

TERKEL ROSENQVIST

Principles of Extractive Metallurgy

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METALLURGY**

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PREFACE

In the past most textbooks on extractive metallurgy have been of a rather descriptive nature. Various processes for the production of various metals have been listed and described, and the emphasis has been on the technology rather than on the basic principles involved. The chemistry of the processes has often been limited to a list of chemical reactions which are believed to have taken place. As the amount of industrial experience increases it becomes more and more difficult to give a comprehensive review of all possible and impossible metallurgical processes. Also, by limiting the teaching to the technology of yesterday the students will be less prepared to develop the technology of tomorrow.

By concentrating on the fundamental principles of metal extraction the author hopes to overcome some of these obstacles. The emphasis of the present text is not on *how* the various processes are performed, but rather on *what* is actually happening and *why* the processes are carried out in a certain way. Such an understanding may show what possibilities exist with respect to future development.

The teaching and learning of the principles of extractive metallurgy is connected with certain inherent difficulties. A metallurgical process is first

of all governed by chemical reactions. The extractive metallurgist, therefore, should be well schooled in chemistry, in particular in chemical thermodynamics and reaction kinetics. Second, the design of a metallurgical reactor is based on the application of engineering principles of heat and mass balance, and of heat and mass flow. Finally, the extractive metallurgist should know something about existing techniques, and he should be trained to use his imagination to improve these techniques.

Present university courses give a certain, but often inadequate, background in chemistry and chemical thermodynamics. Thermodynamics courses are often very formal, and have a tendency to become sterile. In the present text it is, therefore, felt necessary to give a review of thermodynamics, based on first principles and with emphasis on its application to metallurgy. Also, present courses in general engineering are not always geared to the need of the extractive metallurgist. Subjects such as heat transfer and fluid flow are therefore discussed in the present text. The first six chapters, therefore, represent a review of those fundamental principles: Thermodynamics, kinetics, and engineering principles, which are of importance to extractive metallurgy. These chapters may be used as a separate text, or they may be omitted entirely by those readers who already have an adequate background in these fields.

The major part of the text is devoted to the various metallurgical unit processes: roasting, reduction, smelting, electrolysis, etc., and is illustrated by existing techniques for the extraction of the most common metals. The emphasis is mainly on the chemistry and dynamics of the processes, and with only brief reference to reactor design. In the description of metallurgical reactors the principal concern has been to show how these function and not how they actually look. A more detailed discussion of reactor design is considered outside the scope of the text.

Metal extraction is in the end always decided by economic considerations. The most elegant use of thermodynamics and reactor design is of little value if the process is uneconomical or if there is no market for the product. A discussion on plant economics is considered outside the scope of the present text, and only incidental reference is made to the economics of the processes discussed. Both the operating metallurgist and the person engaged in industrial research are well advised, however, always to keep their eyes open to the economic consequences of their activities.

With the exception of certain key publications it has not been possible to include references to all information given. A great deal is part of the common heritage of the metallurgical profession, and the author has drawn information also from other textbooks in the field. As a tribute to these

books and as a guide for the reader who wants further information, each chapter includes a bibliography of recommended reading. Also each chapter includes a list of problems ranging from simple calculations to problems which require imagination and ability for creative synthesis.

The appendixes include tables and graphs of thermodynamic quantities for most substances of metallurgical importance, and may be used to calculate heat (enthalpy) balances and chemical equilibrium constants.

The text is intended to give a broad review of metal extraction based on first principles, and is primarily aimed at the junior or senior undergraduate student. It may be supplemented by more specialized texts on subjects of special interest to the course or to the individual student. Some parts, as for example Chap. 14 and parts of other chapters may also be used at the graduate student level. Furthermore, it is hoped that the text may give some viewpoints of value to the person engaged in metallurgical research and development.

The philosophy of the text has been greatly influenced by the author's work at American universities and by his discussions with American colleagues. Most of the writing was done during the years 1967-68 when the author served as a UNESCO expert at the Middle East Technical University in Ankara, Turkey. The author is indebted to a number of friends and colleagues for encouraging advice and constructive criticism: to Professor Olaf G. Paasche of the Oregon State University and Dr. Jomar Thonstad who both have read the entire manuscript; to Professors Marcus Digre, Håkon Flood, and M. Brostrup Müller who have given valuable advice on Chaps. 7, 11, and 9 and 13, respectively. The appendixes have been compiled with the help of former students: Torgeir Alvsåker, Per-T. Torgersen, and Georg B. Jensen. These people are not responsible for the content of the text, however. That responsibility rests entirely with the author, who welcomes further comments and criticism from readers. Finally the author wishes to thank his secretary, Miss Linda Tidosaar, who, in addition to typing most of the manuscript, also animated him to complete it.

TERKEL ROSENQVIST

LIST OF SYMBOLS

Throughout the world various sets of symbols are used in various fields of science and engineering. Unfortunately, no consistent and unambiguous set has been agreed on. In this text an attempt has been made to use symbols that are most generally accepted. This means that one and the same symbol may be used to denote different quantities. As this is done in definitely different connections and the symbols are explained in the text, this should not represent any problem. In a few cases it is found necessary to use different symbols for the same quantity (in different chapters), this being done in order to avoid confusion.

- A = Helmholtz free energy, area, first component
- a = activity
- B = second component
- C = concentration, third component, molar heat capacity [cal/(mole°C)],
number of components
- c = specific heat [cal/(g°C)]
- D = diffusion coefficient
- d = diameter

- E = internal energy efficiency, electromotive force
 F = number of degrees of freedom, friction energy, radiation efficiency factor, Faraday's number
 f = fugacity, Henrian activity coefficient, friction factor
 G = Gibbs free energy, mass velocity
 g = gravitational acceleration
 H = enthalpy, height
 H_0 = integration constant
 h = heat transfer coefficient, Planck's constant
 I = integration constant, intensity, electric current
 J = flow per unit area
 K = equilibrium constant, proportionality constant
 k = rate constant, heat conductivity, mass transfer coefficient, Boltzmann's constant
 L = length
 M = molecular weight, mass
 m = mass, mass per unit time, molality
 N = mole fraction, Avogadro's number = 6.02×10^{23}
 n = number of moles, charge of ions
 P = pressure, number of phases
 p = pressure, partial pressure
 Q = heat flow (overall)
 q = rate of heat flow, heat flow to system
 R = gas constant = $0.082 \text{ liter-atm/}^\circ\text{K mole}$ = $1.987 \text{ cal/}^\circ\text{K mole}$
 r = radius, roughness, reflectivity
 S = entropy, surface area, standard deviation of mean from true value
 s = distance, standard deviation (scatter, approximate)
 T = absolute temperature $^\circ\text{K}$
 t = temperature $^\circ\text{C}$
 U = overall heat transfer coefficient
 V = volume, number of variables, voltage
 v = linear velocity, bond energy
 W = probability, width
 w = work done on surroundings, exchange bond energy
 X = any state function
 Z = height above base, coordination number

Greek

- α = absorptivity
 β = thermal expansion coefficient, transmissivity

- γ = activity coefficient (Raoultian and for aqueous electrolytes)
 δ = thickness of surface layer
 ϵ = emissivity, void fraction
 η = overvoltage
 θ = time
 κ = electrical conductivity
 λ = wavelength
 μ = viscosity, true value
 ρ = density
 σ = standard deviation (scatter, true)
 ϕ = fractional kinetic energy loss
 ω = angular velocity

Subscripts

- f = fusion, melting
 M = molar quantity (often omitted)
 C = by concentration
 m = mean value
 P = constant pressure
 s = sublimation, at surface, solid
 T = constant temperature
 tot = total
 trf = transformation
 V = constant volume
 v = vaporization, boiling
 vol = by volume
 (underscore) = dissolved

Superscripts

- $^{\circ}$ = standard state
 * = at equilibrium, activated compound
 $\bar{}$ (overbar) = partial quantity, mean value

Some less used symbols are explained in the text.

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INTRODUCTION

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The art of extracting metals from their ores dates back to the dawn of human civilization. The first metals used by man were gold and copper, which were found in nature in metallic or native form. Around 4000 B.C. man learned to produce copper and bronze by the smelting of copper and tin ores in a charcoal fire. Throughout the history of mankind the processes of extractive metallurgy were developed further by trial and error. The knowledge of the smelter or the blacksmith passed on from father to son. New developments were sometimes the result of an ingenious imagination, but perhaps more frequently a result of accidents. A visitor to a modern metallurgical plant will be struck by the large number of complex operations. Particularly in the field of non-ferrous metallurgy the operations vary considerably from one metal to another and even between different plants producing the same metal. In this text we shall see how the many different metallurgical processes may be understood as the result of a relatively small number of fundamental principles.