinetics of heterogeneous reactions are much more complex to interpret than homogeneous reactions. We notice, however, that within the scope of pseudo-steadiness, the validity of the relation of  $\phi E$  (relation [14.3]) is fundamental. It has allowed us to decouple the modeling and to understand a mechanism considering four models:

- the morphological model of growth, which allows us to express the growth space function  $E(\phi, \gamma, t)$ ;
- the physico-chemical model of growth, which allows us to establish the growth reactivity function  $\phi(P_G, T)$  and is dealt with in the same way as a homogeneous reaction mechanism;
- the morphological model of nucleation, which allows us to determine function  $S_L(\tau)$ ; and
- the physico-chemical model of nucleation, which allows us to express function  $\gamma(P_G, T)$  and is also dealt with using homogeneous reaction kinetics methods and considering the thermodynamic influences of the surfaces.

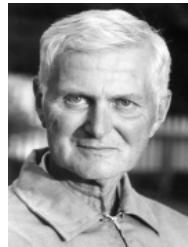
Note that these four models are not completely independent and one hypothesis must be shared between them. For example, both growth models must recognize the same rate-determining steps and the same direction of layer development.

Finally, the application of the same relation [14.3] limits us to growth modeling considering pseudo-steady state modes and a single rate-determining step.

#### 14.8. Important figures in reaction kinetics

Carl Wagner in association with Schottky proposed the point defect-mediated mechanism of mass transport in solids, which Wagner extended to the analysis of electronic defects. For these works and Wagner's subsequent research on local equilibrium, his oxidation rate theory and the concept of counter diffusion of cations, he is considered by some to be the "father of solid state chemistry".

The German chemist Max Volmer made important contributions in electrochemistry, particularly in electrode kinetics. He co-developed the Butler-Volmer equation, which formed the basis of phenomenological kinetic electrochemistry, and discovered the migration of adsorbed molecules, known as Volmer diffusion.



**Prof. Carl Wagner**  
(1901-1976)



**Prof. Max Volmer**  
(1885-1965)

**Figure 14.13. Important chemists**



## Chapter 15

# Kinetics of Non-pseudo-steady State Modes

So far we have concentrated on the study of reactions occurring in a pseudo-steady state mode. Obviously, such a state mode cannot exist throughout the entire reaction. At the beginning of the reaction, the amount of intermediate species starting from zero value must increase. Similarly, at the end of the reaction, for these quantities to become zero they must decrease. During both periods the state is not pseudo-steady as the reaction takes place in the transitory state.

For many reactions, these two periods are short enough, with only very small variations in the extent of the reaction, to be neglected.

In some cases, however, these transitory periods cannot be neglected and a kinetic law that does not correspond to the one deduced with the pseudo-steady state is observed for a significant reaction extent, even if the state tends toward a pseudo-steady state. We will study the example of the paralinear law, which is sometimes obtained during the oxidation of metal plates.

Finally, other reactions are such that they can never reach the pseudo-steady state mode. This is true of those that lead to explosions or ignition. We will see the two classes of systems that can be attributed to these reactions: thermal explosions and branched chain reactions with a positive branching factor.

### 15.1. Partial pseudo-steady state modes

A partial pseudo-steady state mode is a state in which certain intermediates are not pseudo-steady while others are. Such state modes may be treated as several

successive reactions, each following a pseudo-steady state mode and characterized by its own extent and rate.

To illustrate such a state, we will consider reaction [15.R1] in the gas phase and at constant volume, for which the mechanism is given by steps [15.R1a] to [15.R1d] with the rate coefficients  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$ , respectively. The intermediate  $M$  is more stable than others and it is assumed the state mode is pseudo-steady for intermediates  $X_1$  and  $X_2$  but not for  $M$ :



We write the pseudo-steadiness for  $X_1$  and  $X_2$ :

$$\frac{d[X_1]}{dt} = k_1[A] - k_2[X_1][B] = 0 \quad [15.1]$$

$$\frac{d[X_2]}{dt} = k_3[M][B] - k_4[X_2][B] = 0 \quad [15.2]$$

We deduce the intermediate concentrations:

$$[X_1] = \frac{k_1[A]}{k_2[B]} \quad [15.3]$$

$$[X_2] = \frac{k_3[M]}{k_4[X_2]} \quad [15.4]$$

We now write the result for the non-pseudo-steady intermediate  $M$ :

$$\frac{d[M]}{dt} = k_2[X_2][B] - k_3[M][B] = 0 \quad [15.5]$$

The solution to equation [15.5] with the initial condition  $[M] = 0$  at the start is:

$$[M] = \frac{k_1[A]}{k_3} \left\{ 1 - \exp(-k_3[B]t) \right\} \quad [15.6]$$

It is then possible to calculate every concentration as a function of time.

We can also consider that we are dealing with two successive reactions [15.R2] and [15.R3], both of which are pseudo-steady. The first reaction produces  $M$  and the second produces  $C$  from  $M$ :



The first reaction has two steps with an intermediate  $X_1$  and a rate  $v_1$ . The second reaction has also two steps, an intermediate  $X_2$  and a rate  $v_2$ .

We have:

$$\frac{d[M]}{dt} = v_1 - v_2 \quad [15.7]$$

and can calculate:

$$v_1 = k_1[A] \quad [15.8]$$

$$v_2 = k_3[M][B] \quad [15.9]$$

The concentrations of the reactants and products follow:

$$\frac{d[A]}{dt} = -v_1 \quad [15.10]$$

$$\frac{d[B]}{dt} = v_1 - 2v_2 \quad [15.11]$$

$$\frac{d[C]}{dt} = v_2 \quad [15.12]$$

### 15.2. The paralinear law of metal oxidation

Some of the state modes involving two rate-determining steps (mixed) do not compel pseudo-steadiness on all of the intermediate species. This is especially the case with mixed state modes that are not pseudo-steady on an intermediate. We will examine this case in order to develop the method and show that the pseudo-steady state mode appears to be the limit when time tends to infinity. Our goal is not to establish general relations but to explain the procedure to be adopted.

For our example, we will consider reaction [15.R4] with a simple linear reaction scheme involving four steps and three intermediates, which is described by the mechanisms in steps [15.R4a] to [15.R4d]:



We assume that we have mixed kinetics between steps [15.R4b] and [15.R4c] that have set rate constants; the other steps with infinite rate constants are constantly at equilibrium. The reaction is performed at constant concentrations. The equilibrium of the step preceding [15.R4b], which is [15.R3a], allows us to calculate:

$$[X_1] = K_1[A] \quad [15.13]$$

With equilibrium, step [15.R1d] that follows [15.R4c] allows us to calculate:

$$[X_3] = \frac{[C]}{K_4} \quad [15.14]$$

The rate in relation to  $A$  is set by the steps consuming the main reactant  $A$ , in this case step [15.R4a]:

$$r_A = \phi_1 E_1 \quad [15.15]$$

We now assume that any amount of materials is pseudo-steady, with the exception of  $X_2$ ; then follows:

$$\phi_1 E_1 = \phi_2 E_2 \quad [15.16]$$

and:

$$\phi_3 E_3 = \phi_4 E_4 \quad [15.17]$$

The rate can therefore be written:

$$r_A = \phi_2 E_2 \quad [15.18]$$

The amount of  $X_2$  is:

$$\frac{d\{X_2\}}{dt} = n_0 [\phi_2 E_2 - \phi_3 E_3] \quad [15.19]$$

If  $V_2$  denotes the volume of the area or a portion of the area including intermediate  $X_2$ , we have:

$$\{X_2\} = [X_2]V_2 \quad [15.20]$$

and assuming that the intermediate concentrations are very low:

$$\frac{d\{X_2\}}{dt} = V_2 \frac{d[X_2]}{dt} + [X_2] \frac{dV_2}{dt} \approx V_2 \frac{d[X_2]}{dt} \quad [15.21]$$

If, including the reactivities, we have:

$$V_2 \frac{d[X_2]}{dt} = \left( k'_2 K_1 [A][B] - k''_2 [X_2] \right) E_2 - \left( k'_3 [X_2] - \frac{k''_3}{K_4} \right) E_3 \quad [15.22]$$

solving this differential equation allows us to determine the concentration of intermediate  $[X_2]$  as a function of time; which can therefore be included in rate expression [15.6]:

$$r_A = \left( k'_2 K_1 [A][B] - k''_2 [X_2] \right) E_2 \quad [15.23]$$

We notice that with the generic case, the rate is not separable since concentration  $[X_2]$  includes terms  $E_2$  and  $E_3$  according to [15.10].

For example, if we consider the specific case where  $E_2 = E_3 = \frac{V_2}{n_0}$ , which is also the case of an homogeneous reaction, relation [15.10] becomes:

$$V_2 \frac{d[X_2]}{dt} = \left( k'_2 K_1[A][B] - k''_2 [X_2] \right) \frac{V_2}{n_0} - \left( k'_3 [X_2] - \frac{k''_3}{K_4} \right) \frac{V_2}{n_0} \quad [15.24]$$

To simplify the writing of these expressions, we denote the following:

$$M = \frac{(k'_3 - k''_2)}{n_0} \quad \text{and} \quad N = \frac{k'_2 K_1[A][B] + \frac{k''_3}{K_4}}{n_0} \quad [15.25]$$

We can write [15.24] (where  $M$  and  $N$  are independent of time) as:

$$\frac{d[X_2]}{dt} = M[X_2] - N \quad [15.26]$$

which, after integration, gives:

$$[X_2] = [X_2]_0 \exp(-Mt) + \frac{N}{M} (1 - \exp - Mt) \quad [15.27]$$

Hence by using [15.23], the rate has the following forms:

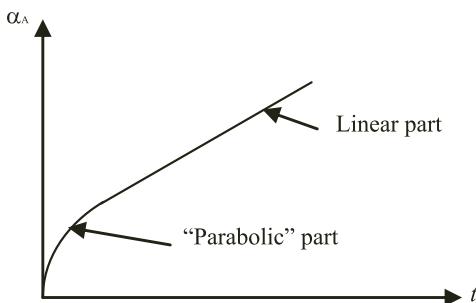
$$r_A = \left( k'_2 K_1[A][B] - k''_2 \left\{ [X_2]_0 \exp - Mt + \frac{N}{M} (1 - \exp - Mt) \right\} \right) \frac{V_2}{n_0} \quad [15.28]$$

Hence the reactivity depends on time but the rate is still separable, even though the two terms may depend on the time, since every reaction step has the same space function.

If time tends toward infinity, we go toward the pseudo-steady state mode:  $[X_i]_{st} = \frac{N}{M}$  and the rate tends toward:

$$r_A = \left( k_2' K_1[A][B] - k_2'' \frac{N}{M} \right) \frac{V_2}{n_0} \quad [15.29]$$

At this limit, concentration  $X_2$  tends toward steadiness and the reactivity becomes independent from time. Only the space function term may depend on the time.



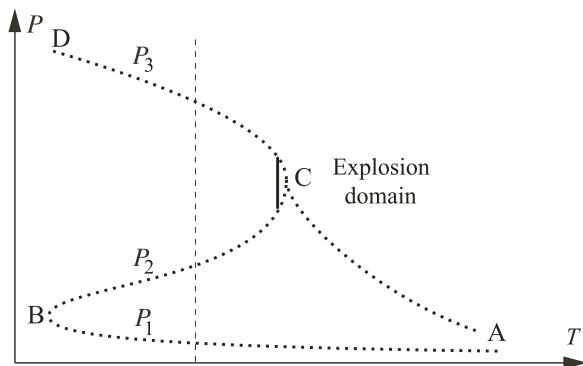
**Figure 15.1.** “Paralinear” curve during metal oxidation

Figure 15.1 gives the appearance the extent of the reaction (with respect to reactant  $A$ ). The curve is concave (called a “parabolic” curve, which is not formally correct) and tends toward the oblique asymptote given by [15.28] if the volume is independent of time. This law is sometimes encountered with the oxidation of metal foils, which is governed by the paralinear law for state mode, whose rate is determined by two interfacial phases.

### 15.3. Thermal runaway and ignition of reactions

When a highly exothermic reaction occurs rapidly at a given temperature, the heat released cannot be removed by conduction or convection to the outside. This results in a rise in temperature, which in turn causes a sharp acceleration of the reaction with more heat production. The rate may become increasingly large and then explosive. This is the theory of explosion by heat accumulation described by van 't Hoff. The explosion threshold is reached when the heat flow supplied by the reaction, given by the product of rate by enthalpy, is no longer compensated for by the heat flow discharged from the reaction medium by conduction or convection.

When considering the combustion of hydrogen or some hydrocarbons, however, if we plot a curve of the limit of inflammation of the mixture in a pressure-temperature space, we obtain curve DCBA as shown in Figure 15.2. This curve divides the plane into two regions: one on the right in which any mixture ignites spontaneously; and a second region to the left of the curve in which the oxidation reaction occurs without inflammation.



**Figure 15.2.** Thresholds of spontaneous ignition

If we consider a certain temperature between point B and point C and the pressure is increased, after the “slow” combustion area we will reach a first pressure threshold  $P_1$ . This is also called the lower ignition pressure; at pressures above this the mixture ignites. By further increasing the pressure we will reach the corresponding pressure threshold  $P_2$ , above which there is no mixture ignition. By further increasing the pressure, we now reach threshold pressure  $P_3$ , from which ignition of the mixture reappears.

The above theory of explosion by accumulation does not explain this phenomenon. At most, we can assign the upper threshold,  $P_3$  (DCA curve), because this theory predicts only one lower level of flammability. The existence of branched chain reactions allows us to explain the existence of the first two critical pressures  $P_1$  and  $P_2$ .

Other factors intervene to modify the values of critical pressures, such as the presence of inert gas which lowers the pressure at both lower and upper threshold pressures of ignition. The lower area of inflammation may eventually disappear. Some substances play a positive catalytic role, for example nitrogen pentoxide for oxidation. Others have a negative role, acting as an inhibitor, for example halogens in oxidation reactions.

### 15.4. Chemical ignition of gaseous mixtures

The inflammation of hydrocarbons is generally explained by the existence of branched chain reactions, and we will now see how the modeling of these reactions contributes to an understanding of the ignition process.

#### 15.4.1. Branched chains with linear branching and chain breaking in the bulk

Looking back at branched chain reactions with linear initiation and breaking in the bulk, we obtain equation [12.63], recalled here:

$$\frac{d[X]}{dt} = v_i + \varphi[X] \quad [15.30]$$

In section 12.6.3 we saw that when the branching factor  $\varphi$  is negative, the solution tends toward a pseudo-steady state. We now consider the case where the branching factor  $\varphi$  is positive:  $\varphi > 0$ .

It is easy to calculate that in this case if  $[X] = 0$  for  $t = 0$ , the solution to equation [15.30] is:

$$[X] = \frac{v_i}{\varphi} \{ \exp(\varphi t) - 1 \} \cong \frac{v_i}{\varphi} \exp(\varphi t) \quad [15.31]$$

We notice that there is no limit to the concentration of the active center for infinities. The rate is therefore given by:

$$v = \frac{v_i}{\varphi \Delta \tau_p} \{ \exp(\varphi t) - 1 \} \cong \frac{v_i}{\varphi \Delta \tau_p} \exp(\varphi t) \quad [15.32]$$

The concentration of the product formed (written as a partial pressure) becomes:

$$[P] = \frac{v_i}{\varphi^2 \Delta \tau_p} \{ \exp(\varphi t) - \varphi t - 1 \} \cong \frac{v_i}{\varphi^2 \Delta \tau_p} \exp(\varphi t) \quad [15.33]$$

We notice that by comparing [15.32] and [15.33], the reaction rate obeys the following relation:

$$v = \varphi[P] \quad [15.34]$$

This expression permits the experimental determination of the branching factor by measuring the rate as a function of the concentration of the product formed.

As in section 12.6.3, we can define dimensionless measures and obtain the dimensionless concentration of the active center:

$$[X] = \{\exp(\varphi t) - 1\} \equiv \exp(\varphi t) \quad [15.35]$$

For the dimensionless concentration of the formed product  $P$ :

$$[P] = \exp(\varphi t) - \varphi t - 1 \equiv \exp(\varphi t) \quad [15.36]$$

We have represented the variations of dimensionless measures according to time and seen that the rate curve in Figure 15.3 takes the shape of curve 1 in Figure 12.1.

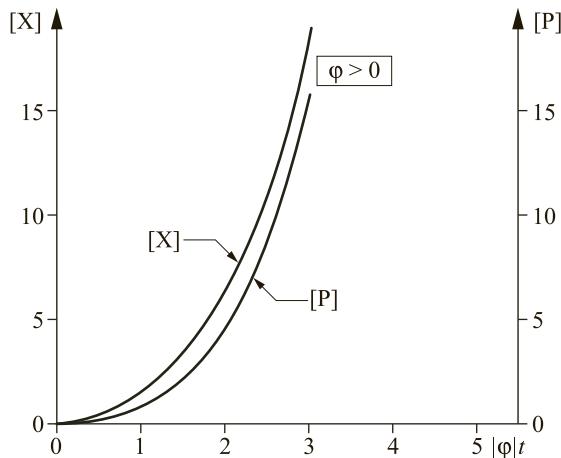


Figure 15.3. Systems without pseudo-steady states

Therefore by following the sign of the branching factor, the reaction may or may not reach a pseudo-steady state.

#### 15.4.2. Branched chains with linear branching and breaking in the bulk and heterogeneous breaking on the walls

This process is characterized by an initiation rate  $v_i$ , a linear branching rate  $(\mu_m - 1)f_{ra}[X]$ , a linear breaking rate in the bulk  $f_r[X]$  and a breaking reaction

on the walls (thus a diffusion term). The summary of the active center concentration will be located on the reactor plane x-axis with the abscissa  $x$  in Figure 12.6:

$$\frac{\partial[X]}{\partial t} = v_i + \{(\mu_m - 1)f_{ra} - f_r\}[X] + D \frac{\partial^2[X]}{\partial x^2} \quad [15.37]$$

#### 15.4.2.1. Calculation of the mean length of the chains

To calculate the mean chain length, we will write the pseudo-steadiness and therefore calculate the mean concentration of active centers in pseudo-steady conditions, which is to look at the roots of:

$$v_i + \{(\mu_m - 1)f_{ra} - f_r\}[X] + D \frac{\partial^2[X]}{\partial x^2} = 0 \quad [15.38]$$

To define the root of this equation, we must consider two possibilities:

– If  $f_r < (\mu_m - 1)f_{ra}$ , in the bulk chains have more chances to be branched. We again find mean concentrations identical to expression [12.29] by replacing  $f_r$  by  $(\mu_m - 1)f_{ra} - f_r$  and according to [12.32], the rate is therefore:

$$v = \frac{v_i}{((\mu_m - 1)f_{ra} - f_r)\Delta\tau_p} \left[ 1 - \frac{\tanh\left(\frac{d}{2}\sqrt{\frac{(\mu_m - 1)f_{ra} - f_r}{D}}\right)}{\frac{d}{2}\sqrt{\frac{(\mu_m - 1)f_{ra} - f_r}{D}}} \right] \quad [15.39]$$

According to [12.33], the mean length of the chains is:

$$\bar{v} = \frac{1}{((\mu_m - 1)f_{ra} - f_r)\Delta\tau_p} \left[ 1 - \frac{\tanh\left(\frac{d}{2}\sqrt{\frac{(\mu_m - 1)f_{ra} - f_r}{D}}\right)}{\frac{d}{2}\sqrt{\frac{(\mu_m - 1)f_{ra} - f_r}{D}}} \right] \quad [15.40]$$

If we only consider the first three terms of the hyperbolic tangent (see relation [12.34]), we have:

$$\bar{v} = \frac{d^2}{12D\Delta\tau_p} \left[ 1 - \frac{((\mu_m - 1)f_{ra} - f_r)d^2}{10D} \right] \quad [15.41]$$

If we take [12.37] into account and in the same way, we must have:

$$((\mu_m - 1)f_{ra})\Delta\tau_p = \delta \quad [15.42]$$

and so:

$$\bar{v}' = \frac{d^2 P^2}{4\lambda_0^2 q} \left[ 1 - \frac{3(\beta - \delta)P^2 d^2}{10\lambda_0^2 q} \right] \quad [15.43]$$

- If  $f_r < (\mu_m - 1)f_{ra}$ , the solutions are different and we find:

$$\left[ \bar{X} \right] = \frac{v_i}{((\mu_m - 1)f_{ra} - f_r)\Delta\tau_p} \left[ I - \frac{\cos \left( x \sqrt{\frac{(\mu_m - 1)f_{ra} - f_r}{D}} \right)}{\cos \frac{d}{2} \sqrt{\frac{(\mu_m - 1)f_{ra} - f_r}{D}}} \right] \quad [15.44]$$

and for the mean length of the chains:

$$\bar{v}' = \frac{v_i}{((\mu_m - 1)f_{ra} - f_r)\Delta\tau_p} \left[ I - \frac{\operatorname{tg} \left( \frac{d}{2} \sqrt{\frac{(\mu_m - 1)f_{ra} - f_r}{D}} \right)}{\frac{d}{2} \sqrt{\frac{(\mu_m - 1)f_{ra} - f_r}{D}}} \right] \quad [15.45]$$

We see that this mean length is infinite for given values of  $f_r$ ,  $\mu_m$  and  $f_{ra}$  if:

$$\frac{d}{2} \sqrt{\frac{(\mu_m - 1)f_{ra} - f_r}{D}} = \frac{\pi}{2} \quad \text{or} \quad d^2 \frac{((\mu_m - 1)f_{ra} - f)_r}{D} = \pi^2 \quad [15.46]$$

#### 15.4.2.2. Justification of the two lower ignition thresholds

Relation [15.45] defines the transition from one state mode with limited chain lengths to a state with unlimited length chains, which is a state mode without pseudo-steadiness, i.e. eventually an explosive state.

It is said that there is a pseudo-steady state mode only if:

$$d^2 \frac{((\mu_m - 1)f_{ra} - f)_r}{D} < \pi^2 \quad [15.47]$$

We know that according to the kinetic theory of gases, the interdiffusion coefficient is proportional to the mean free path  $\lambda$ , at a mean rate of molecules  $\bar{c}$  and inversely proportional to the pressure  $P$ . Therefore taking into account [12.24], [12.25], [12.26], [12.35] and [15.46], the pseudo-steady state mode only exists if:

$$\frac{3(\delta - \beta)P^2d^2}{\lambda_0^2q} < \pi^2 \quad [15.48]$$

hence a limit pressure is:

$$P^2 < \frac{\lambda_0^2q\pi^2}{3(\delta - \beta)d^2} \quad [15.49]$$

It is reasonable to assume that the probability of the chain breaking,  $\beta$ , varies in the gas phase in proportion with the pressure. Indeed, the propagation of chain reactions with or without branching are due to bimolecular collisions; whereas breaking reactions are due to trimolecular collisions. As the number of double collisions varies proportionally to the squared value of the pressure and the number of triple collisions to the cubic value of the pressure, the probability of termination must ultimately vary as the ratio of the cube over the square of the pressure, which is in proportion to the pressure:

$$\beta = bP \quad [15.50]$$

The condition for the existence of a pseudo-steady state mode therefore becomes:

$$\delta - bP - \frac{\lambda_0^2 q \pi^2}{3d^2 P^2} < 0 \quad [15.51]$$

Let us have a look at the following equation:

$$\delta - bP - \frac{\lambda_0^2 q \pi^2}{3d^2 P^2} = 0 \quad [15.52]$$

The equation has two positive roots  $P_1$  and  $P_2$  and condition [15.40] is satisfied outside these roots. Thus we recover the existence of an explosive state mode between two pressures  $P_1$  and  $P_2$  at a given temperature, as shown in Figure 15.2.

We would obtain similar results (to the nearest numerical coefficient) with other forms of reactors.

The presence of an inert gas will reduce the diffusion of active centers toward the walls and lower thresholds  $P_1$  and  $P_2$ .

The composition of the gas phase will also have an influence on the threshold values with the frequency of collisions between reactants.

Thus the theory of branched chain reactions can account for two explosive thresholds restricting an area of lower ignition. Qualitative results are therefore interpreted correctly.

The third pressure threshold ( $P_3$ , see Figure 15.2) is probably attributed to the thermal acceleration, as seen in section 15.3.

#### 15.4.2.3. Calculating the rate as a function of time

To determine the rate versus time, the mean concentration must be calculated and then [12.18] applied. The concentration in the reactor at any point  $x$  and at time  $t$  is the solution to the differential equation:

$$\frac{\partial[X_I]}{\partial t} = \{(\mu_m - 1)f_{ra} - f_r\}[X_I] + D \frac{\partial^2[X_I]}{\partial x^2} \quad [15.53]$$

This equation was studied by Bursian and Sorokin in 1931, which led to the solution as a series.

By calculating:

$$v = \frac{1}{d(\Delta\tau_p)} \int_{-d/2}^{+d/2} [X](x, t) dx \quad [15.54]$$

the rate also is obtained in the form of a series.

Only the first term of this equation can be used, which leads to the following rate:

$$v = \frac{v_i}{\Delta\tau_p} \frac{1}{\{(\mu_m - 1)f_{ra} - f_r - \pi^2 D/d^2\}} \exp\left[\left\{(\mu_m - 1)f_{ra} - f_r - \pi^2 D/d^2\right\}t - 1\right] \quad [15.55]$$

We notice that this solution is identical to expression [15.32] if the following condition is respected:

$$\varphi = \{(\mu_m - 1)f_{ra} - f_r - \pi^2 D/d^2\} \quad [15.56]$$

In fact, we have a solution equivalent to equation [15.36], and therefore the results already obtained in the case of linear branches can be generalized.

The branching factor  $\varphi$  plays an important role. This factor is calculated as discussed in section 12.6.4 with respect to the “chemical” terms to which we add the diffusion term that keeps the same form as in equation [15.47] in  $D/d^2$ ; only the numerical coefficient depends on the shape of the reactor.

In conclusion we see that if we take into account the consumption of reagents, the concept of a chain reaction allows us to account for all the curves in Figure 12.1, particularly the shapes of curves 1 and 2 of this figure, which reactions with limited sequences could not predict. We have also reported an effect of the shape and dimensions of the reactors. Finally, we have accounted for the three explosion threshold pressure limits at constant temperature.



## **APPENDICES**



# Appendix 1

## Point Defects and Structure Elements of Solids

In reactions involving crystallized solids, the intermediates are frequently structure elements among which the point defects play a major role. A branch of chemistry, called “quasi-chemistry” has thus been developed by taking into account these defects in quasi-chemical reactions that feature thermodynamic and kinetic properties. It is often such reactions that constitute the elementary steps of heterogeneous reactions.

### A1.1. Point defects of solids

In a crystalline solid the point lattices are normally occupied by atoms, molecules or ions called components. The lattice thus formed is called the perfect lattice. In practice, this lattice can display irregularities that are called defects.

A point defect is an irregularity at the level of a point lattice and the following can be encountered:

- *the vacancy*: this is the absence of a point lattice of the species that is normally present in the perfect lattice;
- *the interstitial*: this is the presence of an element of the affected solid (atom, molecule or ion) in a position between point lattices;
- *the exchange defect*: this is the replacement of the normal element of a point lattice by another element of the solid;

- *inclusion of a foreign element*: this is a foreign element that has been hammered into an interstitial position in the solid;
- *substitution of a foreign element*: this is a foreign element that has replaced a normal element in the solid at a lattice point.

### A1.2. Definition of a structural element

A structural element is an atom, ion or vacancy (empty space) at a specific site of the crystal. The notion of structural element combines the notions of a chemical species and its surroundings through the nature of the lattice site being considered. A structural element can be:

- an atom of the solid in a normal lattice site (in the sense of an ideal solid);
- an atom of the solid in an abnormal lattice site (substitution of an atom of a different nature and atom in an interstitial position, etc.);
- a vacancy in the normal lattice (empty space in the ideal solid);
- an empty interstitial position that can be regarded as a vacancy in an interstitial position;
- an atom that is foreign to the solid in a specific lattice site (for example, chromium replacing zinc in zinc oxide).

We can thus completely describe the solid from the enumeration of its structure elements by assimilating free electrons and electron holes that might be present in order to be complete.

Structure elements can carry variable charges. The effective charge of a structural element,  $q_e$ , is the difference between its actual charge ( $q_r$ ) and the charge that the structural element occupying the same site in the ideal crystal would have (the normal charge,  $q_n$ ):

$$q_e = q_r - q_n$$

An element is said to be non-ionized if its effective charge is zero.

The normal structure elements of the solid – which means they are present in the ideal solid (atom or ion of the solid in a normal lattice site or an empty interstitial position) – have a zero effective charge.

### A1.3. Symbolic representation of structure elements

Similarly to the emergence of the need for symbolic writing of atoms and molecules in chemistry, it became necessary to create a symbolic system for structure elements. This notation system should provide three types of information about an element:

- the atom or chemical element concerned;
- the lattice site occupied (in reference to the ideal solid);
- the effective (or actual) charge. We usually choose the effective charge because it is null for all normal elements.

The International Union of Pure and Applied Chemistry (IUPAC) has advocated the use of Kröger's notation. Tables A1.1, A1.2, A1.3, A1.4 and A1.5 show all of the notations for the various types of structure elements, applied to the example of alumina. This is a "dummy" example, given as it gathers together all of the cases that will be met.

The symbol ' which figures in the top right-hand side of the element signifies an -1 effective charge. The symbol ° represents the +1 effective charge and the zero effective charge is represented by X (a cross). The presence of this sign is not mandatory, so it can be omitted. Index *i* is assigned to an element in an interstitial position.

Al <sup>3+</sup> ion in normal position ( $q_e = 0$ ).....	Al <sub>Al</sub>
O <sup>2-</sup> ion in normal position ( $q_e = 0$ ).....	O <sub>O</sub>
Empty interstitial position ( $q_e = 0$ ).....	<i>V<sub>i</sub></i>

**Figure A1.1.** Structure elements in the normal location

Free electron ( $q_e = -1$ ) .....	e'
Free electron vacancy ( $q_e = +1$ ) .....	h°

**Figure A1.2.** Free charge symbols

We notice that a vacancy is denoted *V*. To prevent any confusion with the vanadium notation, which has the same symbol, the *International Union of Pure and Applied Chemistry* suggests changing the symbol of vanadium and using Va when dealing with structure elements.

Al <sup>3+</sup> ion in interstitial position ( $q_e = +3$ ) .....	Al <sub><i>i</i></sub> <sup>○○○</sup>
O <sup>2-</sup> ion in interstitial position ( $q_e = -2$ ).....	O <sub><i>i</i></sub> <sup>''</sup>
Al atom in interstitial position ( $q_e = 0$ ) .....	Al <sub><i>i</i></sub>

**Figure A1.3.** Symbols of the structure elements in interstitial positions

Vacancy of Al <sup>3+</sup> ion ( $q_e = -3$ ).....	V <sub>Al</sub> <sup>'''</sup>
Vacancy of O <sup>2-</sup> ion ( $q_e = -2$ ) .....	V <sub>O</sub> <sup>○○</sup>
Vacancy of Al <sup>3+</sup> ion trapping an electron hole ( $q_e = -2$ ) ....	V <sub>Al</sub> <sup>''</sup>
Vacancy of O <sup>2-</sup> ion trapping an electron hole ( $q_e = +1$ )....	V <sub>O</sub> <sup>°</sup>

**Figure A1.4.** Symbols of the vacancies in structure elements

S <sup>2-</sup> substituting O <sup>2-</sup> ( $q_e = 0$ ).....	S <sub>O</sub>
Mg <sup>2+</sup> substituting Al <sup>3+</sup> ( $q_e = -1$ ).....	Mg <sub>Al</sub> <sup>'</sup>
Zr <sup>4+</sup> substituting Al <sup>3+</sup> ( $q_e = +1$ ).....	Zr <sub>Al</sub> <sup>°</sup>
Li <sup>+</sup> in interstitial position ( $q_e = +1$ ) .....	Li <sub><i>i</i></sub> <sup>°</sup>

**Figure A1.5.** Symbols of structure elements substituted by foreign elements

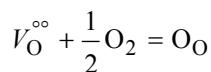
Associations of structure elements are represented by writing them without their effective charge between brackets, and adding the group effective charge after the bracket. For example, the association of the aluminum ion vacancy with an oxygen ion vacancy is denoted:  $(V_{Al}V_O)'$ . We notice that we will obtain the same entity and therefore the same notation of effective charge (-1) if each of these vacancies had trapped an electron and an electron hole, respectively.

With these notations we will be able to write reactions that involve structure elements.

#### A1.4. Reactions involving structure elements in quasi-chemical reactions

Since chemical reactions involve atoms and molecules, ionic reactions and electrochemical involve ions, reactions that are called quasi-chemical reactions involve structure elements.

For instance, by using Kröger's notation the consumption reaction of oxygen vacancies in magnesium oxide by oxygen gas is written as follows:



This shows that the oxygen atom derived from the gas fills the vacancy to place an oxygen atom in the normal position in the solid magnesium oxide.

#### A1.5. Equilibria and reactivities of quasi-chemical reactions

The structure elements of a solid whose proportions vary according to different parameters are regarded as components of a solution. In other words, a solid can be viewed as a solid solution of its structure elements.

This property allows us to apply all the properties of the components of a solution to structure elements. The mass action law of chemical equilibria especially applies to quasi-chemical equilibria using concentrations of structure elements.

For the previous reaction of the oxygen vacancy with the gas, the mass action law for diluted defects will be written as follows at equilibrium:

$$K = [V_O^{\circ\circ}] P_{O_2}^{1/2}$$

The concentration of  $[O_O]$  is very high in the magnesium oxide and so is regarded to be constant, such as water molecules for ionic reactions in aqueous solution. This oxygen belongs to the solvent as well as the magnesium ions in normal cationic positions and the empty interstitial positions.

Similarly, the reactivities of elementary quasi-chemical reactions will be written as a function of the concentrations of the structure elements, through the rate coefficients. So, if the previous reaction was elementary (which is unlikely because it involves a fraction of atom), its reactivity would be:

$$\varphi V_O^\circ P^{1/2}$$

Ultimately, the point defects are reaction intermediates at the solid state in the same way as the radicals and ions in liquid and gas phases.

## Appendix 2

# Notions of Microscopic Thermodynamics

The aim of this appendix is to gather together a few statistical thermodynamics notions and, in particular, to establish the expression of equilibrium constants using partition functions, which is useful in the activated complex theory.

### A2.1. Molecule distribution between the different energy states

Here consider a group of  $N$  molecules that are chemically identical. Among the molecules,  $N_1$  has an energy of  $\epsilon_1$ ,  $N_2$  an energy of  $\epsilon_2$  [...] and  $N_i$  an energy of  $\epsilon_i$ . The number of possibilities  $W$  (number of complexions) by which to distribute  $N$  molecules in the way thus described is:

$$W = \frac{N!}{N_1! N_2! N_3! \dots N_k!} \quad [\text{A2.1}]$$

Using the logarithm of the previous expression, we have:

$$\ln W = \ln N! - \sum_{i=1}^k \ln N_i! \quad [\text{A2.2}]$$

If  $N$  is large, we can use Stirling approximation:

$$\ln N! = N \ln N - N \quad [\text{A2.3}]$$

from which:

$$\ln W = N \ln N - N - \sum_{i=1}^k N_i \ln N_i + \sum_{i=1}^k N_i \quad [A2.4]$$

but since we have:

$$N = \sum_{i=1}^k N_i \quad [A2.5]$$

it follows that:

$$\ln W = N \ln N - \sum_{i=1}^k N_i \ln N_i \quad [A2.6]$$

The most probable state is the one for which  $W$  (or  $\ln W$ ) is at its maximum when it obeys to the following condition:

$$\frac{\delta \ln W}{\delta N_i} = 0 \quad [A2.7]$$

or according to [A2.6]:

$$\sum_{i=1}^k (1 + \ln N_i) \delta N_i = 0 \quad [A2.8]$$

but since  $N$  is a constant, we can write:

$$\sum_{i=1}^k \delta N_i = 0 \quad [A2.9]$$

hence:

$$\sum_{i=1}^k \ln N_i \delta N_i = 0 \quad [A2.10]$$

The total system energy is:

$$E = \sum_{i=1}^k N_i \varepsilon_i \quad [\text{A2.11}]$$

The energy conversion is written  $\delta E = 0$ , or:

$$\sum_{i=1}^k \varepsilon_i \delta N_i = 0 \quad [\text{A2.12}]$$

To solve the system formed by equations [A2.9], [A2.10] and [A2.12], we will apply Lagrange's method. To do so, we multiply relations [A2.10] and [A2.12] by undefined constants  $\alpha$  and  $\beta$ , respectively. The system of three equations becomes:

$$\sum_{i=1}^k \alpha \delta N_i = 0 \quad [\text{A2.13}]$$

$$\sum_{i=1}^k \ln N_i \delta N_i = 0 \quad [\text{A2.14}]$$

$$\sum_{i=1}^k \beta \varepsilon_i \delta N_i = 0 \quad [\text{A2.15}]$$

By adding equations [A2.13], [A2.14] and [A2.15], we obtain:

$$\sum_{i=1}^k (\ln N_i + \alpha + \beta \varepsilon_i) \delta N_i = 0 \quad [\text{A2.16}]$$

The  $\delta N_i$  variations being arbitrary, for condition [A2.16] to be met  $i$  must be:

$$\ln N_i + \alpha + \beta \varepsilon_i = 0 \quad [\text{A2.17}]$$

thus:

$$N_i = \exp(-\alpha) \exp(-\beta \varepsilon_i) = A \exp(-\beta \varepsilon_i) \quad [\text{A2.18}]$$

We can calculate  $A$  by writing that  $N$  is the sum of every  $N_i$ , and obtain:

$$A = \frac{N}{\sum_{i=1}^k \exp(-\beta \varepsilon_i)} \quad [\text{A2.19}]$$

On the other hand, we can demonstrate that  $\beta = 1/k_B T$  (where  $T$  is the absolute temperature and  $k_B$  is Boltzmann's constant with  $k_B = R/N_a$ ).

We obtain the most probable distribution of molecules between the different energy states by calculating:

$$N_i = N \frac{\exp\left(-\frac{\varepsilon_i}{k_B T}\right)}{\sum_{i=1}^k \exp\left(-\frac{\varepsilon_i}{k_B T}\right)} \quad [\text{A2.20}]$$

## A2.2. Partition functions

The exponential sum appearing in expression [A2.20] is found quite frequently in statistical thermodynamics. This sum is also called the partition function of system including  $N$  molecules:

$$Z = \sum_{i=1}^k \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \quad [\text{A2.21}]$$

The system's full partition function includes terms related to the  $i$  different types of energies: nuclear, electronic, molecular vibrations, molecule rotations, as well as translation and interactions between the different types of molecules.

To simplify this, we agree that for a molecule these different types of energies are independent (this is not quite true, especially as the interdependence of the vibration and rotation energies of a molecule are known). We can therefore write the overall energy of a molecule like the sum of the different types of energy contributions:

$$\varepsilon = \varepsilon_n + \varepsilon_e + \varepsilon_v + \varepsilon_r + \varepsilon_t + \varepsilon_I \quad [\text{A2.22}]$$

The partition function becomes:

$$Z = \sum_{i_n} \exp\left(-\frac{\epsilon_{i_n}}{k_B T}\right) \sum_{i_e} \exp\left(-\frac{\epsilon_{i_e}}{k_B T}\right) \sum_{i_v} \exp\left(-\frac{\epsilon_{i_v}}{k_B T}\right) \\ \sum_{i_r} \exp\left(-\frac{\epsilon_{i_r}}{k_B T}\right) \sum_{i_t} \exp\left(-\frac{\epsilon_{i_t}}{k_B T}\right) \sum_{i_I} \exp\left(-\frac{\epsilon_{i_I}}{k_B T}\right) \quad [A2.23]$$

We can show the partial partition functions related to the different types of energies:

$$Z_n = \sum_{i_n} \exp\left(-\frac{\epsilon_{i_n}}{k_B T}\right), \quad [A2.24]$$

$$Z_e = \sum_{i_e} \exp\left(-\frac{\epsilon_{i_e}}{k_B T}\right),$$

$$Z_v = \sum_{i_v} \exp\left(-\frac{\epsilon_{i_v}}{k_B T}\right)$$

$$Z_r = \sum_{i_r} \exp\left(-\frac{\epsilon_{i_r}}{k_B T}\right), \quad [A2.25]$$

$$Z_t = \sum_{i_t} \exp\left(-\frac{\epsilon_{i_t}}{k_B T}\right),$$

$$Z_I = \sum_{i_I} \exp\left(-\frac{\epsilon_{i_I}}{k_B T}\right)$$

The overall partial partition function can therefore be written as the product of the different types of partial partition functions:

$$Z = Z_n Z_e Z_v Z_r Z_t Z_I \quad [A2.26]$$

In chemical reactors, the nucleus energy is not modified; the constant value of this energy will therefore be used as the origin, and the nucleus partition function

will equal one unit. This is the same for the electronic energy of reactions that do not involve atoms in their excited state. Moreover, if we respect the rule of perfect solutions, the interaction term will also be equal to one unit. Finally, with these assumptions the total partition function is written as the product of three terms:

$$Z = Z_v Z_r Z_t \quad [\text{A2.27}]$$

We now have to examine the three partial partition functions of vibration  $Z_v$ , rotation  $Z_r$  and translation  $Z_t$ .

### A2.3. Degrees of freedom of a molecule

The calculation of partial partition functions requires knowledge of the number of degrees of freedom for each type of movement in the molecule.

If a molecule is made of  $N$  atoms, it has a total of  $3N$  degrees of freedom. Usually a molecule has three degrees of freedom of translation. A nonlinear molecule has three degrees of freedom of rotation; whereas a linear molecule only has two. The number of degrees of freedom of vibration is easily deduced:

- linear molecules:  $3N - 5$  degrees of freedom of vibration;
- nonlinear molecules:  $3N - 6$  degrees of freedom of vibration.

For example, a diatomic molecule ( $N = 2$ ), which is obviously linear, will have six degrees of freedom including three of translation, two of rotation and one of vibration.

### A2.4. Elementary partition functions

#### A2.4.1. *Vibration partition function*

For each degree of freedom of vibration, there is a vibration frequency  $v_i$  (in  $\text{s}^{-1}$ ), and the respective partition function is written:

$$z_{v_i} = \frac{1}{1 - \exp\left(-\frac{hv_i}{k_B T}\right)} \quad [\text{A2.28}]$$

This measure has two limit values that are often used (see section A2.4.4):

$$\text{If } h\nu_i \ll k_B T \text{ then } z_{\nu_i} = \frac{k_B T}{h\nu_i} \quad [\text{A2.29}]$$

$$\text{If } h\nu_i \gg k_B T \text{ then } z_{\nu_i} = 1 \quad [\text{A2.30}]$$

When the molecule has  $n$  degrees of freedom of vibration, the overall partition function is:

$$Z_v = \prod_{i=1}^n z_{\nu_i} \quad [\text{A2.31}]$$

#### A2.4.2. Rotation partition function

For a linear molecule with a moment of inertia  $I$  related to the axis perpendicular to the straight line linking atoms and passing by the center of mass, the partition function of rotation is:

$$z_r = \sqrt{\frac{8\pi^2 I k_B T}{\sigma h^2}} \quad [\text{A2.32}]$$

If every atom in the molecule is identical, coefficient  $\sigma$  is equal to 2, otherwise  $\sigma = 1$ .

With nonlinear polyatomic molecules, if  $I_1$ ,  $I_2$  and  $I_3$  are the moments of inertia within three rectangular axes passing through the center of mass, the partition function of rotation is:

$$z_r = \frac{\sqrt{I_1 I_2 I_3}}{\sigma} \left( \frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \quad [\text{A2.33}]$$

where coefficient  $\sigma$  is a number related to the symmetry of the molecule. If there is no symmetry,  $\sigma = 1$ ; for  $\text{NH}_3$  types of molecules,  $\sigma = 3$ ; for  $\text{C}_2\text{H}_4$  molecules,  $\sigma = 3$ ; and for benzene types of molecules,  $\sigma = 12$ .

### A2.4.3. Translation partition function

It is demonstrated that for one degree of freedom of translation, the partition function of translation of a molecule of mass  $m$  per unit of volume is:

$$z_t = \frac{\sqrt{2\pi m k_B T}}{h} \quad [\text{A2.34}]$$

If the molecule has  $n$  degrees of freedom of translation and if the volume  $V$  is available for the system, the partition function of translation is given by:

$$Z_t = z_t^n \cdot V \quad [\text{A2.35}]$$

### A2.4.4. Order of magnitude of partition functions

We notice that in most the cases, the contributions of the elementary partition functions are of the same order of magnitude. Table A2.1 summarizes these approximations.

Partition function by degrees of freedom	Approximation
Vibration	$z_v \approx 1$
Rotation	$z_r \approx 10 \text{ to } 10^2$
Translation per unit of volume	$z_t \approx 10^8$

**Table A2.1.** Order of magnitude of elementary partition functions by degrees of freedom

### A2.5. Expression of thermodynamic functions from partition functions

All the thermodynamic functions of a system can be expressed from the partition functions. We will demonstrate some of them here in order to obtain the equilibrium constant.

### A2.5.1. Internal energy

We have seen that the total energy of the system is expressed by:

$$E = \sum_{i=1}^k \varepsilon_i N_i \quad [\text{A2.36}]$$

with a number  $N_i$  of molecules having an energy  $\varepsilon_i$ , so that:

$$N_i = N_a \frac{\exp\left(-\frac{\varepsilon_i}{k_B T}\right)}{Z} \quad [\text{A2.37}]$$

from which the total energy for one mole of  $N_a$  molecules is:

$$E = k_B T^2 \sum_{i=1}^k \varepsilon_i N_a \frac{\exp\left(-\frac{\varepsilon_i}{k_B T}\right)}{k_B T^2 Z} \quad [\text{A2.38}]$$

using the partition function [A2.21] again, we notice that:

$$\frac{dZ}{dT} = \sum_{i=1}^k \frac{\varepsilon_i}{k_B T^2} \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \quad [\text{A2.39}]$$

Using an arbitrary origin, if  $U_0$  denotes the energy of molecules at absolute zero temperature, and  $U$  the internal energy at temperature  $T$ , we obtain:

$$E = U - U_0 = N_a k T^2 \frac{d \ln Z}{dT} \quad [\text{A2.40}]$$

### A2.5.2. Entropy

Statistical thermodynamics introduces entropy through a number of complexions  $W$  in the following expression:

$$S = k_B \ln W \quad [\text{A2.41}]$$

According to [A2.6],  $W$  is given for one mole:

$$\ln W = N_a \ln N_a - \sum_{i=1}^k N_i \ln N_i \quad [\text{A2.42}]$$

from which we can deduce:

$$S = k_B N_a T \frac{d \ln Z}{dT} + k_B N_a \ln Z \quad [\text{A2.43}]$$

or considering [A2.40]:

$$S = k_B N_a \ln Z + \frac{U - U_0}{T} \quad [\text{A2.44}]$$

### A2.5.3. Free energy

Using the relation defining function  $F$  as well as expressions [A2.40] and [A2.44], we can deduce:

$$F = U - TS = U_0 - k_B N_a T \ln Z \quad [\text{A2.45}]$$

## A2.6. Equilibrium constant and partition functions

We now consider the chemical reaction:

$$0 = \sum_i v_i A_i$$

The equilibrium constant for the concentrations will be:

$$K_c = \prod_i C_i^{v_i} \quad [\text{A2.46}]$$

or:

$$\ln K_c = \sum_i v_i \ln C_i \quad [\text{A2.47}]$$

Moreover, using [A2.45], the associated variation of free energy  $\Delta F$  is:

$$\Delta F = \sum_i v_i F_i = \sum_i v_i U_{0_i} - \sum_i v_i k_B N_a T \ln Z_i \quad [\text{A2.48}]$$

but by the definition of  $\Delta$ , the internal energy is:

$$\sum_i v_i U_{0_i} = \Delta U_0 \quad [\text{A2.49}]$$

Moreover, we know that the partition function  $Z$  includes a translation term proportional to the volume and thus we can write:

$$Z_i = Z_{0_i} V \quad [\text{A2.50}]$$

If we also consider the molar measure ( $R = N_a k_B$ ), and notice that  $C = 1/V_m$  ( $V_m$  molar volume), the associated free energy is therefore:

$$\Delta F = \Delta U_0 - \sum_i v_i R T \ln Z_{0_i} + \sum_i v_i R T \ln C_i \quad [\text{A2.51}]$$

If we consider a constant temperature, function  $F$  is the thermodynamic potential, therefore at equilibrium  $\Delta F = 0$  and we obtain:

$$\frac{\Delta U_0}{R T} - \sum_i v_i \ln Z_{0_i} = \sum_i v_i \ln C_i \quad [\text{A2.52}]$$

from which by comparing equation [A2.47], the equilibrium constant is:

$$K_c = \prod_i (Z_{0_i})^{v_i} \exp\left(-\frac{\Delta U_0}{R T}\right) \quad [\text{A2.53}]$$

The product is extended to all the constituents included in the equation's definition. Hence the equilibrium constant in the perfect solution phase (gaseous, liquid or solid) is defined from the partition functions of the molecules entering into the reaction (reactant and products) using relation [A2.53].



## Appendix 3

### Vibration Frequency of the Activated Complex

To calculate the vibration frequency of the activated complex, we use the surfaces of potential energies. The method used is based on the theory of small vibrations applied to the stationary points of a potential surface, which is either a maximum or minimum of a system at equilibrium; whereas the coordinate variation does not affect the potential energy.

The generic expression of the energy potential  $U$  of a system of particles for displacements  $q_k$  and  $q_j$  of coordinates  $k$  and  $j$  is given by the approximation of Taylor's development:

$$U = U_0 + \sum_k \frac{\partial U}{\partial q_k} q_k + \frac{1}{2} \sum_k \frac{\partial^2 U}{\partial q_k \partial q_j} q_k q_j \quad [\text{A3.1}]$$

At equilibrium, the maximum potential is:

$$\frac{\partial U}{\partial q_k} = 0 \quad [\text{A3.2}]$$

and [A3.1] becomes:

$$U = U_0 + \frac{1}{2} \sum_k \frac{\partial^2 U}{\partial q_k \partial q_j} q_k q_j \quad [\text{A3.3}]$$

The origins can be changed so that the energy potential is zero. Thus [A3.3] can be simplified and the energy potential can be written:

$$U = \sum_{k,j} b_{k,j} q_k q_j \quad [\text{A3.4}]$$

This expression gives the energy potential around a maximum for vibrations.

The kinetic energy is given by:

$$T = \sum_{k,j} a_{k,j} \frac{\partial q_k}{\partial t} \frac{\partial q_j}{\partial t} \quad [\text{A3.5}]$$

Coefficients  $a_{l,j}$  and  $a_{k,j}$  are related to the masses and the particle coordinates of the constituents of the activated complex.

The difference between kinetic and potential energies is the Lagrangian,  $L$ :

$$L = T - U \quad [\text{A3.6}]$$

Relations [A3.4] and [A3.5] give:

$$L = \sum_{k,j} a_{k,j} \frac{\partial q_k}{\partial t} \frac{\partial q_j}{\partial t} - \sum_{k,j} b_{k,j} q_k q_j \quad [\text{A3.7}]$$

The derivation of relation [A3.7]:

$$\frac{\partial L}{\partial \frac{\partial^2 q_k}{\partial t^2}} = \sum_k a_{k,j} \frac{\partial q_k}{\partial t} \quad [\text{A3.8}]$$

and:

$$\frac{\partial L}{\partial q_k} = - \sum_k a_{k,j} \frac{\partial q_k}{\partial t} \quad [\text{A3.9}]$$

The differentiation of relation [A3.9] according to time gives:

$$\frac{\partial}{\partial t} \left( \frac{\partial L}{\partial \left( \frac{\partial q_l}{\partial t} \right)} \right) = \sum a_{l,j} \frac{\partial^2 q_j}{\partial t^2} \quad [\text{A3.10}]$$

or Lagrange's equation of movement is written:

$$\frac{\partial}{\partial t} \left( \frac{\partial L}{\partial \left( \frac{\partial q_k}{\partial t} \right)} \right) - \frac{\partial L}{\partial q_k} = 0 \quad [\text{A3.11}]$$

When applied to equations [A3.9] and [A3.10], for  $k = 1$  we obtain:

$$\sum_j a_{1,j} \frac{\partial^2 q_j}{\partial t^2} + b_{1,j} q_j = 0 \quad [\text{A3.12}]$$

Similarly, for  $k = 2$ :

$$\sum_j a_{2,j} \frac{\partial^2 q_j}{\partial t^2} + b_{2,j} q_j = 0 \quad [\text{A3.13}]$$

We thus obtain  $n$  linear equations of this type when  $k$  varies between one and  $n$ ,  $n$  being the number of normal vibration frequencies of the active complex. Since these movements are vibrations, the solutions of this system will be written as:

$$q_j = A_j \exp(2\pi i \nu t) = A_j \exp(i\lambda t) \quad [\text{A4.14}]$$

(here,  $i$  is the pure imaginary number  $i^2 = -1$ ).

We define:

$$\lambda = 2\pi\nu \quad [\text{A3.15}]$$

Substituting equation [A3.15] into equation [A3.12], we obtain  $n$  equations of the following type:

$$\sum_{j=1}^n \left[ -a_{k,j} A_j \lambda^2 \exp(i\lambda t) + b_{k,j} A_j \exp(i\lambda t) \right] = 0 \quad [\text{A3.16}]$$

which is:

$$\sum_{j=1}^n \left[ -a_{k,j} \lambda^2 + b_{k,j} \right] A_j = 0 \quad [\text{A3.17}]$$

This results in a set of equations for  $A$  and the determinants of coefficients of  $A_j$  is zero:

$$\begin{vmatrix} b_{1,1} - a_{1,1} \lambda^2 & b_{1,2} - a_{1,2} \lambda^2 & \dots & b_{1,n} - a_{1,n} \lambda^2 \\ b_{2,1} - a_{2,1} \lambda^2 & b_{2,2} - a_{2,2} \lambda^2 & \dots & b_{2,n} - a_{2,n} \lambda^2 \\ \dots & \dots & \dots & \dots \\ b_{n,1} - a_{n,1} \lambda^2 & b_{n,2} - a_{n,2} \lambda^2 & \dots & b_{n,n} - a_{n,n} \lambda^2 \end{vmatrix} = 0 \quad [\text{A3.18}]$$

[A3.18] is an equation of the degree  $n$ , which gives  $n$  values for  $\lambda$  and therefore  $n$  values of  $v$  by using [A3.15].

If  $n \geq 3$ , it is not possible to strictly solve the equation and a numerical method must be used.

To solve equation [A3.18], coefficients  $a$  and  $b$  for the system must be known. Taking the example of an activated complex, with three aligned atoms of mass  $m_1$ ,  $m_2$  and  $m_3$ , the values of  $a_{k,j}$  coefficients (where  $M$  is the sum of the masses) are:

$$\begin{cases} a_{1,1} = \frac{m_1(m_2 + m_3)}{2M} \\ a_{1,2} = \frac{m_1 m_3}{M} \\ a_{2,2} = \frac{m_3(m_2 + m_1)}{2M} \end{cases} \quad [\text{A3.19}]$$

To calculate the  $b$  coefficients, the potential surface energy gives the coordinates  $r_1^\neq$  and  $r_2^\neq$  of the activated complex. In the vicinity of this point, the potential energy can be approximately represented by:

$$U = \frac{1}{2} f_{1,1} (r_1 - r_1^\neq)^2 + f_{1,2} (r_1 - r_1^\neq) (r_2 - r_2^\neq) + f_{2,2} (r_2 - r_2^\neq)^2 \quad [\text{A3.20}]$$

The three unknowns –  $f_{1,1}$ ,  $f_{1,2}$  and  $f_{2,2}$  – can be estimated by taking three points of coordinates  $r_1$  and  $r_2$  and solving the equation for these points (where  $U$  is read directly from the chart). The  $b_{j,k}$  coefficients are therefore:

$$\begin{cases} b_{1,1} = \frac{1}{2} f_{1,1} \\ b_{1,2} = f_{1,2} \\ b_{2,2} = \frac{1}{2} f_{2,2} \end{cases} \quad [\text{A3.21}]$$



## Notations and Symbols

A: pre-exponential term or frequency term

$[A_i]$ : concentration of component  $A_i$

$[A_i]_0$ : initial concentration of component  $A_i$

$\{A_i\}$ : amount of component  $A_i$

$\{A_i\}_0$ : initial amount of component  $A_i$

$|A_i|$ : activity of component  $A_i$

$|A_i||$ : activity of component  $A_i$

$[A^\ddagger]$ : concentration of the activated complex  $A^\ddagger$

$[A]$ : dimensionless concentration of component  $A$

$a$ : lattice parameter

$a$ : mesh parameter

$a$ : Morse law constant

AP: proton affinity of a molecule

$B$ : Hückel coefficient

$C$ : concentration

$D$ : diffusion coefficient

$D$ : coefficient of dissociation of a diatomic molecule

$D$ : dielectric constant of the medium

$d$ : density

$d$ : width of a reactor $E$ : space function $E_{\text{I}}$ : diatomic attractive energy, Morse $E_{\text{II}}$ : Anti-Morse diatomic repulsive energy $E_0^{\neq}$ : activation energy at absolute zero $E_{1/2}$ : the potential of half a polarographic wave $E_a$ : activation energy of an elementary reaction $(E_a)_i$ : apparent activation energy of a reaction in a mode determined by step  $i$  $E_D$ : activation energy of diffusion $E_k$ : space function of an elementary step,  $k$  $E_k$ : apparent activation energy of a reaction in a state mode determined by step  $i$  $E_p$ : potential energy of a set of atoms $e$ : electrode potential $e_0$ : thickness of a plate $e_{\text{th}}$ : thermodynamic equilibrium potential $e_p(t, \tau)$ : function space at time  $t$  of growth of a nucleus born at time  $\tau$  $f_{\text{het}}$ : spreading coefficient $\overline{F_i^{\text{ex}}}$ : excess molar free energy $f'_k$  and  $f''_k$ : speed factors of step  $k$  and its opposite $f'_r$ : rate factor of the breaking step of a chain reaction $f'_{ra}$ : rate factor of the branching step in a branched chain reaction $f_t$ : partition function of translation $G$ : shape function of diffusion $g_i^0$ : Gibbs free energy of pure  $i$  $h$ : Planck's constant $h$ : Thiele number/modulus $H$ : reaction enthalpy $H_0$ : Hammett acidity function

*I*: light intensity

$I_\infty$ : reaction end intensity at the peak of a diffractogram *X*

$I_0$ : initial intensity at the peak of a diffractogram *X*

*i*: polarization current

$i_{\text{ox}}$ : oxidation current

$i_{\text{red}}$ : reduction current

*J*: diffusion flux

*k*: rate coefficient of an elementary reaction

K: equilibrium constant

$K_m$ : Michaelis constant

$K_c^\neq$ : equilibrium constant of the activated complex with respect to concentrations

$K_p^\neq$ : equilibrium constant of the activated complex with respect to partial pressures

$k', k''$ : rate coefficient of two opposing elementary steps

$k_0^s$ : rate coefficient for infinite dilution

$k_k$ : rotary power of component  $A_k$

$k_B$ : Boltzmann constant

$k_I$ : rate coefficient in solvent *I*

$k_p$ : rate coefficient with respect to partial pressures

L: Lagrangian

$\bar{L}$ : mean length of a cylindrical pore

$M_A$ : molar mass of component *A*

*m*: mass

*N*: number of non-nucleated spots at time *t*

$N_0$ : Initial number of grain

$N_a$ : Avogadro's number

$n_R$ : refractive index

$n_0$ : initial amount of the reference reactant

- $n^*$ : dimension of the minimum nucleus
- $n^\neq$ : dimension of the agglomerate to the maximum of Volmer's curve
- $n_i$ : amount of component  $i$  (in moles)
- $P$ : gas pressure
- $P_0$ : pressure at the start of a reaction
- $P_m$ : molecular polarization
- $P_\infty$ : pressure at the end of a reaction
- $P^0$ : pressure at equilibrium
- $p$ : spreading parameter
- $p_j$ : reaction probability following path  $j$
- $p(v)$ : probability that a molecule will have rate  $v$
- $Q$ : Coulomb integral of a diatomic molecule
- $Q$ : quantity of heat involved
- $q$ : average number of collisions required for an active center to react
- $q_k$ : exchange flow of component  $k$  between a system and the outside
- $R$ : ideal gas constant
- $r$ : distance between atoms in a bond
- $r$ : rate of a reaction
- $\bar{r}$ : mean radius of a cylindrical pore
- $r_A$ : rate of a reaction with respect to component  $A$
- $r_{\rho[i]}$ : rate of step  $\rho$  in a mode determined by step  $i$
- $r_g(t, \tau)$ : growth rate at time  $t$  of a nucleus born at time  $\tau$
- $r_{[i]}$ : rate of a reaction in a state mode determined by step  $i$
- $r_0$ : equilibrium distance between atoms in a diatomic molecule
- $r_0$ : initial radius of a cylindrical or spherical grain
- $r_i, r_e$ : radius of internal and external interfaces
- $S$ : surface entropy
- $S_{BET}$ : specific surface of a solid
- $S_e$ : external surface of a solid grain

- $S_i, S_e$ : surface of inner and outer interfaces  
 $S_L(\tau)$ : area available for nucleation at time  $\tau$   
 $S_O$ : opening area of a pore; initial area of a solid  
 $S_p$ : area of the active interface  
 $T$ : temperature  
 $t$ : time  
 $t_f$ : time required for consumption of a grain  
 $U$ : potential energy  
 $V$ : volume  
 $V_{mA}$ : molar volume of  $A$   
 $V_p$ : porous volume per gram of solid  
 $v$ : surface or volume rate of a reaction  
 $\bar{v}$ : average speed of a ball  
 $v_A$ : volumetric or surface rate of a reaction with respect to component  $A$   
 $v_a$ : absolute rate of a reaction  
 $v_i$ : volumetric rate of the initiation of a chain reaction  
 $v_p$ : volumetric rate of the propagation of a chain reaction  
 $(v_a)_A$ : absolute rate of a reaction with respect to component  $A$   
 $v_k^0$ : molar volume of component  $k$  that is pure in its phase  
 $x_i$ : molar fraction of  $i$   
 $Y$ : thickness of a diffusion layer  
 $Z$ : partition function  
 $Z^\ddagger$ : partition function of the activated complex  
 $z$ : expansion coefficient  
 $z_A$ : electrovalence of ion  $A$   
 $z_r$ : elementary partition function of rotation  
 $z_t$ : elementary partition function of translation per length in units  
 $z_v$ : elementary partition function of vibration  
 $\alpha$ : exchange integral of a diatomic molecule

- $\alpha$ : fractional extent of a reaction
- $\alpha$ : probability that an active center  $X$  generates another active center
- $\alpha$ : transmission coefficient of the activated complex
- $\alpha_\infty$ : fractional extent at equilibrium
- $\alpha'$ : multiplication factor over all active centers
- $\alpha_A$ : fractional extent with respect to component  $A$
- $\beta$ : breakage probability of a chain
- $\beta$ : molarity of an elementary reaction
- $\beta_i$ : arithmetic stoichiometric coefficient of  $A_i$
- $\beta_i$ : order with respect to component  $A_i$
- $\beta_{j,\rho}$ : arithmetic stoichiometric coefficient of component  $X_j$  in the  $\rho$ -th reaction
- $\delta$ : branching probability of a chain reaction
- $\delta$ : length of the activation peak
- $\delta^*$ : probability of branching to a link in a chain reaction
- $\Delta$ : deviation from stoichiometry
- $\Delta G$ : Gibbs free energy of a reaction
- $\Delta H_i$ : enthalpy associated with reaction  $i$
- $\Delta I$ : light intensity absorbed
- $\Delta \tau$ : lifetime of an intermediate
- $\Delta Y$ : Laplacian of  $y$  is the function which is in Cartesian coordinates  $(x, y, z)$ :

$$\Delta Y = \frac{\partial^2 Y}{\partial x^2} + \frac{\partial^2 Y}{\partial y^2} + \frac{\partial^2 Y}{\partial z^2}$$

and which has another form in spherical or cylindrical coordinates.

- $\Delta(F_0^\neq)$ : standard free energy of activation
- $\Delta(G_0^\neq)$ : standard Gibbs free energy of activation
- $\Delta(H_0^\neq)$ : standard enthalpy of activation

$\Delta m$ : variation in solid mass between times 0 and  $t$

$\Delta(S_0^\neq)$ : standard entropy of activation

$\Delta\tau_p$ : average lifetime of the active center involved in the propagation

$\Delta_{X,i}(G)$ : Gibbs free energy of the formation of an agglomerate of size  $i$

$\Delta_{X,i}(G)^\neq$ : Gibbs free energy of formation of the agglomerate at the maximum of the Volmer curve

$\epsilon$ : dielectric constant

$\phi_g$ : surface rate of nucleation

$\phi_{[i]}$ : reactivity of a reaction determined by step  $i$

$\phi_k$ : reactivity of an elementary step  $k$

$\phi_{\rho[i]}$ : reactivity of step  $\rho$  in a mode determined by step  $i$

$\varphi$ : branching factor of a branched chain reaction

$\Gamma(\tau)$ : frequency of nucleation

$\gamma_A$ : activity coefficient of  $A$  relative to concentrations in vapor

$\gamma$ : specific frequency surface nucleation

$\gamma_A$ : activity coefficient of  $A$  relative to concentrations in solution

$\gamma_s$ : surface tension, specific frequency of nucleation

$\eta$ : overpotential

$\eta_k$ : stoichiometric abundance of component  $A_k$

$\chi_A$ : magnetic susceptibility of solid  $A$

$\Lambda$ : equivalent conductivity

$\lambda$ : mean free path of a gas molecule

$\lambda$ : wavelength of radiation

$\lambda_k$ : multiplying coefficient of step  $k$

$\mu$ : chains multiplying factor

$\mu$ : reduced mass

$\mu_m$ : mean number of active centers formed from one active center

$v_A$ : algebraic stoichiometric coefficient of  $A$

$v_i$ : algebraic stoichiometric coefficient of  $A_i$

$v_{jp}$ : algebraic stoichiometric coefficient of component  $X_j$  in the  $\rho$ -th reaction

$\Pi$ : thermodynamic equilibrium potential

$\theta$ : degree of recovery of a surface

$\theta$ : polarization angle

$\theta_\infty$ : degree of recovery at equilibrium

$\rho$ : mass density

$\aleph$ : affinity of a reaction

$\Xi$ : temperature coefficient of a reaction

$\xi$ : extent of a reaction

$\xi_A$ : extent of a reaction with respect to component  $A$

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