PHYSICAL CHEMISTRY OF METALLURGICAL PROCESSES

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I had been planning to write a book on Physical Chemistry of Metallurgical Processes based on my experiences of teaching a graduate course with the same title at the Department of Materials Science and Engineering, Massachusetts Institute of Technology and association/interaction with the faculty members of the Department of Metallurgy and Metallurgical Engineering, University of Utah, Salt Lake City, during my 3 years (1978–1981) of visit to the United States. But while taking account of rapid development of the theoretical knowledge in recent years in gas–solid (roasting and reduction) and liquid–solid (leaching and precipitation) reactions, I was in a dilemma regarding the extent to which mathematical expressions should be incorporated in the book. After spending a lot of time on the mathematical contents while teaching the same course at the Department of Metallurgical Engineering, Banaras Hindu University, I concluded that it should be possible to discuss the new developments in a satisfactory manner without going into the use of advanced mathematics by giving more emphasis on thermodynamics that brings out more convincing evidence as compared to kinetics involving complex expressions. This decision has helped me in the preparation of a book of reasonable size covering various process steps in production of different types of metals, namely common, reactive, rare, and refractory.

In the past, during 1950–1970, most textbooks on extractive metallurgy described processes for production of different metals emphasizing the technology rather than the basic principles involved. The physical chemistry of the processes has been restricted to mere listing of chemical reactions expected to be taking place. However, the book entitled Physical Chemistry of Iron and Steel Making by Professor R. G. Ward published in 1962 has been an exception. With rapid increase in the number of extraction processes on the industrial scale, it became difficult to bring out the comprehensive idea of all metallurgical fundamentals for the development of future technology.
During 1970–1995, Professors C. Bodsworth, W. G. Davenport, J. F. Elliott, F. Habashi, E. Jackson, J. J. Moore, R. H. Parker, R. D. Pehlke, T. Rosenqvist, H. Y. Sohn, M. E. Wadsworth and Dr. E. T. Turkdogan paid due attention to the physicochemical aspects of metallurgical fundamentals in their books. I have benefited from their texts while preparing this manuscript and owe them most sincerely. In addition, I have tried to collect information on this subject from different journals and proceeding volumes. For the benefit of readers, important references have been listed in each chapter. This may also be considered as a tribute to various academicians, researchers, and investigators associated with the publication of various books and research articles in different journals.

By giving more emphasis on the physical chemistry of different metallurgical processes, I aim to solve some of the problems. Attention has not been paid to how different processes are carried out; instead, the emphasis has been on why the step has been adapted in a particular manner. These queries, with a clear understanding of the physical chemistry, may open ways and means for future developments. Lecturing on physical chemistry of metallurgical processes is associated with a number of challenging exercises and difficulties. It requires not only a thorough understanding of chemical reactions taking place in a process, but also a sound knowledge of chemical thermodynamics and reaction kinetics. In addition, technical principles of heat and mass transfer are also needed in designing a metallurgical reactor. Lastly, the chemical-extractive metallurgist must know about the existing processes and should be capable of employing his imagination in encouraging students/investigators in improving the existing techniques.

Currently, university courses provide inadequate background in chemical/metalurgical thermodynamics. At the majority of institutions, thermodynamics courses are formal. Often teachers feel satisfied by solving a few problems by plugging data in the thermodynamic expressions derived in the class. In this book, the thermodynamic interrelationships concerning the problems have been summarized in Chapter 1, and for clarity the thermodynamics quantities have been defined together with an explanation of their physical significance. It has been presumed that readers are familiar with the undergraduate course in chemical/metallurgical thermodynamics. For details, readers are advised to consult the textbooks and necessary compilations listed in this book. Reaction kinetics of different processes has not been covered in detail, and topics on heat and mass transfer have not been included with the primary objective of publishing a book of reasonable volume. Depending upon the response from readers, it may be taken up in the second volume or edition.

The book deals with various metallurgical topics, namely, roasting of sulfide minerals, sulfide smelting, slag, reduction of oxides and reduction smelting, interfacial phenomena, steelmaking, secondary steelmaking, role of halides in extraction of metals, refining, hydrometallurgy, and electrometallurgy in different chapters. Each chapter is illustrated with appropriate examples of application of the technique in extraction of some common, reactive, rare, or refractory metal together with worked-out problems explaining the principle of the operation. The problems require imagination and critical analysis. At the same time, they also encourage readers for creative application of thermodynamic data. Exercises have not been given because I am confident that the worked-out examples provide ample platform for the
framework of additional problems. In selecting these problems, I am grateful to the late Professor John F. Elliott of MIT and late Dr. Megury Nagamori of the Noranda Research Center, Canada. I am not consistent in using the SI unit throughout the book. Based on my long teaching experience of about four decades, I strongly feel that the use of different units will make students mature with regard to the conversion from one unit to another. The principal objective of the book is to enlighten graduate students of metallurgy and metallurgical engineering specializing in chemical-extractive metallurgy and chemical engineering with the basic principles of various unit operations involved in the extraction of different types of metals. It will also be useful to senior undergraduate students of metallurgy and chemical technology.

However, the success of the process is dictated by economic evaluation. The use of thermodynamic principles and reactor design becomes insignificant if the process is uneconomical and/or the product has poor demand. This aspect has not been considered in this book. I advise the industrial metallurgists and researchers to be careful about the economic consequences of their work.

I am grateful to a number of friends and colleagues for necessary help in the preparation of the manuscript. It is not possible to mention all, but I shall be failing in my duty if I do not thank Professor H. Y. Sohn of the University of Utah, Salt Lake City, USA, Professor Fathi Habashi of the Laval University, Canada, and Professor T. R. Mankhand of the Banaras Hindu University for their advice and constructive criticism and also Dr. C. K. Behera and Dr. S. Jha of the Banaras Hindu University for their assistance in the preparation of diagrams and the manuscript. I am also thankful to library staffs of the Department of Metallurgical Engineering for their active cooperation in locating the reference materials. Although due acknowledgments have been given to authors at appropriate places in the texts for adapting their tables and figures published in various books and journals, I take this opportunity to thank the publishers (authors as well) listed below for giving permission to reproduce certain figures and tables:

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Bodsworth, C. (1990) The Extraction and Refining of Metals, CRC Press, Tokyo for Fig. 10.1.

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X. ELSEVIER


XI. GORDON & BREACH


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2. Balagiva, K., Quarrel, A. G. and Vajragupta, P. (1946) A laboratory investigation of the phosphorus reaction in the basic steelmaking process, J. Iron Steel Inst. 153, pp 115–145 for Fig. 7.3.

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XIX. THE INDIAN INSTITUTE OF METALS


Last but not the least, I am extremely grateful to Mrs. Abida Khatoon for taking care of the family, and for offering moral support and patience for my long hours spent working on the book.

M. SHAMSUDDIN
The limited availability of textbooks in chemical and extractive metallurgy is evident from their paucity in different library websites. Hence, there is a need to enrich the extractive metallurgy library. In this field, hardly one or two books are published within a span of 5–10 years. Considering the requirement and circumstances, this book by Professor M. Shamsuddin, which discusses the physical chemistry of various steps involved in the extraction of different types of metals, is an important contribution in the field of chemical metallurgy. It is well known that the exploitation of many low-grade and complex ores/minerals has been possible in recent years by a thorough understanding of slag–metal reactions with the aid of thermodynamics and reaction kinetics. The fundamental principles of chemical metallurgy are based on physical chemistry that includes thermodynamics and kinetics. In general, textbooks on physical chemistry deal mainly with contents that are appreciated by the students of chemistry but are of less interest to metallurgists and chemical engineers. In this book, physical chemistry is presented for aspects concerning chemical metallurgy with appropriate examples drawn, as much as possible, from extractive metallurgical processes.

The physical chemistry principles that are key to extraction technologies play a decisive role in the development and improvement of processing methods. As a consequence, metallurgists and chemical engineers often face the problem in selecting the appropriate technique for treatment of the concentrate. In order to overcome such a challenging task, a sound knowledge of physical chemistry of different extraction methods is extremely useful. Since the chemistry of the extraction process varies according to the nature of the metal, which may fall under the categories of common, rare, reactive or refractory, a comprehensive and collective treatment in one book is very much desired at the present time. Depending on the interest, one may further
study the details in a book/monograph dealing with the particular metal. This is the main objective of this book.

This is a very special book for three reasons: Firstly, it includes discussions on physicochemical principles involved in different steps, namely, roasting of sulfide minerals, matte smelting/convert ing, reduction smelting, iron- and steelmaking, deoxidation, refining, degassing, leaching, purification of leach liquor, precipitation, cementation, etc., during extraction/production of not only common metals but also rare, reactive, and refractive metals by pyro- and hydrometallurgical methods. Secondly, it provides a number of worked-out examples in each chapter, which make understanding of the process easier. Thirdly, the author has systematically summarized and presented scattered information on physicochemical aspects of metal extraction from previously published books and journal articles.

The book will undoubtedly fulfill the need of students and teachers by providing information on the principles and methods of extraction of different metals: common, rare, reactive, and refractory in one place. I am confident that the book will be in demand throughout the world by universities and institutes offering courses in Metallurgy, Chemical Engineering and Technology, and also by various metallurgical and chemical research laboratories. It will be more useful to students of metallurgical engineering specializing in chemical/extractive metallurgy, but the basic principles of various unit operations involved in extraction will also be appreciated by chemical engineering students.

In addition to his long tenure at Banaras Hindu University, Professor Shamsuddin has had diversified interactions with faculty members of two premier institutions, namely the Department of Metallurgical Engineering, University of Utah, Salt Lake City, and the Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, on various aspects of metal extraction, thermodynamics, and kinetics. I have no reservation in stating most strongly that this book on Physical Chemistry of Metallurgical Processes will achieve a high standard in the field of chemical/extractive metallurgy and be appreciated by metallurgists and chemical engineers.

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LIST OF SYMBOLS

\begin{itemize}
\item \( A \) \quad \text{Area of surface, pre-exponential factor, frequency factor}
\item \( a \) \quad \text{Raoultian activity}
\item \( \text{atm} \) \quad \text{Atmosphere (pressure)}
\item \( B, b \) \quad \text{Basicity}
\item \( c \) \quad \text{Concentration, constant}
\item \( C \) \quad \text{Heat capacity, component, constant}
\item \( C_p \) \quad \text{Heat capacity at constant pressure}
\item \( C_v \) \quad \text{Heat capacity at constant volume}
\item \( d \) \quad \text{Diameter}
\item \( D \) \quad \text{Diffusion coefficient}
\item \( D_P \) \quad \text{Dephosphorization index}
\item \( D_S \) \quad \text{Desulfurization index}
\item \( e \) \quad \text{Electron charge, interaction coefficient}
\item \( E \) \quad \text{Energy, electrode potential, emf, electron field mobility}
\item \( E_A \) \quad \text{Activation energy}
\item \( E_{\eta} \) \quad \text{Activation energy for viscous flow}
\item \( f \) \quad \text{Henrian activity coefficient, fraction reacted}
\item \( F \) \quad \text{Degree of freedom, Faraday constant}
\item \( f(\theta) \) \quad \text{Shape factor}
\item \( (g) \) \quad \text{Gaseous phase}
\item \( g \) \quad \text{Acceleration due to gravity}
\item \( G \) \quad \text{Free energy}
\item \( G^\circ \) \quad \text{Free energy of activation}
\item \( h \) \quad \text{Planck constant, height (metal head)}
\item \( H \) \quad \text{Enthalpy}
\end{itemize}
J  Flux, (mass transferred per unit area per unit time), Joule

k  Rate constant, partition/segregation/distribution coefficient, Sievert’s constant, Boltzmann constant, kilo

\( k_m \)  Mass transfer coefficient

\( K \)  Equilibrium constant, distribution coefficient

\( K' \)  Equilibrium quotient of cations

\( L \)  Latent heat of transformation, liter

\( L^c \)  Latent heat of evaporation

\( L^f \)  Latent heat of fusion

(l)  Liquid state, liter

ln  Napierian logarithm (loge)

m  Mass

\( M \)  Atomic/molecular weight

n  Number of moles/atoms

\( N \)  Avogadro’s number

\( N' \)  Electrically equivalent ionic fraction

p  Partial pressure

\( P \)  Total pressure

\( p_i \)  Partial pressure of the component i

\( p^o \)  Partial pressure of the pure component

q  Quantity of heat

\( Q' \)  Total extensive thermodynamic quantity

\( Q \)  Molar extensive thermodynamic quantity

r  Radius, rate of evaporation

\( R \)  Gas constant, rate of reaction

(s)  Solid phase

S  Entropy

t  Time

\( T \)  Absolute temperature (Kelvin), temperature (°C)

\( T^e \)  Temperature of evaporation

\( T^f \)  Temperature of fusion

U  Internal energy

\( v \)  Rate of rise of the deoxidation product, volume

V  Volume

\( \omega \)  Weight, work done

x  Atom/mole fraction, ionic fraction, distance in the direction of x

z  Valence, a factor in reduction of an oxide, electrochemical equivalent

**GREEK SYMBOLS**

\( \alpha \)  Stoichiometry factor, separation factor

\( \gamma \)  Raoultian activity coefficient

\( \gamma^* \)  Raoultian activity coefficient at infinite dilution
LIST OF SYMBOLS

δ Thickness of the stagnant boundary layer
ε Interaction parameter
η Viscosity, overvoltage due to polarization
θ Contact angle made by nucleus with the substrate
μ Chemical potential (partial molar free energy), mobility
ρ Density
σ Interfacial surface tension
Φ Fugacity

PREFIXES

Δ Change in any extensive thermodynamic property (between product and reactant), e.g., \( \Delta G, \Delta H, \Delta S, \Delta U, \Delta V \)
d Very small change in any thermodynamic variable, e.g., \( dG, dT, \) and \( dP \)

SUFFIXES

The physical state of a substance is indicated by the following symbols, placed in bracket ( ) after the chemical formulae of the substance.
aq Dissolved in water at infinitely dilute concentration, e.g., \( M^{2+}(aq) \)
g Gaseous, e.g., \( \text{Cl}_2(g) \)
l Liquid, e.g., \( \text{H}_2\text{O}(l) \)
s Solid, e.g., \( \text{SiO}_2(s) \)

SUBSCRIPTS

a Anode potential \( E_a \), anode polarization \( \eta_a \)
c Cathode potential \( E_c \), cathode polarization \( \eta_c \)
cell \( E_{\text{cell}}, \Delta G_{\text{cell}} \)
f Formation, e.g., \( \Delta G_f \)
M Metal, e.g., \( E_M \)
sol Solution, e.g., \( \Delta G_{\text{sol}} \)
vol Volume, e.g., \( \Delta G_{\text{vol}}, \Delta H_{\text{vol}} \)

SUPERSCRIPTS

‡ Transition of activated state
\( _i \) Partial molar functions, e.g., \( \bar{G}_i \)
° Thermodynamic standard state, e.g., \( \Delta G^\circ \)
id  Ideal thermodynamic functions, e.g., $\Delta G^{M,id}$
M   Mixing, e.g., $\Delta G^M$, $\Delta H^M$
xs  Excess thermodynamic functions, e.g., $G^{xs}$

**ADDITIONAL SYMBOLS**

( ) Solute in slag phase
[ ] Solute in metallic phase, e.g., [S], concentration of a species in solution, e.g., [CN$^-$]
{ } Gaseous phase
$c_i^m$ Concentration of the metal at the interface
$c_b^m$ Concentration of the metal in the bulk of the metal phase
$c_i^s$ Concentration of the slag at the interface
$c_b^s$ Concentration of the slag in the bulk of the slag phase
$\frac{dc}{dx}$ Concentration gradient
$\frac{dm}{dt}$ Rate of mass transfer
$k_m^m$ Mass transfer coefficient in the metal phase
$k_m^s$ Mass transfer coefficient in the slag phase
INTRODUCTION

Metals generally occur in combined states in the form of ores and minerals as oxides, for example, cassiterite (SnO$_2$), cuprite (Cu$_2$O), chromite (Fe$_3$O$_4$), hematite (Fe$_2$O$_3$), pyrolusite (MnO$_2$), rutile (TiO$_2$), wolframite [Fe(Mn)WO$_4$]; sulfides, for example, chalcopyrite (CuFeS$_2$), cinnabar (HgS), galena (PbS), molybdenite (MoS$_2$), pentlandite [(NiFe)$_9$S$_8$], sphalerite (ZnS), stibnite (Sb$_2$S$_3$); silicates, for example, beryl (3BeO·Al$_2$O$_3$·6SiO$_2$), zircon [Zr(Hf)SiO$_4$]; titanate, for example, ilmenite (FeO·TiO$_2$); carbonates, for example, azurite [2CuCO$_3$·Cu(OH)$_2$], dolomite (MgCO$_3$·CaCO$_3$), malachite [CuCO$_3$·Cu(OH)$_2$], magnesite (MgCO$_3$); phosphate, for example, monazite [Th$_3$(PO$_4$)$_4$]; vanadate, for example, carnotite (K$_2$O·2UO$_3$·V$_2$O$_5$) and so on. A few precious metals like gold, silver, and platinum are found in the native or uncombined form because they are least reactive. As naturally occurring ores and minerals are associated with gangue such as silica, alumina etc., the first step in the extraction of metals is the removal of gangue from the ore containing the metal value by mineral beneficiation methods incorporating comminution, preliminary thermal treatment and concentration by magnetic separation, heavy media separation, jiggling, tabling, and flotation. The choice of the method depends upon the nature of the gangue and its distribution in the ore and the degree of concentration of the metal value required, which depends on the extraction technology to be adopted. The extraction methods incorporate various steps to obtain the metal from the concentrate, ore or some mixture, or from chemically purified minerals; occasionally, the mineral may be first converted to a more amenable form. The mineral beneficiation step lies
between mining and extraction. The extraction processes are classified into three main groups, namely:

1. **Pyrometallurgical** methods including smelting, converting, and fire refining are carried out at elevated or high temperatures. A step called roasting or calcination may also be incorporated in the flow sheet in the treatment of sulfide or carbonate minerals.

2. **Hydrometallurgical** methods incorporate leaching of metal values from the ores/minerals into aqueous solution. The resultant solution is purified before precipitation of the metal by pH and $P_O_2$ control, gaseous reduction, or cementation. Roasting or calcination also forms an important step in the treatment of sulfide and carbonate ores. In the production of rare metals like uranium, thorium, zirconium and so on, the leach liquor may be purified by fractional crystallization, ion exchange, and/or solvent extraction techniques.

3. **Electrometallurgical** methods use electrical energy to decompose the pure mineral that is present in aqueous solutions or in a mixture of fused salts. If the metal is extracted from the electrolyte using an insoluble anode the method is called electrowinning. On the other hand if the impure metal (in the form of the anode) is refined using a suitable electrolyte, the method is known as electrorefining.

The choice of the technique mainly depends on the cost of the metal produced, which is related to the type of ore, its availability, cost of fuel, rate of production, and the desired purity of the metal. The fuel or energy input in the process flow sheet may be in the form of coal, oil, natural gas, or electricity. Being an electrically based process electrothermic smelting is an expensive method. This process can only be adopted if cheap hydroelectric power is available. Highly reactive metals like aluminum and magnesium can be produced in relatively pure states by fused salt electrolysis. Electrowinning is often employed as a final refining technique in hydrometallurgical extraction. Hydrometallurgy seems to be a better technique for the extraction of metals from lean and complex ore although it is slower than pyrometallurgical methods. Major quantities of metals are obtained by the pyrometallurgical route as compared to the hydrometallurgical route because kinetics of the process is much faster at elevated temperatures. This is evident from the discussion in the following chapters on matte smelting, slag, reduction smelting, steelmaking, refining, and halides, which deal with the pyrometallurgical methods of extraction. Separate chapters have been included on hydrometallurgy and electrometallurgy.

In addition to the well-established tonnage scale production of the ferrous and six common nonferrous metals (aluminum, copper, lead, nickel, tin, zinc), in recent years many other metals, namely, beryllium, uranium, thorium, plutonium, titanium, zirconium, hafnium, vanadium, columbium, tantalum, chromium, tungsten, molybdenum and rare earths have gained prominence in nuclear power generation, electronics, aerospace engineering, and aeronautics due to their special combination of nuclear, chemical, and physicochemical properties. Many of these metals are categorized as rare despite their more abundant occurrence in nature compared to copper, zinc, or
nickel. This is due to the diversified problems associated with their extraction and conversion to usable form. Production of some of these metals in highly pure form on tonnage scale has been possible recently by efficient improvement of the conventional extraction methods as well as through the development of novel unit processes.

On account of the refractory nature of the minerals and stability of the oxides and carbides of many rare metals direct smelting of the ores with carbon is not feasible for rare metal extraction. The refining methods like fire refining, liquation, distillation and so on are also not applicable. Hence, the flow sheets for rare metal extraction and refining involve many steps, each with the specific objective of successfully removing a particular impurity. On account of the co-occurrence of chemically similar elements, for example, uranium/thorium, columbium/tantalum, zirconium/hafnium and rare earths there are often problems in rare metal extraction. For the separation of such elements, unconventional techniques like ion exchange and solvent extraction have to be incorporated in the process flow sheet for production of high-purity metals. Finally, during the reduction and consolidation stages one has to be extremely careful because rare metals in general, and titanium, zirconium and hafnium in particular, are very sensitive to atmospheric gases that affect their physical, chemical, and mechanical properties.

It would be appropriate to outline here the general steps in the extraction of rare metals:

1. **Physical mineral beneficiation:** Beach sand, a source of many rare metals like titanium, zirconium, hafnium, and thorium, is processed by exploiting the characteristic differences in the size, shape, density, and electromagnetic and electrostatic behavior of mineral constituents, that is, rutile, ilmenite, zircon, monazite and so on.

2. **Selective chemical ore breakdown:** In order to bring the metal values to an extractable state, hydrometallurgical unit processes like acid or alkali leaching or pyrometallurgical techniques like fusion with alkalis and alkali double fluorides are employed.

3. **Ion exchange:** The technique developed long back for purification and deionization of water is currently used extensively for concentration and purification of lean leach liquor and for separation of chemically similar elements.

4. **Solvent extraction:** An analytical technique once developed for selective transfer of specific metal ions from aqueous solution to an organic phase, has presently come up to the stage of large-scale unit process for purification and separation of a number of rare and nuclear metals.

5. **Halogenation:** For the production of oxygen-free reactive metals like titanium, uranium, zirconium and so on it has become essential to adopt intermediate routes by converting oxides into chlorides or fluorides prior to reduction.

6. **Metallothermic reduction:** The traditional “thermit process” has been very successfully employed in rare metal extraction. For example, uranium tetrafluoride is reduced with calcium for tonnage production of uranium metal required in atomic reactors. Similarly, magnesium is used for the production of titanium and zirconium from their respective tetrachlorides.
7. Consolidation and vacuum refining: As most of the metals mentioned above are high melting and very corrosive in the molten state they pose problems during melting and consolidation. Special consumable electrode arc melting with super-cooled copper hearths have been developed for the production of titanium and zirconium alloys. Electron beam melting technique has been practiced for melting and refining of columbium and tantalum. The high superheat at temperatures around 3000°C under vacuum helps in removing all impurities including oxygen, nitrogen, and carbon.

8. Ultra-purification: The performance of rare and reactive metals during usage depends on purity. For proper assessment it is important that metals are free from impurities. Similarly, high order of purity is specified for semiconducting elements like silicon and germanium, required in electronic industry. In recent years a number of ultra-purification methods, for example, thermal decomposition, zone refining, and solid-state electrolysis have been developed for large-scale purification of these metals.

A number of textbooks dealing with ironmaking, steelmaking, extraction of nonferrous metals and principles of extractive metallurgy are available. Each book has some edge over the other in certain aspects of presentation in terms of theory and practice. Some emphasize on technology and some on principles. Thermodynamics and kinetics have been discussed. In this book an attempt has been made to discuss the physical chemistry of different steps, for example, roasting, sulfide smelting/converting, reduction smelting, steelmaking, deoxidation, degassing, refining, leaching, precipitation, cementation involved in the extraction of metals. A chapter on slag which plays an important role in the extraction of metals from sulfide as well as oxide minerals, has been included. Similarly, another chapter highlights the significance of interfacial phenomena in metallurgical operations. The physicochemical aspects of desulfurization, dephosphorization, decarburization, and silicon and manganese reactions in steelmaking have been discussed along with brief accounts on various steelmaking processes highlighting the differences in their chemistry of refining and pretreatment of hot metal. Role of halides, ion exchange, and solvent extraction in metal production and refining have been discussed in different chapters. Methods of construction of predominance area diagrams applicable in selective roasting and leaching have been explained with suitable and appropriate examples in Chapters 2 and 11. At the of end the book, flow sheets demonstrating various steps in the extraction of copper, lead, nickel, zinc, tungsten, beryllium, uranium, thorium, titanium, zirconium, aluminum, and magnesium from their respective ores have been presented.

Relevant worked out examples have been included in each chapter to illustrate principles. While reading the topics on continuous smelting and submerged lance technology in different books and journals one may feel that the chapter on roasting is outdated but one must realize that these developments have been possible only after a sound understanding of the physical chemistry and thermodynamics of all the steps involved in the extraction of metals. Although, currently, almost the entire production of steel comes from top-blown (LD), bottom-blown (OBM) and combined-blown
(Hybrid) converters and electric arc furnaces a discussion on the obsolete Bessemer process has been included to highlight the contributions of Henry Bessemer whose invention laid the foundation for the modern steelmaking processes. Readers may also raise questions on SI units not being used uniformly throughout the book. I want to stress here that based on my 40 years of teaching experience I strongly feel that solving problems in different units will make students mature with respect to conversion from one system to another. As some basic knowledge of under-graduate level chemical/metallurgical thermodynamics is necessary to understand the worked out problems in different chapters, a brief account on thermodynamic quantities and their interrelationships has been included in this chapter.

1.1 THERMODYNAMIC QUANTITIES AND THEIR INTERRELATIONSHIPS

1.1.1 General Thermodynamics

First law of thermodynamics: Energy can neither be produced nor destroyed in a system of constant mass, although it can be converted from one form to another. According to the first law of thermodynamics, the total heat content of the system, called enthalpy \( H \) is expressed as:

\[
H = U + pv
\]

that is, heat content (enthalpy) = internal energy \( U \) + energy term, dependent on the state of the system \( pv \), where \( p \) and \( v \) are, respectively, the pressure and volume of the system.

Heat capacity at constant volume and constant pressure: Heat capacity, \( C \) may be defined as the ratio of the heat, \( Q \) absorbed by a system to the resulting increase in temperature \( (T_2 - T_1) \), that is, \( \Delta T \). Since the heat capacity usually varies with temperature,

\[
C = \lim_{T_1 \to T_2} \frac{Q}{\Delta T} = \frac{q}{dT}
\]

where \( q \) = quantity of heat, \( dT \) = small rise in temperature.

At constant volume, \( q_v = \Delta U_v \)

\[
\therefore \ C_v = \frac{dU_v}{dT} = \left[ \frac{\partial U}{\partial T} \right]_v
\]

Hence, the heat capacity of a system at constant volume is equal to the rate of increase of internal energy content with temperature at constant volume.

Similarly, at constant pressure,

\[
C_p = \frac{dH}{dT} = \left[ \frac{\partial H}{\partial T} \right]_p
\]
Thus, the heat capacity of a system at constant pressure is consequently equal to the rate of the increase of heat content with temperature at constant pressure. The well known expression \( C_p - C_v = R \) can be established from the knowledge of differential calculus.

**Effect of temperature on heat of reaction:** The variation of the heat of reaction with temperature can be expressed as:

\[
\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \, dT
\]  

(1.5)

Where \( \Delta H_1 \) and \( \Delta H_2 \) are the heat of reaction at temperatures \( T_1 \) and \( T_2 \), respectively and \( \Delta C_p \) is the difference in the total heat capacities of the reactants and products taking part in the reaction. Equation 1.5 known as Kirchhoff’s equation, is often used to calculate the heat of reaction at one temperature, if that is known at another temperature. In case reactant(s) and/or product(s) undergo any transformation at \( T_t \) the above equation is modified as:

\[
\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_t} \Delta C_p(T_1 \rightarrow T_t) \, dT + \int_{T_t}^{T_2} \Delta C_p(T_t \rightarrow T_2) \, dT \quad (T_1 \leq T_t \leq T_2)
\]  

(1.6)

According to the first law of thermodynamics, the total energy of the system and surroundings remains constant. The thermodynamic variables like enthalpy, entropy, and free energy changes for the reaction depend only on the initial and final states, not on the path chosen. This is the basis of Hess law of constant heat summation. The law states that the overall heat change of a chemical reaction is the same whether it takes place in one or several stages, provided the temperature and either the pressure or the volume remains constant.

**Second law of thermodynamics:** The first law of thermodynamics is concerned with the quantitative aspects of inter-conversion of energies. This law neither allows us to predict the direction of conversion nor the efficiency of conversion when heat energy is converted into mechanical energy. In the last half of the nineteenth century many scientists put their concentrated efforts to apply the first law of thermodynamics to the calculation of maximum work obtained from a perfect engine and prediction of feasibility of a reaction in the desired direction. These considerations led to the development of the second law of thermodynamics, which has had a far-reaching influence on the subsequent development of science and technology. The Carnot cycle made it possible to assess the efficiency of engines and it also showed that under normal conditions all the heat supplied to the system cannot be converted into work even by perfect engines. A perfect engine would convert all the heat supplied into work if the lower temperature of the process could be made equal to zero. This proof of practical impossibility of complete conversion of heat energy into mechanical work/energy was the starting point of the second law of thermodynamics. Based on this law, the concept of entropy was introduced by Clausius.