Jorge Ancheyta

CHEMICAL REACTION KINETICS

Concepts, Methods and Case Studies

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About the Author

Jorge Ancheyta, PhD, graduated with a bachelor's degree in Petrochemical Engineering (1989), master's degree in Chemical Engineering (1993) and master's degree in Administration, Planning and Economics of Hydrocarbons (1997) from the National Polytechnic Institute (IPN) of Mexico. He splits his PhD between the Metropolitan Autonomous University (UAM) of Mexico and the Imperial College London, UK (1998), and was awarded a postdoctoral fellowship in the Laboratory of Catalytic Process Engineering of the CPE-CNRS in Lyon, France (1999). He has also been visiting professor at the Laboratoire de Catalyse et Spectrochimie (LCS), Université de Caen, France (2008, 2009 and 2010), Imperial College London, UK (2009), and Mining University at Saint Petersburg, Russia (2016).

Prof. Ancheyta has worked for the Mexican Institute of Petroleum (IMP) since 1989, and his present position is Manager of Products for the Transformation of Crude Oil. He has also worked as professor at the undergraduate and postgraduate levels for the School of Chemical Engineering and Extractive Industries at the National Polytechnic Institute of Mexico (ESIQIE-IPN) since 1992 and for the IMP postgrade since 2003. He has been supervisor of more than 100 BSc, MSc and PhD theses. Prof. Ancheyta has also been supervisor of a number of postdoctoral and sabbatical year professors.

Prof. Ancheyta has been working in the development and application of petroleum refining catalysts, kinetic and reactor models, and process technologies, mainly in catalytic cracking, catalytic reforming, middle distillate hydrotreating and heavy oils upgrading. He is author and co-author of a number of patents and books and about 200 scientific papers; he has been awarded the highest distinction (Level III) as National Researcher by the Mexican government and is a member of the Mexican Academy of Science. He has also been guest editor of various international journals, for example *Catalysis Today*, *Petroleum Science and Technology*, *Industrial Engineering Chemistry Research*, *Chemical Engineering Communications* and *Fuel*. Prof. Ancheyta has also chaired numerous international conferences.

Preface

Reaction kinetics is mainly focused on studying the rate at which chemical reactions proceed. It is also used to analyse the factors that affect the reaction rates and the mechanisms by means of which they take place.

The study of the chemical kinetics of a reaction is a fundamental tool to perform in the design of chemical reactors, to predict the reactor's performance and to develop new processes. In fact, the first step for designing a chemical reactor is always the generation of experimental data whereby the reaction rate expressions are determined.

Chemical Reaction Kinetics: Concepts, Methods and Case Studies is devoted to describing the fundamentals of reaction kinetics, with particular emphasis on the mathematical treatment of the experimental data. The book is organized in six chapters, each one having detailed deductions of the kinetic models with examples.

Chapter 1 deals with the definitions of the main concepts of stoichiometry, reacting systems, chemical kinetics and ideal reactors.

Chapter 2 gives details about the mathematical methods to determine the reaction order and the reaction rate coefficient for irreversible reactions with one component. The methods described here include the integral method, differential method, total pressure method and half-life time method.

Chapter 3 reports the mathematical methods for evaluating the kinetics of irreversible reactions with two or three components by employing the integral method, differential method and initial reaction rate method. All of the mathematical treatments are performed according to the type of feed composition: stoichiometric, non-stoichiometric and with a reactant in excess.

Chapter 4 describes the reversible reactions of first order, second order and combined orders.

Chapter 5 presents the mathematical treatment of complex reactions, that is, simultaneous or parallel irreversible reactions and consecutive or in-series irreversible reactions, with the same order or with combined orders.

Chapter 6 is devoted to special topics in kinetic modelling, which include reconciliation of data generated during experiments to minimize the inconsistencies of mass balances due to experimental errors, a method for sensitivity analysis to assure that kinetic parameters are properly estimated and the convergence of the objective function to the global minimum is achieved, estimation of kinetic parameters of enzymatic reactions by means of different approaches, estimation of kinetic parameters of catalytic cracking reaction using a lumping approach and estimation of kinetic parameters of hydrodesulphurization of petroleum distillates.

Each chapter illustrates the application of the different methods with detailed examples by using experimental information reported in the literature. Step-by-step solutions are provided so that the methods can be easily followed and applied for other situations. Some exercises are provided at the end to allow the reader to apply all of the methods developed in the previous chapters.

Chemical Reaction Kinetics: Concepts, Methods and Case Studies is oriented to cover the contents of undergraduate and postgraduate courses on reaction kinetics of chemical engineering and similar careers. It is anticipated that *Chemical Reaction Kinetics: Concepts, Methods and Case Studies* will become an outstanding and distinctive textbook because it emphasizes detailed description of fundamentals, mathematical treatments and examples of chemical reaction kinetics, which are not described with such details in previous textbooks related to the topic. The particular manner in which the kinetic models are developed will help the readers adapt to their own reaction studied and experimental data.

I would like to acknowledge Prof. Miguel A. Valenzuela from the School of Chemical Engineering and Extractive Industries at the National Polytechnic Institute of Mexico, who contributed some ideas during the preparation of the Spanish version of this book, and also to hundreds of students who during more than 20 years of delivering lectures encouraged me to write this book.

Jorge Ancheyta

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Fundamentals of Chemical Reaction Kinetics

In homogeneous reacting systems, all the reactants and products are in the same phase. If the reaction involves a catalyst, it is also in the same phase. To determine the rates of reaction, experimental information is needed, which is generated by using properly designed small-scale reactors and experiments. These reaction rates cannot be directly measured, but they are obtained by means of experimental data such as the variation of time with respect to concentration of reactants or products, partial pressures and total pressure, among others.

To obtain the kinetic expression that represents the studied reaction, there are various approaches that correlate the experimental data with the variables that affect them.

When a reaction proceeds, one or more reactants can take part. It can be carried out in either liquid or gas phase, the reaction extent is measured by means of variations of reactants or product properties, or simply the reaction mechanisms are unknown. In any case, it is necessary before starting with the mathematical treatment of the experimental data to know the fundamentals of stoichiometry, thermodynamics and kinetics that will be further used for elucidating the specific mathematical expression for each type of reaction. This chapter is then devoted to introducing the readers to these topics.

1.1 Concepts of Stoichiometry

1.1.1 Stoichiometric Number and Coefficient

A chemical reaction can be represented as follows:

$$aA + bB + \ldots \rightarrow rR + sS + \ldots \tag{1.1}$$

where A, B, R and S are the chemical species, and a, b, r and s are their corresponding stoichiometric coefficients, which are the positive numbers before the chemical formula that balance the reaction.

Chemical Reaction Kinetics: Concepts, Methods and Case Studies, First Edition.
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Eq. (1.1) can be transformed as follows (Chopey, 1994):

$$-aA - bB - \ldots + rR + sS + \ldots = 0 \tag{1.2}$$

or with positive values:

$$\upsilon_1 A_1 + \upsilon_2 A_2 + \upsilon_3 A_3 + \ldots + \upsilon_{n-1} A_{n-1} + \upsilon_n A_n = 0 \tag{1.3}$$

which can be generalized as:

$$\sum_{i=1}^{n} \upsilon_i A_i = 0 \tag{1.4}$$

where A_i is the chemical formula and υ_i is the corresponding stoichiometric numbers.

Stoichiometric numbers (υ_i) are numerically equal to stoichiometric coefficients (*a*, *b*, *r* and *s*), but they have a negative sign for reactants and positive sign for products.

Example 1.1 Determine the stoichiometric coefficients and numbers for the following reaction for synthesis of ammonia:

$$N_2 + 3H_2 \rightarrow 2NH_3 \quad (aA + bB \rightarrow rR)$$

Solution

According to stoichiometry, the stoichiometric coefficients and numbers are:

Stoichiometric coefficient	Stoichiometric number
$a = 1$	$\nu_{N2} = -1$
$b = 3$	$\nu_{H2} = -3$
$r = 2$	$\nu_{NH3} = 2$

1.1.2 Molecularity

Molecularity is defined as the number of molecules of reactants that take part in a chemical reaction. Most of the reactions exhibit a molecularity of one or two, and in rare cases it reaches the value of three (Hill, 1977).

Molecularity is an appropriate concept for a process in which a simple or elemental step is occurring. Reactions in which one or several reactants produce one or several products in a simple path are scarce. For complex reactions, it is necessary to know the molecularity of each individual step of the reaction.

Table 1.1 Chemical reactions with different molecularity.

Molecularity	Examples	
1	$A \rightarrow R$	$n\text{-}C_4H_{10} \rightarrow i\text{-}C_4H_{10}$
	$A \rightarrow R + S$	$SO_2Cl_2 \rightarrow SO_2 + Cl_2$
	$A \rightarrow Products$	$(CH_3)_2O \rightarrow CH_4 + H_2 + CO$
2	$A + B \rightarrow R + S$	$O_3 + NO \rightarrow O_2 + NO_2$
	$A + B \rightarrow 2R$	$H_2 + Br_2 \rightarrow 2HBr$
	$A + B \rightarrow R$	$C_2H_4 + HI \rightarrow C_2H_5I$
	$2A \rightarrow Products$	$2N_2O \rightarrow 2N_2 + O_2$
3	$A + B + C \rightarrow Products$	$C_2H_5NO_2 + C_5H_5N + I_2 \rightarrow C_2H_4INO_2 + C_5H_5NH^+ + I^-$
	$2A + B \rightarrow Products$	$2NO + O_2 \rightarrow 2NO_2$

Based on this concept, the chemical reactions can be classified mainly as mono-molecular, bi-molecular and tri-molecular. A mono-molecular reaction involves one molecule of reactant. In a bi-molecular reaction, two molecules of reactants (either the same or different) are combined to form one or more products. Tri-molecular reactions are rare since they need the simultaneous collision of three molecules to produce one or several products. Examples of the different types or reactions according to their molecularity are shown in Table 1.1.

1.1.3 Reaction Extent

To follow the performance of a chemical reaction, it is necessary to define a parameter which properly represents the conversion of the reactants. In 1920, De Donder (1920) introduced the concept of reaction extent (ξ), by considering that the change in the number of moles of the chemical species is directly related to the stoichiometric number as follows:

$$\frac{\Delta n_2}{\Delta n_1} = \frac{\upsilon_2}{\upsilon_1} \quad or \quad \frac{\Delta n_3}{\Delta n_1} = \frac{\upsilon_3}{\upsilon_1}$$

or, in differential form:

$$\frac{dn_2}{dn_1} = \frac{\upsilon_2}{\upsilon_1} \qquad or \qquad \frac{dn_2}{\upsilon_2} = \frac{dn_1}{\upsilon_1}$$

$$\frac{dn_3}{dn_1} = \frac{\upsilon_3}{\upsilon_1} \qquad or \qquad \frac{dn_3}{\upsilon_3} = \frac{dn_1}{\upsilon_1}$$

For all chemical species, these equations can be generalized in the following manner:

$$\frac{dn_1}{\upsilon_1} = \frac{dn_2}{\upsilon_2} = \frac{dn_3}{\upsilon_3} = \dots = \frac{dn_i}{\upsilon_i} \tag{1.5}$$

Defining the parameter ξ, as the reaction extent:

$$\frac{dn_i}{\upsilon_i} = d\xi \tag{1.6}$$

The integration of Eq. (1.6) gives:

$$\int_{n_{io}}^{n_i} dn_i = \upsilon_i \int_0^{\xi} d\xi$$

$$\xi_i = \frac{n_i - n_{io}}{\upsilon_i} \tag{1.7}$$

It is then observed that if a moles of A_1 react with b moles of A_2 to produce r moles of A_{n-1} and s moles of A_n, the reaction extent ξ is equal to 1. Therefore, in general, it can be stated that ξ_a moles of A_1 react with ξ_b moles of A_2 to produce ξ_r moles of A_{n-1} and ξ_s moles of A_n.

1.1.4 Molar Conversion

The molar fractional conversion (x_i) is an intensive normalized parameter referred preferably to the limiting reactant; it is defined as the fraction of such a reactant that is transformed into products (Froment *et al.*, 2010):

$$x_i = \frac{\textit{Moles of reactant "i" transformed}}{\textit{Initial moles of reactant "i"}} = \frac{n_{io} - n_i}{n_{io}} \tag{1.8}$$

where $0 \le x_i \le 1$.

Subindex "$_o$" refers to the number of moles at zero time (i.e. the beginning of the reaction). Conversion can be correlated with reaction extent by means of Eqs. (1.7) and (1.8):

$$n_i = n_{io} + \upsilon_i \xi_i \tag{1.9}$$

$$n_i = n_{io} - n_{io} x_i \tag{1.10}$$

where:

$$\xi_i = -\frac{n_{io}}{\upsilon_i} x_i \tag{1.11}$$

The maximum reaction extent (ξ_i^{max}) can be calculated from Eq. (1.11) for the maximum conversion value ($x_i^{max} = 1$):

$$\xi_i^{\max} = -\frac{n_{io}}{\upsilon_i} \tag{1.12}$$

which implies that the minimum and maximum values of ξ_i are in the following range:

$$0 \le \xi_i \le -\frac{n_{io}}{v_i}$$

1.1.5 Types of Feed Composition in a Chemical Reaction

When a chemical reaction involves more than one reactant, the feed composition is different depending on the relative initial concentrations of the chemical species:

- *Stoichiometric feed composition*: This occurs when the ratio between the stoichiometric coefficients of the reactants is equal to the ratio between the amount of moles or the molar initial concentrations of reactants.
- *Non-stoichiometric feed composition*: This is when the ratio between the stoichiometric coefficients of the reactants is different from the ratio between the amount of moles or the molar initial concentrations of reactants.
- *Equimolar feed composition*: This is when the same amount of reactants are used at the beginning of the reaction to keep the ratio between the amount of moles or the molar initial concentration equal to unity no matter the stoichiometric coefficients of the reaction.
- *Reactant in excess*: This is when the ratio between the amount of moles or the molar initial concentrations of the reactants with respect to the limiting reactant is much higher than the ratio between the stoichiometric coefficients.

Some feed compositions can be considered close to the stoichiometric feed composition, and this happens when the ratio between the amount of moles or the molar initial concentrations of reactants is more or less the same as the ratio between the stoichiometric coefficients.

If at the beginning of the reaction there are inert components, although they are not reacting, they must be considered to define the type of feed composition.

Example 1.2 Define the different feed compositions for the following reaction of formation of nitrogen dioxide:

$$2NO + O_2 \rightarrow 2NO_2 \quad (2A + B \rightarrow 2R)$$

Solution

If a feed consists of 4 moles of NO and 2 moles of O_2, the ratio of moles between them is $n_{O2}/n_{NO} = 2/4 = 0.5$, and the ratio between stoichiometric coefficients is $b/a = 1/2 = 0.5$. Since $n_{O2}/n_{NO} = b/a$, the feed composition is stoichiometric.

If the feed consists of 3 moles of NO and 2 moles of O_2, the ratio of moles between them is $n_{O2}/n_{NO} = 2/3 = 0.66$, and the ratio between stoichiometric coefficients is $b/a = 1/2 = 0.5$. Since $n_{O2}/n_{NO} \neq b/a$, the feed composition is non-stoichiometric.

If the feed consists of 4 moles of NO and 4 moles of O_2, the ratio of moles between them is $n_{O2}/n_{NO} = 4/4 = 1$, and therefore the feed composition is equimolar. This feed composition is also non-stoichiometric since $n_{O2}/n_{NO} \neq b/a$.

If the feed consists of 1 mol of NO and 20 moles of O_2, the ratio of moles between them is $n_{O2}/n_{NO} = 20/1 = 20$, and the ratio between stoichiometric coefficients is $b/a = 1/2 = 0.5$. Since $n_{O2}/n_{NO} >> b/a$, it is considered that reactant B (O_2) is in excess.

If the feed consists of 4 moles of NO and 1.8 moles of O_2, the ratio of moles between them is $n_{O2}/n_{NO} = 1.8/4 = 0.45$, and the ratio between stoichiometric coefficients is $b/a = 1/2 = 0.5$. Since $n_{O2}/n_{NO} \approx b/a$, the feed composition is assumed to be close to stoichiometric.

An equimolar feed composition would also be 4 moles of NO, 4 moles of O_2 and 4 inert moles.

1.1.6 Limiting Reactant

The limiting reactant is the chemical species that in a chemical reaction is consumed before all of the other reactants (Himmelblau, 1970). If the reaction is carried out with only one reactant, the limiting reactant concept does not have meaning since it is obvious that it is the limiting one.

For reactions between two or more components with stoichiometric feed composition, any of the reactants can be the limiting one since they are consumed at the same rate. For other feed compositions, the definition of *limiting reactant* will depend on such a composition and on the reaction stoichiometry.

To know the limiting reactant in certain reactions, the concept of *reaction extent* can be used according to the following definition: "the limiting reactant is the chemical species that has the lowest value of maximum reaction extent (ξ_i^{max})."

Example 1.3 Determine the limiting reactant if, in the following reaction, 5 moles of ethylene bromide (A) and 2 moles of potassium iodide (B) are fed:

$$C_2H_4Br_2 + 3KI \rightarrow C_2H_4 + 2KBr + KI_3 \quad (A + 3B \rightarrow R + 2S + T)$$

Solution

The number of moles of each reactant in the feed and the corresponding stoichiometric numbers are:

$$n_{Ao} = 5\,\text{moles}, n_{Bo} = 2\,\text{moles}, \upsilon_A = -1 \text{ and } \upsilon_B = -3.$$

According to Eq. (1.12):

$$\xi_A^{\max} = -\frac{n_{Ao}}{\upsilon_A} = -\frac{5}{-1} = 5$$

$$\xi_B^{\max} = -\frac{n_{Bo}}{\upsilon_B} = -\frac{2}{-3} = {}^{2}/_{3}$$

Since $\xi_B^{\max} < \xi_A^{\max}$, thus the limiting reactant is *B*.

The results of this example can be confirmed by analysing the stoichiometry of the reaction, in which for each mole of *A*, 3 moles of *B* are required. For the case of this example, if 5 moles of *A* are used, then 15 moles of *B* will be required to complete the reaction, and if only 2 moles of *B* are present, then *B* is consumed first and *A* is in excess.

1.1.7 Molar Balance in a Chemical Reaction

If, in the reaction $aA + bB \longrightarrow rR + sS$, *A* is assumed to be the limiting reactant, and n_{Ao}, n_{Bo}, n_{Ro} and n_{So} are the number of moles of *A*, *B*, *R* and *S*, respectively, at the beginning of the reaction, then from Eq. (1.7) for reactant *A*:

$$n_A = n_{Ao} + \upsilon_A \xi_A$$

Substituting Eq. (1.11) in this equation:

$$n_A = n_{Ao} + \upsilon_A\left(-\frac{n_{Ao}x_A}{\upsilon_A}\right) = n_{Ao} - n_{Ao}x_A = n_{Ao}(1 - x_A) \tag{1.13}$$

For reactant *B*:

$$n_B = n_{Bo} + \upsilon_B \xi_A$$

$$n_B = n_{Bo} + \upsilon_B\left(-\frac{n_{Ao}x_A}{\upsilon_A}\right)$$

Since $\upsilon_B = -b$ and $\upsilon_A = -a$, then:

$$n_B = n_{Bo} + (-b)\left(-\frac{n_{Ao}x_A}{-a}\right) = n_{Bo} - \frac{b}{a}n_{Ao}x_A \tag{1.14}$$

which can also be written as follows to introduce the ratio n_{Bo}/n_{Ao}:

$$n_B = n_{Ao}\left(\frac{n_{Bo}}{n_{Ao}} - \frac{b}{a}x_A\right)$$

Defining the following feed molar ratio of B with respect to A:

$$M_{BA} = {}^{n_{Bo}}/_{n_{Ao}}$$

$$n_B = n_{Ao}\left(M_{BA} - \frac{b}{a}x_A\right) \tag{1.15}$$

Following the same procedure for R and S:

$$n_R = n_{Ro} + \frac{r}{a}n_{Ao}x_A \tag{1.16}$$

$$n_R = n_{Ao}\left(M_{RA} + \frac{r}{a}x_A\right) \tag{1.17}$$

$$n_S = n_{So} + \frac{s}{a}n_{Ao}x_A \tag{1.18}$$

$$n_S = n_{Ao}\left(M_{SA} + \frac{s}{a}x_A\right) \tag{1.19}$$

where:

$$M_{RA} = {}^{n_{Ro}}/_{n_{Ao}} \text{ and } M_{SA} = {}^{n_{So}}/_{n_{Ao}}$$

1.1.8 Relationship between Conversion and Physical Properties of the Reacting System

When it is not possible to generate experimental information in terms of common properties (concentration, total pressure, partial pressure, etc.), it is necessary to measure the reaction extent as a function of any physical property of the system, such as absorbance, electric conductivity, refractive index and the like, since they are additive functions of the contributions of all chemical species and in general they vary linearly with the concentration (Levenspiel, 1972).

For any physical property (λ), the contribution of all the chemical species can be represented by:

$$\lambda = \sum_{i=1}^{n} y_i\lambda_i \tag{1.20}$$

The relationship between λ and C_i can be written as:

$$\lambda_i \propto C_i \quad or \quad \lambda_i = k_{\lambda i}C_i \tag{1.21}$$

Dividing Eq. (1.7) between the volume to obtain the volumetric reaction extent ($\xi_i^{'}$):

$$\xi_i' = \frac{\xi_i}{V} = \frac{n_i - n_{io}}{V\upsilon_i} = \frac{\frac{n_i}{V} - \frac{n_{io}}{V}}{\upsilon_i} = \frac{C_i - C_{io}}{\upsilon_i}$$

$$C_i = C_{io} + \upsilon_i\xi_i'$$

And, substituting in Eq. (1.21):

$$\lambda_i = k_{\lambda i}\left(C_{io} + \upsilon_i \xi_i'\right) = k_{\lambda i} C_{io} + k_{\lambda i}\upsilon_i \xi_i'$$

Substituting λ_i in Eq. (1.20) and considering a constant value of ξ_i' for a specific chemical species:

$$\lambda = \sum_{i=1}^{n} y_i\left(k_{\lambda i} C_{io} + k_{\lambda i}\upsilon_i \xi_i'\right) = \sum_{i=1}^{n} y_i k_{\lambda i} C_{io} + \ \xi_i' \sum_{i=1}^{n} y_i k_{\lambda i}\upsilon_i \tag{1.22}$$

Since $k_{\lambda i}$ and υ_i are constant, the following equation can be derived:

$$\sum_{i=1}^{n} y_i k_{\lambda i}\upsilon_i = k_{\lambda i}\upsilon_i \sum_{i=1}^{n} y_i = k_{\lambda i}\upsilon_i = K_\lambda$$

Moreover, at zero time, Eq. (1.20) is:

$$\lambda_o = \sum_{i=1}^{n} y_i \lambda_{io} = \sum_{i=1}^{n} y_i k_{\lambda i} C_{io}$$

Substituting K_λ and λ_o in Eq. (1.22):

$$\lambda = \lambda_o + K_\lambda \xi_i' \ \text{ or } \ \lambda - \lambda_o = K_\lambda \xi_i' \tag{1.23}$$

Applying Eq. (1.23) at the maximum point of reaction extent:

$$\lambda_\infty - \lambda_o = K_\lambda \xi_i'^{\max} \tag{1.24}$$

Dividing Eq. (1.23) by Eq. (1.24):

$$\frac{\lambda - \lambda_o}{\lambda_\infty - \lambda_o} = \frac{K_\lambda\ \xi_i'}{K_\lambda\ \xi_i'^{\max}} = \frac{\xi_i'}{\xi_i'^{\max}} = \frac{\xi_i / V}{\xi_i^{\max} / V} = \frac{\xi_i}{\xi_i^{\max}} \tag{1.25}$$

Since the maximum reaction extent (ξ_i^{max}) is:

$$\xi_i^{\max} = -\frac{n_{io}}{\upsilon_i}$$

the ratio (ξ_i/ξ_i^{max}) is:

$$\frac{\xi_i}{\xi_i^{\max}} = \frac{\left(-n_{io}/_{\upsilon_i}\right)x_i}{\left(-n_{io}/_{\upsilon_i}\right)} = x_i \tag{1.26}$$

And, finally, Eq. (1.25) is:

$$x_i = \frac{\lambda - \lambda_o}{\lambda_\infty - \lambda_o} \tag{1.27}$$

where:

λ: Physical property at time t;
λ_o: Physical property at time zero ($t = 0$);
λ_∞: Physical property that does not change with time; and
x_i: Conversion.

Example 1.4 Reactant A is prepared under refrigeration and is introduced in a small capillary that acts as a reaction vessel, in which the decomposition reaction $A \longrightarrow R + S$ is carried out. The vessel is rapidly introduced in a bath containing water at the boiling point. During handling, there is no reaction. During the experiments, several data of the capillary length occupied by the reacting mixture (L) were collected (Levenspiel, 1979). Evaluate the values of conversion for the capillary length at different times indicated in Table 1.2.

Solution

In this case, Eq. (1.27) can be written as:

$$x_A = \frac{L - L_o}{L_\infty - L_o}$$

where:

L: Capillary length at time t;
L_o: Capillary length at time zero ($t = 0$);
L_∞: Capillary length that does not change with time; and
x_A: Conversion of reactant A.

In this equation, the initial capillary length (L_o) is unknown. However, from the analysis of the stoichiometry, it is deduced that the reaction is

Table 1.2 Data and results of Example 1.4.

Time (min)	Capilar length (cm)	x_A
0.5	6.1	0.2979
1.0	6.8	0.4468
1.5	7.2	0.5319
2.0	7.5	0.5957
3.0	7.85	0.6702
4.0	8.1	0.7234
6.0	8.4	0.7872
10.0	8.7	0.8511
∞	9.4	1.0000

irreversible; hence, at $t = \infty$, the conversion is 100% ($x_A = 1.0$), that is, all the reactant A has been transformed into R and S. In other words, 1 mole of reactant has been transformed into 2 moles of products. This indicates that at $t = \infty$, the number of moles is duplicated, as well as the volume and the capillary length, so that:

$$L_\infty = 2\,L_o$$

$$L_o = L_\infty/2 = 9.4/2 = 4.7cm$$

The application of the previous equation, at $t = 1$ min, gives:

$$x_A = \frac{L - L_o}{L_\infty - L_o} = \frac{6.8 - 4.7}{9.4 - 4.7} = 0.2979$$

The results of conversion for all the capillary lengths are reported in Table 1.2.

1.2 Reacting Systems

1.2.1 Mole Fraction, Weight Fraction and Molar Concentration

If the total number of moles and weight of all the chemical species present in the reacting mixture are n_t and w_t, respectively, and if n_i moles and w_i weight units of component i are present, the mole or molar fraction (y_i) and the weight fraction (y_{wi}) of species i in the system are defined as:

$$y_i = \frac{n_i}{n_t} \quad \text{(mole fraction)} \tag{1.28}$$

$$y_{wi} = \frac{w_i}{w_t} \quad \text{(weight fraction)} \tag{1.29}$$

By definition, the sum of fractions of all the components must be equal to unity:

$$\sum_{i=1}^{n} y_i = y_1 + y_2 + \ldots + y_n = \frac{n_1}{n_t} + \frac{n_2}{n_t} + \ldots + \frac{n_n}{n_t} = \frac{n_1 + n_2 + \ldots + n_n}{n_t} = \frac{n_t}{n_t} = 1$$

$$\sum_{i=1}^{n} y_{wi} = y_{w1} + y_{w2} + \ldots + y_{wn} = \frac{w_1}{w_t} + \frac{w_2}{w_t} + \ldots + \frac{w_n}{w_t} = \frac{w_1 + w_2 + \ldots + w_n}{w_t} = \frac{w_t}{w_t} = 1$$

To convert a mole fraction in a weight fraction or vice versa, the following relationship is used, which is obtained by using the definition of number of moles ($n = w/MW$):

$$y_i = \frac{n_i}{n_t} = \frac{{}^{w_i}/_{MW_i}}{{}^{w_t}/_{MW_t}} = \frac{w_i MW_t}{w_t MW_i} = y_{wi}\left(\frac{MW_t}{MW_i}\right) \tag{1.30}$$

where the molecular weight of the mixture (MW_t) is:

$$MW_t = \sum_{i=1}^{n} y_i MW_i \tag{1.31}$$

The molar concentration is defined as the ratio between the number of moles of a chemical species (n_i) by unit of the system volume (V) and is related with density (ρ_i) as follows:

$$C_i = \frac{n_i}{V} = \frac{{}^{w_i}/_{PM_i}}{V} = \frac{w_i}{V\ PM_i} = \frac{\rho_i}{PM_i} \tag{1.32}$$

Example 1.5 Evaluate the initial mole and weight fractions of the reactants if the following reaction of nitrogen dioxide formation starts with 3 moles of NO and 2 moles of O_2.

$$2NO + O_2 \rightarrow 2NO_2 \quad (2A + B \rightarrow 2R)$$

Solution

Mole fractions. Using Eq. (1.28):

$$y_{NOo} = \frac{n_{NOo}}{n_{to}} = \frac{n_{NOo}}{n_{NOo} + n_{O2o}} = \frac{3}{3+2} = 0.6$$

$$y_{O2o} = \frac{n_{O2o}}{n_{to}} = \frac{n_{O2o}}{n_{NOo} + n_{O2o}} = \frac{2}{3+2} = 0.4$$

Weight fractions. Using Eq. (1.29):

$$w_{NOo} = (n_{NOo})(MW_{NO}) = (3)(30) = 90\ g$$

$$w_{O2o} = (n_{O2o})(MW_{O2}) = (2)(32) = 64\ g$$

$$w_{to} = w_{NOo} + w_{O2o} = 90 + 64 = 154\ g$$

$$y_{wNOo} = \frac{w_{NOo}}{w_{to}} = \frac{90}{154} = 0.584$$

$$y_{wO2o} = \frac{w_{O2o}}{w_{to}} = \frac{64}{154} = 0.416$$

Using Eq. (1.30):

$$MW_t = y_{NO} MW_{NO} + y_{O2} MW_{O2} = 0.6(30) + 0.4(32) = 30.8\ g/gmol$$

$$y_{wNOo} = y_{NOo}\left(\frac{MW_{NO}}{MW_t}\right) = 0.6\left(\frac{30}{30.8}\right) = 0.584$$

$$y_{wO2o} = y_{O2o}\left(\frac{MW_{O2}}{MW_t}\right) = 0.4\left(\frac{32}{30.8}\right) = 0.416$$

1.2.2 Partial Pressure

Partial pressure is defined as the pressure that a gas in a mixture of gases would exert if it alone occupied the whole volume occupied by the mixture at the same temperature. Therefore, partial pressure p_i of gas i in a mixture of gases is calculated by multiplying its mole fraction (y_i) by the total pressure of the system (P):

$$p_i = y_i P$$

This is the so-called Dalton law, which also states that the total pressure exerted of a mixture of gases is equal to the sum of partial pressures of all the gases of the mixture (Smith *et al.*, 1980):

$$\sum_{i=1}^{n} p_i = \sum_{i=1}^{n} y_i P = P \sum_{i=1}^{n} y_i = P$$

Partial pressure of a gas in a mixture of gases is related to its molar concentration by means of the ideal gas law:

$$\begin{aligned} p_i V &= n_i RT \\ p_i &= y_i P = \left(\frac{n_i}{V}\right) RT = C_i RT \end{aligned} \tag{1.33}$$

where R is the universal gas constant, the common values of which are:

$$R = 1.987\frac{Cal}{gmol\ K} = 1.986\frac{BTU}{lbmol\ R} = 82.057\frac{atm\ \ cm^3}{gmol\ K} = 8.314\frac{J}{gmol\ K} = 0.08205\frac{atm\ \ lt}{gmol\ K}$$

$$= 10.73\frac{psia\ \ ft^3}{gmol\ K} 0.7302\frac{atm\ ft^3}{lbmol\ R} = 62.361\frac{mmHg\ lt}{gmol\ K} = 1.315\frac{atm\ ft^3}{lbmol\ K} = 8.31\frac{KPa\ lt}{gmol\ K}$$

$$5.83 \times 10^{-4}\frac{KWh}{lbmol\ R} = 7.82 \times 10^{-4}\frac{hp\ h}{lbmol\ R}$$

1.2.3 Isothermal Systems at Constant Density

When a system operates at constant density, the corresponding volume refers to the reacting mixture and not to the volume of the reactor. To this type of system belongs those reactions conducted in liquid phase or gas phase that either do not experience change in the number of moles or are carried out in hermetic vessels.

For an homogeneous reaction, which is carried out in the hermetic vessel shown in Figure 1.1, in gas phase, isothermally, with change in the number of moles and consequently with an increase or decrease in the

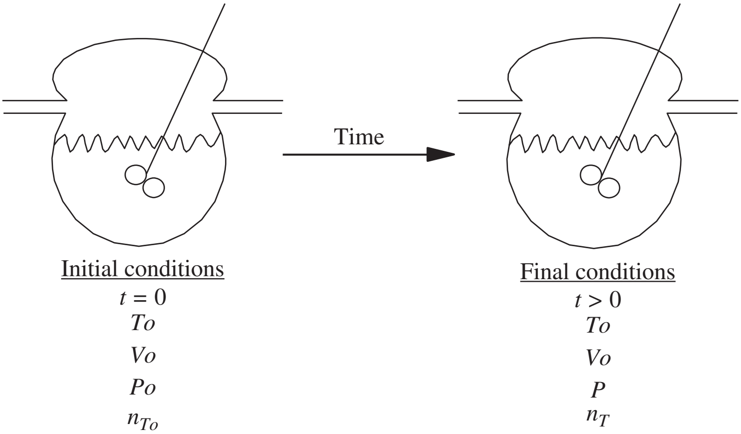

Figure 1.1 Reacting system at constant density.

pressure by expansion or compression due to the reaction, the molar balance at any time for the reaction $aA + bB \rightarrow rR + sS$ is the following:

$$n_A = n_{Ao} - n_{Ao}x_A$$

$$n_B = n_{Bo} - \frac{b}{a}n_{Ao}x_A$$

$$n_R = n_{Ro} + \frac{r}{a}n_{Ao}x_A$$

$$n_S = n_{So} + \frac{s}{a}n_{Ao}x_A$$

Assuming that the system follows the ideal gas law ($PV = nRT$) for the system at constant density, then at the beginning of the reaction (Figure 1.1):

$$P_oV_o = n_{To}RT_o \tag{1.34}$$

$$n_{To} = n_{Ao} + n_{Bo} + n_{Ro} + n_{So} \tag{1.35}$$

and at time t:

$$PV_o = n_TRT_o \tag{1.36}$$

$$n_T = n_A + n_B + n_R + n_S \tag{1.37}$$

Substituting the equations of the molar balance (Eqs. 1.13, 1.15, 1.17 and 1.19) in Eq. (1.37):

$$n_T = n_{Ao} + n_{Bo} + n_{Ro} + n_{So} + \frac{r}{a}n_{Ao}x_A + \frac{s}{a}n_{Ao}x_A - n_{Ao}x_A - \frac{b}{a}n_{Ao}x_A$$

$$n_T = n_{To} + \frac{n_{Ao}}{a}(r + s - a - b)x_A = n_{To} + \frac{n_{Ao}\Delta n}{a}x_A \tag{1.38}$$