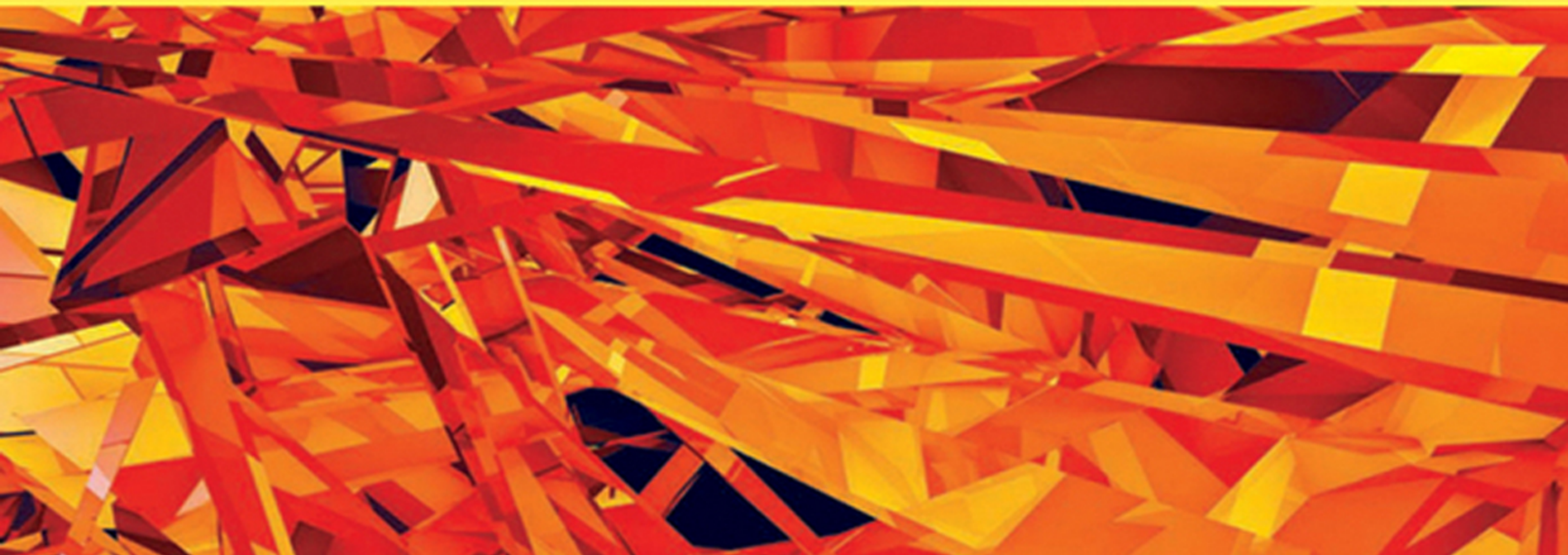
Extractive Metallurgy 1

Basic Thermodynamics and Kinetics

Alain Vignes



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Preface

Extractive metallurgy is the art of extracting metals from their ores and refining them.

This book deals with the processes, operations, technologies and processing routes of extractive metallurgy, i.e. the (production) extraction of metals from ores, concentrates (enriched ores), scraps and other sources and their refining to liquid metals before casting or to solid metals.

In many books dealing with metallurgy, the introduction starts by recalling the steps of the progress of metallurgy. These steps, according to and since Lucrèce, are identical to those of human progress: the copper age, the bronze age, the iron age, the silicon age[1]. According to Mohen[2], the considerable role attributed to the three principal metals in the development of human societies must not be overstressed or overvalued. It is nonetheless true that “metallurgy is the most advanced prehistoric manifestation of the mastery of natural resources” (Mohen). Extracting copper from its ore dates back to the middle of the fifth millennium before our age and extracting iron from its ore dates from the beginning of the second millennium before our age.

The winning (production) of metals and alloys today is still one of the basic industries of the transformation of matter. Metals and alloys still are essential resources for metallic, mechanic, electromagnetic, electric and even electronic industries (silicon is treated as a metal).

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1 S.L. SASS, *The Substance of Civilization: Materials and Human History from the Stone Age to the Age of Silicon*, Arcade Publishing, 1999.

2 J.P. MOHEN, *Métallurgie préhistorique*, Masson, Paris, 1990.

This industry is characterized by:

– Production (of primary metal) ranging from 1,345 million tons (Mt) of steel a year to 138,000 tons of titanium, in 2007[3].

Steel	Aluminum	Copper	Zinc	Lead	Nickel	Magnesium	Titanium
1,345	38	15.6	10.6	7.0	1.66	0.79	0.138

Table 1. *World Metal Production in 2007*

– Very high growth rates in the years 1950 to 1973, and again since 2000. The production of steel was 200 million tons in 1950. The production of aluminum increased from 2 million tons in 1950 to 10 million tons in 1973, reaching 38 million tons in 2007. If in developed countries the growth in terms of tonnage has strongly slowed in recent decades, this is due to a smaller consumption of these products owing to the increase in mechanical and physical properties of the materials and parts forged from these materials, thus requiring less material for the same usage. However the annual production of steel in China increased from 182 million tons in 2002 to 489 million tons in 2007[4].

– Production costs varying by a factor of 20 to 25 between steel and titanium. The three principal costs in metal production are investment, ore and energy consumption. The energy consumption is about 20 GJ/ton of steel, 80 GJ/ton of aluminum and 160 GJ/ton of titanium. Hence the permanent research into improvements of the processes or operations and/or the development of new processes.

– Very high recycling rates. Recycled steel represents 46% of iron sources in worldwide steel production. The "electric furnace processing route" produces 35% of steel. It uses 75% less energy than the integrated route. The recycling rate of aluminum represents 25% of total production and the energy consumption from recycled aluminum represents 5% (energy reflow) of energy consumption from the ore. The production of primary zinc is 7.4 million tons and from recycled zinc is 2.1 million tons. In the case of lead, the production from recycled lead is greater than 50%.

– Very high quality products with degrees of purity (i.e. contents of harmful impurities) for the finished products, comparable to the purity of materials for electronics and with very narrow concentration ranges of the alloying elements, to obtain physical or mechanical properties with very small dispersions. For metal castings reaching 300 tons, steel grades with carbon content of less than 25 ppm,

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[3] US Geological Survey, *Minerals Commodity Summaries and Minerals Yearbook*, 2007.

[4] Source: IISI (International Iron and Steel Institute).

and sulfur and phosphorus content of less than 20 ppm or even 10 ppm can be guaranteed. The impurities in liquid aluminum after electrolysis and refining are <3 ppm for Li, <1 ppm for Ni and <1/10 ppm for H. The contents of each impurity in copper for electric wire must be <1 ppm. Achieving these chemical performances coupled to research into the lowest energy consumption requires perfect mastery of the process and thus a profound knowledge of its technology.

– The energy consumption and reduction of pollution (rejected CO_2, SO_2 and dust) from the production of metals have become major objectives, leading to the development of new processes or product lines.

– Non-ferrous metal ores often have very low contents of many rare or noble metals, whose extraction and recuperation often constitutes essential steps for the global production economy. Such extraction requires very complex processing routes for recovering rare or precious metals.

Often the metal can or could be produced via several processing routes. The industrial processing routes for a given metal are to a large extent dependent on economic considerations, i.e. the cost of raw materials, cost of energy, cost of equipment and market conditions.

The raw materials for the production of metals and alloys are the ores on one hand and recovered and recycled products on the other:

– the ores. The ores of Sn, Fe, Mn, Cr, Al, Ni are oxides. The ores of many non-ferrous metals, e.g. Cu, Ni, Pb, Zn, Cd, Mo, are sulfides;

– the recycled metals (Fe, Al, Cu, Zn, Pb);

– the steel plant dust containing metals or oxides (Zn, Cd, Pb);

– the residues from leaching operations, e.g. the red muds, a residue containing titanium, vanadium, gallium produced by bauxite leaching during the Bayer process, the gold cyanide sludge;

– the drosses, slags and scoria treated to recover rare metals or to eliminate harmful components.

The operations of mineralogy are known as ore-dressing. In the general case, the ore must be concentrated to free it from minerals of no value, called the gangue, whose main components are oxides (SiO_2, Al_2O_3, CaO, MgO). This is done using physical operations: grinding (comminution) or fragmentation of the ore to small sizes to allow easy separation, then separation by sedimentation and enrichment by flotation, magnetic sorting etc., leading to a raw material enriched in components.

The operations of extractive metallurgy treat ores, concentrates and recycled metals. These are mixtures of oxides or sulfides. The processing routes of the ore's treatment, raw or enriched, together with the technologies used in these routes depend first of all on the ore's nature and its metal content.

Thus iron ore is practically pure iron oxide (hematite or magnetite), with a content of iron of the order of 65% and several percent of silica (SiO_2). The basic treatment will be the direct reduction of the iron oxide.

Alternatively, the ores can be treated to give an essentially pure chemical compound of the metal and this compound may be converted to give the metal. For example, aluminum's ore (bauxite), is composed of alumina (Al_2O_3, 30–60%), iron oxide (Fe_2O_3, 1–30%) and silica (1–10%). The first phase of the ore's treatment will be the separation of these oxides to obtain the pure alumina, which will be reduced in a second phase by electrolysis in molten salts.

The copper sulfide ores, whose copper content is very low, exceptionally reaching 5%, undergo processes of mineralogy (flotation) to obtain concentrates containing Cu (20–25%), Fe (30%) and S (30%). The separation of copper sulfide from iron sulfide via a selective roasting constitutes the first step of the treatment. The second step is a copper converting.

Zirconium ore, zircon (silicate of zirconium and hafnium, i.e. $ZrSiO_4$ and $HfSiO_4$), is converted into gas chlorides whose separation is possible before the reduction of zirconium chloride to very pure zirconium.

Extraction and refining operations may be carried out by pyrometallurgical, hydrometallurgical, halide and electrometallurgical processes:

– *pyrometallurgy* involves processes carried out at high temperatures divided into:

- *primary pyrometallurgy*, which converts the ore or concentrate to impure metal generally in liquid form. The main operations are oxide reduction, sulfide roasting, smelting and converting;

- *secondary pyrometallurgy* is the treatment of the liquid metal, obtained either directly in the first step or by remelting metallic recycled products. It consists of several refining operations, mainly the removal of harmful elements left in the liquid metal (deoxidation, dehydrogenation, etc.) and addition of the alloying elements;

– *hydrometallurgy* consists of operations of primary metallurgy performed in aqueous solutions, at relatively low temperatures and often under high pressure, such as leaching, precipitation and solvent extraction;

– *hydroelectrometallurgy* consists of salt electrolysis in an aqueous solution, yielding the metal in a solid state. Electrorefining constitutes a refining process of the metal obtained in a first electrolysis;

– *pyroelectrometallurgy* consists of processes employing electrolysis (reduction), either of mattes or oxides (e.g. Al_2O_3) or chlorides (e.g. $MgCl_2$) into molten salts, yielding the metal in a liquid state;

– *chlorometallurgy* consists of the following processes:

- *chlorination* of a highly reactive metal oxide, such as titanium or zirconium,
- *separation* of the chlorides via physical processes: distillation and extractive distillation,
- *reduction* of chlorides by metallothermic reduction.

The upholding into operation of an existing processing unit, the improvement of an industrial operation, the implementation of a new technology (not formerly used in the unit) and the development of a new process all fall within technical considerations, as well as economic considerations. In this series, economical considerations will not be discussed, for obvious reasons, but sound economic decisions rest on in-depth technical analyses of the processes and operations. Such in-depth analyses are based on process engineering principles. These methods use mathematical models allowing us to simultaneously take into account the elementary processes and their couplings[5]. These mathematical models are sets of fundamentally-based differential equations derived from thermodynamics, kinetics, heat flow, fluid flow, mass transfer and electromagnetic phenomena. Modeling will thus be at the heart of all the analyses here. The solutions to these differential equations, via analytical or numerical methods, allow us to achieve sound quantitative previsions. Analytical solutions of these equations of partial derivatives have been established in numerous instances, but only for specific cases. They are nonetheless interesting as they reveal the influence of certain factors or parameters on the processes. This leads to very useful dimensionless numbers. These analytical solutions and the dimensionless equations are presented and used in these volumes. For the numerical methods of the solution of equation systems, the reader is referred to specialized publications.

The subject of extractive metallurgy is also addressed in two other publications written by myself and published by ISTE. This volume deals with the fundamentals

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[5] J. SZEKELY, “The mathematical modeling revolution in extractive metallurgy”, *Metallurgical Transactions B*, Vol. 19B, p. 525-540, 1988, and H.Y. SOHN, “The coming-of-age of process engineering in extractive metallurgy”, *Metallurgical Transactions B*, Vol. 22B, p. 737-754, 1991.

of thermodynamics and kinetics of the extraction processes. The second volume, *Metallurgical Reaction Processes*, deals with the extraction and refining unit processes. The third volume, *Processing Operations and Routes*, deals with the operations and technologies used in industrial production and industrial processing routes, i.e. the combination of steps or operations used to convert the available ore to metal, illustrated by flowsheets.

This book is intended not only for students of metallurgical and mechanical engineering who want to acquire the bases of this technology, decreasingly taught in universities and engineering schools, but also for engineers confronted with a new production problem, either directly (management of a industrial operation or development of a new process) or indirectly (in the definition of a materials' specification).

It is conceived to be accessible to any student or engineer with general chemistry and physics training. It only necessitates elementary knowledge in chemistry, thermodynamics and chemical kinetics. One of the objectives of this book is to allow the easy consultation of books and technical publications dealing with this field.

This book is the result of my chemical engineering training, courses taught in the Écoles des Mines of Nancy and Paris (France), visits to industrial plants, research performed in collaboration with industry, studies and common work as a consultant and as an industrialist in direct contact with numerous producers of metallic parts. I would like to thank, more particularly, engineers from the research centers of Arcelor-Mittal (IRSID), Alcan (ex-Péchiney), Cezus and Eramet for their advice and authorized opinions.

I would most particularly like to thank Professors Jean Philibert and André Pineau. Finally this book is dedicated to Professors Pierre Le Goff and Pierre-Marie Fourt.

Alain VIGNES

February 2011

Chapter 1

Metallurgical Thermochemistry

1.1. Introduction

The industrial *processing route* for the production of a metal, from its ore or concentrate to a refined metal, consists of a combination or sequence of *operations* (illustrated conveniently by means of a flowsheet, see [VIG 11c], Chapter 10), performed in *reactors*. In a *unit operation* a single *extraction process* is performed, such as the roasting of a sulfide ore or the reduction of an oxide or a transfer process (removal of a component from a phase) such as a solvent extraction. *In some operations, such as in blast furnaces, several processes occur in sequence* from iron ore to hot metal *in the same reactor*.

These operations are carried out in different conditions: discontinuous (batch, closed), continuous (open) and semi-continuous (semi-batch), see Figure 1.2.1.

Metallurgical processes, occurring in the operations of extraction and refining of metals and alloys, involve homogeneous chemical reactions or heterogeneous chemical reactions (between reactants present in two phases, the reaction occurring at the interface between the two phases).

In the first part of this chapter the physical quantities allowing the quantitative description of the state (and its evolution) of a reaction mixture undergoing a chemical reaction are defined. The second part deals with the fundamentals of thermodynamics for these reactions.

The thermodynamic analysis of reactions constitutes the first unavoidable step of the study of these extraction processes.

Thermodynamics provides three important pieces of information:

– it allows the calculation of the energy balance, i.e. the energy (thermal or electric) that needs to be provided or extracted for the reaction to occur at a certain temperature and pressure;

– it allows the calculation of the maximum possible degree of advancement (i.e. the extent) of a reaction and the maximum possible fractional conversion of the reactants, in different operating conditions, which constitute what can be called the *thermodynamic modeling* of a process.

– it allows the determination of operating conditions (T, P, initial composition of the reaction mixture), optimizing the maximum possible fractional conversion of the reactants.

The thermodynamic quantities and data necessary for the prediction of operating conditions of processes are of two types:

– *thermodynamic functions*: enthalpy, Gibbs free energy (free enthalpy), affinity of a reaction, activity of a phase's component, law of mass action, equilibrium constant of a reaction;

– *phase diagrams*: graphs that show which phases (and their extension) are present in a binary, ternary system. The coordinates of these diagrams are various parameters: for instance: temperature (ordinate) and composition (abscissa), see section 1.4. These equilibrium diagrams are quantitatively related to the thermodynamic functions of the systems they describe.

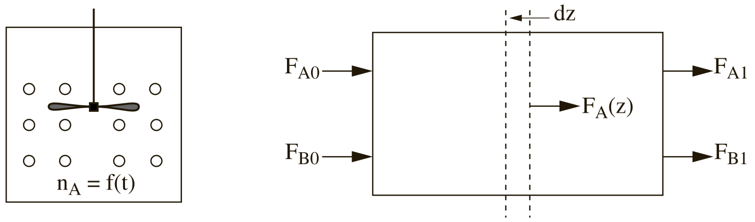
A thermodynamic analysis is often sufficient to predict the maximum possible extent of reactions carried out at high temperatures, especially in the case of reactions between fluid phases, for which the process rates are not limited by slow diffusion phenomena in solid phases or by chemical reactions. It can then be considered that the reaction is indeed occurring: until the total consumption of a reactant or until it nearly reaches equilibrium state for a closed system; or is occurring through a succession of equilibrium states, in the case of a semi-batch system during the continuous injection of a reactant.

The extent of this presentation comes from the fact that in the literature (books and publications) dealing with this field, many definitions and expressions can be found for the same quantities, especially for the activities of components. All these different definitions are presented in this chapter in order to help the reader interpret and understand future readings.

1.2. Quantities characterizing the state of a system and its evolution

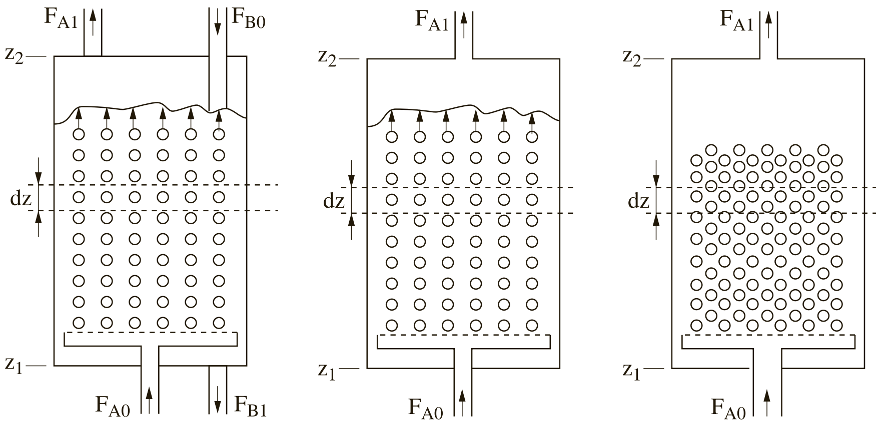
The progress of a chemical reaction can be expressed by a single quantity: the degree of advancement (or extent) ξ, see equation [1.2.5]. The fractional conversion of the reactants, see equation [1.2.7], depends on the degrees of advancement of the reactions occurring during the process. The corresponding equations depend on the type of operations, see Figure 1.2.1.

1.2.1. *The types of operations*



a) Batch (closed) system

b) Steady-state (open) flow system



c) Steady-state countercurrent flows system

d) Semi-batch (fluid-fluid) system

e) Semi-batch (solid-fluid) system

Figure 1.2.1. *Types of operations and contacting patterns for fluid-fluid (c and d) and fluid-solid (e) systems*

The different operations can be performed under three modes: a discontinuous mode, a continuous mode and a semi-continuous mode:

– In a *discontinuous operation*, the reactants are charged into the reactor, mixed and left to react for a certain time. The reaction mixture is then discharged. These reactors are qualified as *batch (closed)*, as there is no flow of matter in or out of the reactor, see Figure 1.2.1a.

– In a *continuous operation*, the reactor is an *open system* that has one or more openings through which the reactants are introduced and one or more exits from where the products of the process are extracted. Thus, there is one (in the case of a homogeneous reaction) or several flows of matter (in the case of a heterogeneous reaction) getting in and out of the reactor. The steady state is the normal operating regime of this operation: steady state plug flow for a homogeneous system (reaction), see Figure 1.2.1b; or steady-state countercurrent or co-current flows for a two-phase system with various contacting patterns, see Figure 1.2.1c.

– in a *semi-continuous operation*, in a *semi-open (semi-batch) system reactor*, one of the reactants or one phase is introduced at the start of the operation (discontinuous charging, for example a charge of solid particles or a liquid phase). The other reactant is continuously introduced during the operation (continuous feed), for instance a gas phase injected as bubbles into a liquid bath, see Figure 1.2.1d, or a gas phase blown through a bed of solid particles, see Figure 1.2.1e. The reactions proceed as long as the reactants are added.

1.2.2. *Stoichiometric description of a chemical system*

We consider the following reaction (homogeneous or heterogeneous) occurring in the indicated direction:

$$\nu_A A(\alpha) + \nu_B B(\beta) \rightarrow \nu_R R(\alpha) + \nu_S S(\beta) \qquad [1.2.1]$$

A, B, R and S are the components (elements, molecules or compounds), and α and β are the phases in which the components are present.

Although the number of molecules can vary in a system during the reaction, the number of elements (“*chemical elements*”) does not vary. Thus, the stoichiometric coefficients ν of the reaction are not arbitrary. They satisfy the conservation equations of the elements, see equations [1.2.12b].

Besides this, during the reaction there is conservation of matter. The mass conservation law leads to the *stoichiometric equation* between the stoichiometric coefficients:

$$\nu_A M_A + \nu_B M_B = \nu_R M_R + \nu_S M_S \qquad [1.2.2]$$

For a system in which several chemical reactions may occur, it is important to have a criterion that gives the number r of independent (distinct) reactions necessary to determine the chemical composition of the system when the equilibrium state has been reached. This number is equal to the difference between the number n of non-inert (reacting) components, and the number e of the chemical elements [PRI 54]:

$$r = n - e \qquad [1.2.3]$$

1.2.2.1. *The Gibbs phase rule*

The phase rule that gives the number of *intensive variables w* (T, P and mole fractions) determining the physicochemical state of a multiphase system at equilibrium can be either written as:

$$w = (n - r) + 2 - \phi \qquad [1.2.4a]$$

where ϕ is the number of phases at the same pressure p and at the same temperature T, [PRI 54] or as:

$$w = C_{(\text{independent})} + 2 - \phi \qquad [1.2.4b]$$

where the number of independent components is equal, at most, to the number of chemical elements [ROS 83].

For instance, a system composed of three phases and three components: $CO_3Ca(s)$, $CaO(s)$ and $CO_2(g)$, undergoing the following reaction:

$$CO_3Ca(s) = CaO(s) + CO_2(g)$$

is mono-variant w = 1 and at equilibrium, its physicochemical state is entirely determined by the set temperature. At a temperature T, the pressure of CO_2 at equilibrium with the two solid phases is determined. If the reaction is carried out in the presence of an inert gas under a pressure P, the reaction and CO_2 gas release against the pressure P, will only occur at one temperature fixed by P.

DUHEM THEOREM.– Regardless of the number of phases, components and chemical reactions occurring in the system, the equilibrium states of a closed system, whose initial masses (or number of moles) of each component in each phase is given, are completely determined by two independent variables.

1.2.3. *Evolution of a system's state: degree of advancement of a reaction*

The fractional conversion rates of the reactants can be expressed as a function of a single quantity: the *degree of completion or degree of advancement (extent)* of the reaction ξ.

1.2.3.1. *For a closed system*

The reaction mixture (mono- or multiphase) within a closed container contains n_j molecules of each component j:

– at the initial state: n_{A0} n_{B0} n_{R0} n_{S0} $\{\sum n_{j0} + n_{inert}\}$;

– at a time t: $n_A(t)$ $n_B(t)$ $n_R(t)$ $n_S(t)$ $\{\sum n_j(t) + n_{inert}\}$.

In the course of reaction [1.2.1], the variations of the number of moles of each component are proportional to the corresponding stoichiometric coefficients of the reaction (*law of definite proportions*):

$$dn_A / -\nu_A = dn_B / -\nu_B = dn_R / \nu_R = dn_S / \nu_S = d\xi \qquad [1.2.5]$$

where $\xi(t)$ is the reaction's degree of advancement, at time t. It is an *extensive variable* that can take any positive value.

Convention: the stoichiometric coefficients v are all positive (an inverse convention is often used).

For a degree of advancement ξ of the reaction, $\nu_R \, . \, \xi$ moles of R and $\nu_S \, . \, \xi$ moles of S are produced, $\nu_A \, . \, \xi$ moles of A and $\nu_B \, . \, \xi$ moles of B have been consumed. The molar balance of each component is written:

$$n_A(t) - n_{A0} = -\nu_A \, . \, \xi(t) \qquad [1.2.6a]$$

$$n_B(t) - n_{B0} = -\nu_B \, . \, \xi(t) \qquad [1.2.6b]$$

$$n_R(t) - n_{R0} = +\nu_R \, . \, \xi(t) \qquad [1.2.6c]$$

$$n_S(t) - n_{S0} = +\nu_S \, . \, \xi(t) \qquad [1.2.6d]$$

The state at time t of a mono- or a multiphase reaction mixture, in which a chemical reaction is occurring, is determined by the initial number of moles of each component n_{ij}, by the degree of advancement of the reaction $\xi(t)$ and by two physical variables (T and P).

The *fractional conversion of a reactant*[1] is the ratio of the number of moles of reactant having reacted to the number of moles initially present:

$$\chi_A(t) = (n_{A0} - n_A(t)) / n_{A0} \qquad [1.2.7]$$

with the following relationship between the fractional conversion of reactants A and B:

$$n_{A0} \cdot \chi_A / \nu_A = n_{B0} \cdot \chi_B / \nu_B \qquad [1.2.8]$$

The fractional conversion of a reactant is an intensive variable, independent of the initial number of moles, ranging from 0 (initial state) to 1 (final state).

These fractional conversions can be expressed as a function of the degree of advancement ξ of the reaction by:

$$\chi_A(t) = \nu_A . \xi(t) / n_{A0} \qquad [1.2.9a]$$

$$\chi_B(t) = \nu_B . \xi(t) / n_{B0} \qquad [1.2.9b]$$

1.2.3.2. *Closed system within which several chemical reactions occur*

The molar balance of each component can be expressed as a function of the degrees of advancement of the reactions occurring, by:

$$n_j(t) = n_{j0} + \sum(\pm\nu_{jr}) \cdot \xi_r \qquad [1.2.10]$$

where the sign before the stoichiometric coefficient is negative if the component is a reactant for a reaction r, and positive if the component (possibly the same one) is a product in a reaction r'. The fractional conversions, at time τ, for the reactants in one or more reactions are given by:

$$\chi_A(t) = \{\sum\nu_A \cdot \xi(\tau)\} / n_{A0} \qquad [1.2.11]$$

EXAMPLE.– For a system that initially involves two reactants: an oxide and carbon, undergoing simultaneous reactions:

$$1/y\ M_xO_y(s) + CO(g) \rightarrow x/y\ M(s) + CO_2(g) \qquad (R)$$

$$C(s) + CO_2(g) \rightarrow 2\ CO(g) \qquad (B)$$

---

[1] The fractional conversion makes sense only for reactants.

where ξ_R is the degree of advancement of the oxide reduction by carbon monoxide and ξ_B is the degree of advancement of the Boudouard reaction (B). The state of the system may be described by these degrees of advancement. For example, the numbers of molecules (or masses) of each component present at a specific time are given by the following balances:

$$n_{MxOy} = n^\circ_{MxOy} - \xi_R/y$$

$$n_M = (x/y)\ \xi_R$$

$$n_C = n^\circ_C - \xi_B \qquad [1.2.12a]$$

$$n_{CO} = -\xi_R + 2\ \xi_B;$$

$$n_{CO2} = \xi_R - \xi_B$$

$$p_{CO} = \{-\xi_R + 2\ \xi_B\}\ P / \xi_B$$

$$p_{CO2} = \{\xi_R - \xi_B\}\ .\ P / \xi_B$$

The state of the system may also be described by the conservation equations of elements M, C and O:

– for the metal M: $n^\circ_{MxOy} = n_{MxOy} + xn_M$;

– for the carbon: $n^\circ_C = n_C + n_{CO} + n_{CO2}$; and [1.2.12b]

– for the oxygen: $n^\circ_{MxOy} = n_{MxOy} + yn_{CO} + 2\ yn_{CO2}$.

It is easy to verify that these two sets of equations are equivalent.

1.2.3.3. *Open system*

In the *law of definite proportions*, see equation [1.2.5], in terms of F, the molar flow rates of each constituent in and out of the reactor can be expressed by:

$$\frac{\left(F_{A0} - F_{A1}\right)}{-\nu_A} = \frac{\left(F_{B0} - F_{B1}\right)}{-\nu_B} =$$

$$\frac{\left(F_{\mathrm{Re}0} - F_{R1}\right)}{\nu_R} = \frac{\left(F_{S0} - F_{S1}\right)}{\nu_S} \qquad [1.2.13]$$

For an open system and a single phase in convective flow within a tubular reactor, the fractional conversion of reactants A and B presents in this phase, between the entry and exit of the reactor (see Figure 1.2.1.b) can be expressed by:

$$\chi_{A1} = \frac{\left(F_{A0} - F_{A1}\right)}{F_{A0}} \qquad [1.2.14a]$$

$$\chi_{B1} = \frac{\left(F_{B0} - F_{B1}\right)}{F_{B0}} \qquad [1.2.14b]$$

The degree of advancement of the reaction in moles per time unit reached at the exit of the reactor, can be written as:

$$\xi_1 = \frac{\left(F_{A0} - F_{A1}\right)}{\nu_A} = \frac{\left(F_{B0} - F_{B1}\right)}{-\nu_B} \qquad [1.2.15]$$

Under a steady-state flow regime, these two quantities do not vary over time, but vary from point-to-point along the flow path:

$$\chi_A(z) = \frac{\left(F_{A0} - F_A(z)\right)}{F_{A0}} \qquad [1.2.16]$$

and:

$$\xi(z) = \frac{\left(F_{A0} - F_A(z)\right)}{\nu_A} = \frac{\left(F_{B0} - F_B(z)\right)}{\nu_B} \qquad [1.2.17]$$

with:

$$\frac{\left(F_{A0} \cdot \chi_A(z)\right)}{\nu_A} = \frac{\left(F_{B0} \cdot \chi_B(z)\right)}{\nu_B} \qquad [1.2.18]$$

For a length dz, we have:

$$\left(\frac{F_{A0}}{\nu_A}\right) \cdot \left(\frac{d\chi_A}{dz}\right) = \left(\frac{F_{B0}}{\nu_B}\right) \cdot \left(\frac{d\chi_B}{dz}\right) \qquad [1.2.19]$$

For a two-phase system α and β, *with concurrent flows of both phases*, with reactant A present in phase α and reactant B in phase β, the previous relationships are all valid.

For a two-phase system *with countercurrent flows of both phases*, see Figure 1.2.1c, with reactant A present in phase α and reactant B in phase β, we have:

$$\left(\frac{F_{A0}}{\nu_A}\right)\cdot\left(\frac{d\chi_A}{dz}\right) = -\left(\frac{F_{B0}}{\nu_B}\right)\cdot\left(\frac{d\chi_B}{dz}\right) \qquad [1.2.20]$$

when $z = z_1$, $\chi_A(z_1) = 0$ and when $z = z_2$: $\chi_B(z_2) = 0$ and:

$$\chi_B(z) - \chi_B(z_1) = -\left(\frac{\nu_B}{\nu_A}\right)\left(\frac{F_{A0}}{F_{B0}}\right)\cdot\chi_A(z) \qquad [1.2.21]$$

1.2.3.4. *Semi-batch system*

1.2.3.4.1. First case

A gas $A(\alpha)$ is blown through a stationary liquid bath β, or through a fluidized bed of particles B, see Figures 1.2.1d and 1.2.1e and section 18.4.

When the flow rate of gas A is such that phase β can be considered homogeneous, the composition of this phase evolves over time. The fractional conversion of reactant $B(\beta)$ for a blowing time τ is:

$$\chi_B(\tau) = \{n_{B0} - n_B(\tau)\} / n_{B0} \qquad [1.2.22]$$

For a steady flow of phase α, the inlet molar flow rate of reactant A (F_{Ae}) is constant during the operation, but the outlet molar flow rate $F_{As}(t)$ varies over time. The number of moles of $B(\beta)$ that still have to be consumed decreases with time. The fractional conversion of reactant A at each instant is given by:

$$\chi_A(t) = \{F_{A0} - F_{A1}(t)\} / F_{A0} \qquad [1.2.23]$$

It decreases over time. A global fractional conversion, during time τ, can thus be defined by:

$$\chi_A(\tau) = \frac{F_{A0}.\tau - \int F_{A1}(t)\,dt}{F_{A0}.\tau} \qquad [1.2.24]$$

Equation [1.2.8] is therefore written:

$$\frac{\{F_{A0}.\tau.\chi_A(\tau)\}}{\nu_A} = \frac{\{n_{B0}.\chi_B(\tau)\}}{\nu_B} \qquad [1.2.25]$$

where F_{A0} . τ is the number of moles of reactant A injected into the reactor over a time τ. Equation [1.2.25] is equivalent to equations [1.2.8] and [1.2.18]. During this time τ, a number of moles of reactant A equal to $\{F_{A0} . \tau . \chi_A(\tau)\}$ have reacted.

1.2.3.4.2. Second case

A gas A(α) is blown through a fixed bed of solid particles B, see Figure 1.2.1e and Figure 3.3.2 in [VIG 11c].

When the height of the bed is such that the fractional conversion of the stationary reactant B varies along the length z of the fixed bed, the fractional conversion of reactant A – $\chi_A(z, t)$ – and of reactant B – $\chi_B(z, t)$ – depend on z and t. Along a length dz of the particle bed, we thus have:

$$\left(\frac{F_{A0}}{\nu_A}\right).\left(\frac{d\chi_A}{dz}\right) = \left(\frac{n_{B0}}{\nu_B}\right).\left(\frac{d\chi_B}{dt}\right) \qquad [1.2.26]$$

when $z = z_1$, $\chi_A(z_1) = 0$ and when $t = 0$, $\chi_B = 0$.

During time τ, if F_{A0}. τ moles of A pass through the fixed bed of B particles, the fractional conversion of both reactants are connected by equation [1.2.25].

1.2.4. *Characteristic quantities of a phase's composition*

Many quantities characterizing the composition of a phase are used. Every one of them is used for a special purpose, hence the necessity of introducing and defining them with precision.

We consider in a phase, in convective or non-convective flow, an elementary volume that is small enough that its composition may be considered uniform (this elementary volume being in motion or not).

Let $m_j(t)$ be the mass and $n_j(t)$ the number of moles of component j, of molar (atomic) mass M_j, at a given time in the elementary volume V. This mass $m_j(t)$ varies over time, following the advancement of the reaction(s). It can also vary by inlet or outlet of matter from the considered volume:

$$n_j = m_j / M_j \qquad [1.2.27]$$

The *(mass) density* $\boldsymbol{\rho}$ of the phase is defined as:

$$\rho = \sum m_j / V \qquad [1.2.28]$$

The *molar* (*mole) fraction* of component j is defined as:

$$x_j = n_j / \sum n_j = n_j / n \quad \text{with} \quad \sum x_j = 1 \qquad [1.2.29]$$

where n is the total number of moles present in the elementary volume (this number is not usually constant).

The *mass fraction* of component j is defined as:

$$w_j = m_j / \sum m_j \quad \text{with} \quad \sum w_j = 1 \qquad [1.2.30]$$

Metallurgists often use the *mass percentage*, represented by %j, for components present in low concentrations:

$$\%j = 100 w_j \qquad [1.2.31]$$

The relation between the molar fraction and the mass percentage is:

$$x_j = \{\%j / M_j\} / \sum\{(\%j) / M_j)\} \qquad [1.2.32]$$

and in a *binary* solution, very dilute in component j:

$$x_j \approx (\%j) \, . \, \{M_s / 100\, M_j\} \qquad [1.2.33]$$

where M_s is the molar mass of the "solvent".

The *molar concentration*, or *molality* C_j, of component j, which is often represented by [A] for component A, is the number of moles n_j per unit volume:

$$C_j = n_j / V, \quad C_A = [A] = n_A / V \quad \text{and} \quad C = \sum C_j \qquad [1.2.34]$$

For a dilute solution, for the elements present in low concentrations:

$$x_j = C_j \times v_{MS} \qquad [1.2.35]$$

where v_{MS} is the specific molar volume of the solvent. For instance, in the case of water, $v_{Ms} = 18$ cm^3/mol.