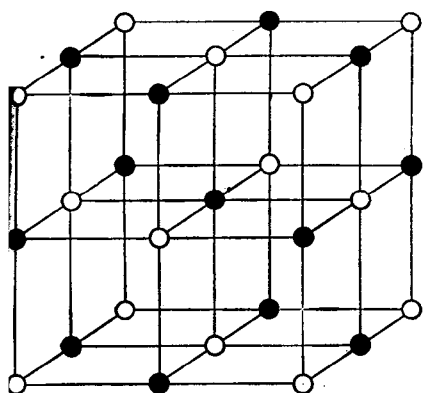# C. BODSWORTH AND H. B. BELL
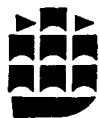
PHYSICAL CHEMISTRY OF IRON & STEEL MANUFACTURE

SECOND EDITION

Physical chemistry of iron and steel manufacture

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LONGMAN

Preface to first edition

The development of the iron and steel manufacturing processes to their present standard of efficiency has been brought about largely by trial and error and by experience gained under production conditions. In comparison, our knowledge of the physico-chemical factors which determine the rate and extent of the various refining reactions is still at a comparatively early stage of development. However, progress in this field has been rapid during the past twenty-five years or so and it is now possible to define precisely the equilibrium conditions and the factors affecting the kinetics of many of these reactions.

The art, as distinct from the science, of ferrous extraction and refining operations has been fully described in many textbooks. No recent publications have brought together the wealth of physico-chemical data pertinent to this field which is now available, or have shown how these data can be used to further the understanding and control of the existing processes and assist in the development of new processes. This text is concerned mainly with the application of the physico-chemical data and only brief reference is made to processing operations, although more such detail is given for some of the newer methods of production of iron and steel.

The text has been prepared primarily for use by students studying ferrous extraction and refining operations, the research worker engaged in obtaining fundamental information in this field and the process metallurgist who wishes to apply the rapidly developing theoretical treatment to the process he is operating. To meet individual requirements the text is divided into four parts.

Part One contains an explanation of those aspects of chemical thermodynamics, kinetic theory and the structure and properties of liquid slags which are subsequently applied to the extraction and refining

processes in the remainder of the book. Thermodynamic theory is covered in sufficient detail to meet the needs of those process metallurgists with only a limited knowledge of the subject and for use in connection with lecture courses dealing with the application of chemical thermodynamics to metallurgical problems. The mathematical treatment has been simplified so far as possible without undue approximations. Some topics are dealt with in more detail than is subsequently necessary in the text to enable the reader to understand the theoretical background of any relevant thermodynamic papers in the scientific and technological journals. The process metallurgist may choose to omit part of these chapters, but it is important to become familiar with the relations between the concepts of activity, activity coefficient, free energy and the equilibrium constant (Sections 1.7, 1.8 and 1.10) and the methods used to assess the activities of solutes in multi-component solutions (Section 2.5).

Thermodynamics deals only with equilibrium conditions. These conditions may not be achieved in a reasonable period of time in an industrial process, so it is necessary to examine the factors affecting the kinetics of the reactions. The application of kinetic theory to ferrous extraction and refining operations has so far produced only a little quantitative data, but qualitative explanations can be advanced for most of the non-equilibrium conditions which are encountered. A brief introduction is given, therefore, to those aspects of the theory which have been applied successfully to this field.

The theoretical approach is explained in the second part in relation to the gas–solid, gas–liquid and slag–metal reactions in the blast furnace and, in the third part, in relation to the Bessemer converter, open-hearth and electric-arc furnace processes, together with some of the newer processes which have been proposed for the production of iron and steel. Some cross-reference between chapters is unavoidable but, so far as possible without introducing excessive repetition, the chapters dealing with each of the processes are self-contained. The reader who is interested only in steel-making can, if he so chooses, omit the chapters dealing with iron-making.

Part Four contains more advanced chapters in which detailed consideration is given to the factors affecting the activities of various oxides in liquid slags and the distribution of carbon, oxygen, phosphorus, sulphur and other elements between gas, metal and slag. Available data are critically assessed and methods are described for calculating equilibrium conditions. Tables of interaction coefficients are given in an appendix.

As the contents of the book were planned originally it was intended

to include chapters dealing with dissolved gases and with vacuum melting and casting. However, as the writing proceeded it became evident that the limited quantitative data available for these topics were better introduced in relation to the various refining processes and the distribution of specific elements than in isolated chapters.

Contrary to usual practice, the names of authors are largely excluded from the text. This is not intended in any way as disrespect of their contributions, but if the normal practice had been adopted certain names such as Chipman, Richardson, Schenck and their associates would appear several times on most of the pages. Omission of names makes the text easier to read, but requires more effort in consulting the references on the part of the reader who wishes to distinguish between the contributions made by the various research and development groups. However, the author believes that the improved continuity of the text fully justifies this additional effort. References are given at the end of each chapter and signalled in the text by the use of figures in square brackets, e.g., [1]. More than 500 references are included, which have been selected to draw attention to the various types of approach to each of the problems considered and also to provide the process metallurgist with further reading on the practical applications of some of the more recent refining techniques.

Preface to second edition

In the second edition the overall format of the first edition has been retained, but incorporation of the developments which have occurred during the intervening years has necessitated extensive rewriting. On the process side the most notable change since the first edition was prepared has been the growth in importance of the oxygen converter and the simultaneous decline in the open-hearth process. This has resulted also in a retardation in the development of methods for direct reduction, but other processes such as electro-slag refining and continuous steel-making are now in commercial operation or in the pilot plant stage of development. Apart from measurements of interaction coefficients, sulphide capacities and some slag activities, progress has been relatively slow in the thermodynamic field, but there have been significant developments in studies of the kinetics of reactions.

These changes are reflected in the contents of the second edition. The opportunity has been taken also to convert to the SI system of units. An endeavour has been made to avoid too great an increase in the size of the book but, to meet numerous requests, Chapter 1 has been retained together with a condensed treatment of the Bessemer converter and open-hearth processes.

I am grateful to Dr H. B. Bell for preparing a new section on the oxygen converter processes and rewriting parts of Chapters 6 and 7 describing the blast-furnace process.

Acknowledgements

Notation

The notation selected for the various quantities are those in most common use and are largely based upon the recommendations of the International Union of Pure and Applied Physics (1955) and the International Union of Pure and Applied Chemistry (1955).

Square and round brackets surrounding a molar quantity denote components of the metal and slag respectively.

The meanings of all the symbols used are listed in the following Table for ready reference.

Symbol	Meaning	Traditional units	SI units
A	Helmholtz function	cal/mol	J/mol
a	Activity		
c	Concentration		
C_p	Molar heat capacity at constant pressure	cal/deg/mol	J/deg/mol
C_v	Molar heat capacity at constant volume	cal/deg/mol	J/deg/mol
D	Diffusion coefficient	cm^2/sec	m^2/sec
E	Activation energy for diffusion	cal/mol	J/mol
f	Activity coefficient (Henry)		
f_Y^X	Interaction coefficient; the effect of element X upon the activity coefficient of element Y		

Symbol	Meaning	Traditional units	SI units
$\mathscr{F}$	Fugacity		
G	Gibbs function or Gibbs free energy	cal/mol	J/mol
G^0	Standard free energy	cal/mol	J/mol
$\bar{G}$	Partial molar free energy	cal/mol	J/mol
G^M	Integral molar free energy of mixing	cal/mol	J/mol
G_A^M	Relative partial molar free energy of a component A	cal/mol	J/mol
G_A^E	Excess partial molar free energy of a component A	cal/mol	J/mol
H	Enthalpy, heat content	cal/mol	J/mol
H^0	Standard enthalpy	cal/mol	J/mol
$\bar{H}$	Partial molar enthalpy	cal/mol	J/mol
H^M	Integral molar enthalpy (or heat) of mixing	cal/mol	J/mol
H_A^M	Relative partial molar enthalpy of a component A	cal/mol	J/mol
J	Joule		
k	Boltzmann's constant	$1\cdot38 \times 10^{-16}$ erg/deg $3\cdot30 \times 10^{-22}$ cal/deg .	$1\cdot38 \times 10^{-23}$ J/deg
K	Equilibrium constant		
K'	Apparent equilibrium constant		
κ	Henry's law constant		
ln	Natural logarithm; $\log_e$		
log	Common logarithm; $\log_{10}$		
L_{tr}	Latent heat of transformation	cal/mol	J/mol
M	Molecular weight	grams	grams
N	Mole fraction		
N_0	Avogadro's number	$6\cdot02 \times 10^{23}$/mol	$6\cdot02 \times 10^{23}$/mol
n	Number of moles		
P	Pressure	atmospheres	Newton/m^2

Symbol	Meaning	Traditional units	SI units
p	Partial pressure	atmospheres	Newton/m^2
Q	Arrhenius activation energy	cal/mol	J/mol
q	Heat absorbed	cal/mol	J/mol
r	Radius		
R	Gas constant	1·986 cal/deg	8·3143 J/deg
S	Entropy	cal/deg	J/deg
S^0	Standard entropy	cal/deg	J/deg
$\bar{S}$	Partial molar entropy	cal/deg/mol	J/deg/mol
S_A^M	Relative partial molar entropy of a component A	cal/deg/mol	J/deg/mol
S_A^E	Excess partial molar entropy of a component A	cal/deg/mol	J/deg/mol
T	Temperature	deg Kelvin	deg Kelvin
U	Internal energy	cal/mol	J/mol
V	Volume	mol; cm^3	mol; m^3
W	Work done by a system	cal	J
γ	Activity coefficient (Raoult)		
γ^0	Activity coefficient at infinite dilution		
ϵ_X^Y	Interaction parameter $\dfrac{\partial \ln f_X}{\partial N_Y}$		
e_X^Y	Interaction parameter $\dfrac{\partial \log f_X}{\partial \text{wt-\% } Y}$		
ζ	Viscosity	dynes sec/cm	Nsec/m^2
k	Rate constant		
μ	Chemical potential	cal/mol	J/mol
ρ	Density	grams/ml	kg/m^3
σ	Surface tension	dynes/cm	Newton/m
ω	Probability factor; number of distributions		
(g)	Gas		
(s)	Solid		
(l)	Liquid		

Contents

PART ONE   THEORY

PART FOUR   SLAG–METAL REACTIONS

PART 1

THEORY

Thermodynamic functions

1.1 Internal energy

The classical theory of thermodynamics is based on two fundamental laws which are simply statements of the results of practical observations regarding the interconversion of different forms of energy. A corollary to the second law is now classed as a third law of thermodynamics. By the application of certain well established mathematical procedures it is possible to derive from these laws a large number of relations which can be employed for the solution of many different types of problems. In this book consideration will be restricted mainly to those relations which determine the conditions for chemical equilibrium and whether or not, under specified conditions, a reaction can occur spontaneously.

A chemical *reaction* can be defined as a process whereby a system is transferred from one state to another. The *system* is here defined as that part of the universe selected for consideration. It may contain any number of atoms, chemical substances or other entities but, for convenience, it is customary to select the boundaries of the system so that the various parts are in some way interconnected. The system may be separated by a real or an imaginary boundary, through which energy can be exchanged with the surroundings. In some instances it is desirable to include the immediate surroundings in the part of the universe considered, in which case it is referred to as an *isolated system*.

A *homogeneous system* contains only one phase, such as a gas, a mixture of gases or a liquid or solid solution, whereas a *heterogeneous system* contains more than one phase. In relation to iron and steel refining, the gas, liquid slag and liquid metal may usually be considered as homogeneous systems. Mixtures of two or more of these are