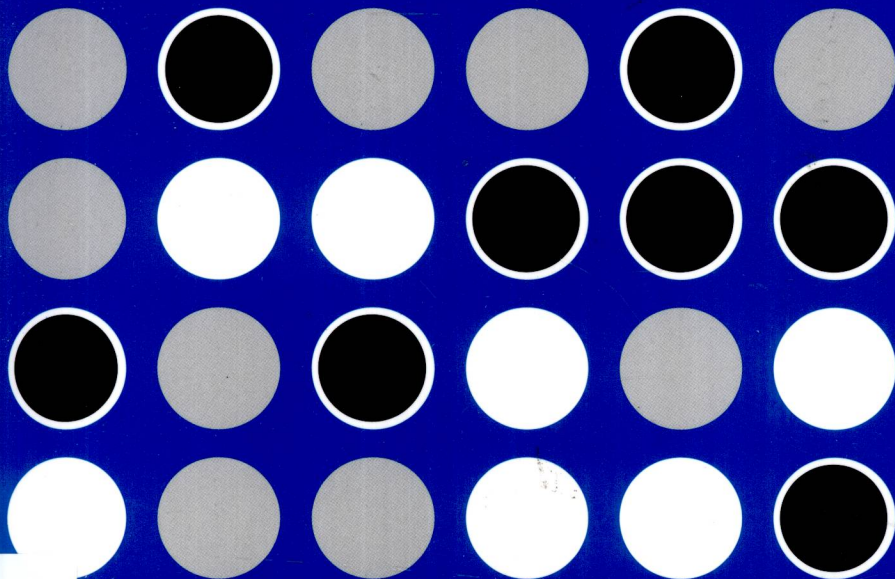


# Phase Transformations in Metals and Alloys

THIRD EDITION

DAVID A. PORTER,  
KENNETH E. EASTERLING,  
and MOHAMED Y. SHERIF



CRC Press  
Taylor & Francis Group

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# **Phase Transformations in Metals and Alloys**

THIRD EDITION

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## ***Preface to the Third Edition***

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The fundamental theories of phase transformations in metals and alloys remain largely unchanged, so the third edition is essentially an expanded version of the second edition with additional material covering some of the more important application developments of the last 17 years. A section addressing the computation of phase diagrams has been added to Chapter 1 and recent developments in metallic glasses have been treated in Chapter 4. Chapter 5 contains most new material: the Scheil method of calculating a CCT diagram from a TTT diagram is now given; the treatment of the nucleation and growth of polygonal ferrite and bainite has been expanded to include new theories, while new case studies cover copper precipitation hardening of very low-carbon bainitic steel and very fine carbide-free bainite were added. In Chapter 6, a more detailed treatment of stress-assisted and strain-induced martensite is included to provide a theoretical background to transformation-induced plasticity (TRIP) steels.

**David A. Porter and Mohamed Y. Sherif**  
*August 2008*

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## *Preface to the Second Edition*

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In the ten years since this book was first published there have been many new developments in the metallurgical field. Rapidly solidified metals and glasses have come of age; new Al-Li alloys are now used in modern aircraft; microalloyed (structural) and high purity (pipeline) steels have become more sophisticated; radically new oxide-dispersed steels have appeared; a number of new memory metals have been developed; the list could go on. In spite of this, the underlying principles governing all of these developments have obviously not changed over the years. This is really the strength of the present text book. From the beginning we aimed to spell out these principles in a nice, readable way, and one in which undergraduates could appreciate and be capable of developing for themselves. The present text is thus deliberately little changed from the original. We have, however, hopefully corrected any errors, expanded the lists of further reading, and perhaps, most importantly, included a complete set of solutions to exercises. We hope that the revised edition continues to be enjoyed and appreciated in the many Schools of Metallurgy, Materials Science and Engineering Materials we know to be using our text throughout the world.

In completing this revised edition we are grateful to the many people, students and professors alike, who have written to us over the last decade. Particular thanks are due to Dr Wen-Bin Li (University of Luleå) for using a fine tooth-comb in bringing out both obvious and less obvious errors in the original text. There remain, (inevitably), a few 'points of contention' concerning our description of certain phenomena, as raised by some of our correspondents, but there is nothing unhealthy about that. We should finally like to thank Dr John Ion (University of Lappeenranta, Finland) for his help in compiling the Solutions to Exercises chapter.

**David Porter and Kenneth Easteriing**

*September 1991*

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## *Preface to the First Edition*

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This book is written as an undergraduate course in phase transformations for final year students specializing in metallurgy, materials science or engineering materials. It should also be useful for research students interested in revising their knowledge of the subject. The book is based on lectures originally given by the authors at the University of Luleå for engineering students specializing in engineering materials. Surprisingly we found no modern treatments of this important subject in a form suitable for a course book, the most recent probably being P.G. Shewmon's *Transformations in Metals* (McGraw-Hill, 1969). There have, however, been some notable developments in the subject over the last decade, particularly in studies of interfaces between phases and interface migration, as well as the kinetics of precipitate growth and the stability of precipitates. There have also been a number of important new practical developments based on phase transformations, including the introduction of TRIP steels (transformation induced by plastic deformation), directionally aligned eutectic composites, and sophisticated new structural steels with superior weldability and forming properties, to mention just a few. In addition, continuous casting and high speed, high energy fusion welding have emerged strongly in recent years as important production applications of solidification. It was the objective of this course to present a treatment of phase transformations in which these and other new developments could be explained in terms of the basic principles of thermodynamics and atomic mechanisms.

The book is effectively in two parts. Chapters 1-3 contain the background material necessary for understanding phase transformations: thermodynamics, kinetics, diffusion theory and the structure and properties of interfaces. Chapters 4-6 deal with specific transformations: solidification, diffusional transformations in solids and diffusionless transformations. At the end of the chapters on solidification, diffusion-controlled transformations and martensite, we give a few selected case studies of engineering alloys to illustrate some of the principles discussed earlier. In this way, we hope that the text will provide a useful link between theory and the practical reality. It should be stated that we found it necessary to give this course in conjunction with a number of practical laboratory exercises and worked examples. Sets of problems are also included at the end of each chapter of the book.

In developing this course and writing the text we have had continuous support and encouragement of our colleagues and students in the Department of Engineering Materials. Particular thanks are due to Agneta Engfors for her patience and skill in typing the manuscript as well as assisting with the editing.

**David Porter and Kenneth Easterling**

*February 1980*

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# Contents

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Preface to the Third Edition .....	xi
Preface to the Second Edition .....	xiii
Preface to the First Edition .....	xv

<b>1 Thermodynamics and Phase Diagrams .....</b>	<b>1</b>
1.1 Equilibrium .....	1
1.2 Single Component Systems .....	4
1.2.1 Gibbs Free Energy as a Function of Temperature .....	4
1.2.2 Pressure Effects .....	7
1.2.3 The Driving Force for Solidification .....	9
1.3 Binary Solutions .....	11
1.3.1 The Gibbs Free Energy of Binary Solutions .....	11
1.3.2 Ideal Solutions .....	13
1.3.3 Chemical Potential .....	16
1.3.4 Regular Solutions .....	17
1.3.5 Activity .....	21
1.3.6 Real Solutions .....	23
1.3.7 Ordered Phases .....	24
1.3.8 Intermediate Phases .....	26
1.4 Equilibrium in Heterogeneous Systems .....	29
1.5 Binary Phase Diagrams .....	31
1.5.1 A Simple Phase Diagram .....	32
1.5.2 Systems with a Miscibility Gap .....	33
1.5.3 Ordered Alloys .....	34
1.5.4 Simple Eutectic Systems .....	34
1.5.5 Phase Diagrams Containing Intermediate Phases .....	35
1.5.6 The Gibbs Phase Rule .....	35
1.5.7 The Effect of Temperature on Solid Solubility .....	40
1.5.8 Equilibrium Vacancy Concentration .....	41
1.6 The Influence of Interfaces on Equilibrium .....	43
1.7 Ternary Equilibrium .....	46
1.8 Additional Thermodynamic Relationships for Binary Solutions .....	51
1.9 Computation of Phase Diagrams .....	53
1.9.1 Pure Stoichiometric Substances .....	54
1.9.2 Solution Phases .....	57
1.9.2.1 Substitutional Solutions .....	57
1.10 The Kinetics of Phase Transformations .....	59

References .....	60
Further Reading .....	60
Exercises .....	61
<b>2 Diffusion .....</b>	<b>65</b>
2.1 Atomic Mechanisms of Diffusion.....	66
2.2 Interstitial Diffusion .....	69
2.2.1 Interstitial Diffusion as a Random Jump Process .....	69
2.2.2 Effect of Temperature—Thermal Activation .....	72
2.2.3 Steady-State Diffusion.....	74
2.2.4 Nonsteady-State Diffusion .....	75
2.2.5 Solutions to the Diffusion Equation.....	76
2.3 Substitutional Diffusion.....	80
2.3.1 Self-Diffusion.....	80
2.3.2 Vacancy Diffusion.....	85
2.3.3 Diffusion in Substitutional Alloys .....	87
2.3.4 Diffusion in Dilute Substitutional Alloys .....	96
2.4 Atomic Mobility .....	96
2.5 Tracer Diffusion in Binary Alloys.....	99
2.6 Diffusion in Ternary Alloys .....	101
2.7 High-Diffusivity Paths.....	103
2.7.1 Diffusion along Grain Boundaries and Free Surfaces....	103
2.7.2 Diffusion along Dislocations.....	107
2.8 Diffusion in Multiphase Binary Systems.....	108
References .....	110
Further Reading .....	111
Exercises .....	111
<b>3 Crystal Interfaces and Microstructure .....</b>	<b>115</b>
3.1 Interfacial Free Energy .....	116
3.2 Solid/Vapour Interfaces .....	117
3.3 Boundaries in Single-Phase Solids .....	121
3.3.1 Low-Angle and High-Angle Boundaries .....	122
3.3.2 Special High-Angle Grain Boundaries .....	126
3.3.3 Equilibrium in Poly crystalline Materials.....	128
3.3.4 Thermally Activated Migration of Grain Boundaries ....	133
3.3.5 The Kinetics of Grain Growth.....	143
3.4 Interphase Interfaces in Solids .....	146
3.4.1 Interface Coherence .....	146
3.4.2 Second-Phase Shape: Interfacial Energy Effects .....	153
3.4.3 Second-Phase Shape: Misfit Strain Effects .....	158
3.4.4 Coherency Loss .....	164
3.4.5 Glissile Interfaces .....	167
3.4.6 Solid/Liquid Interfaces .....	172

3.5	Interface Migration .....	175
3.5.7	Diffusion-Controlled and Interface-Controlled Growth.....	179
	References .....	184
	Further Reading .....	185
	Exercises .....	186
<b>4</b>	<b>Solidification.....</b>	<b>189</b>
4.1	Nucleation in Pure Metals .....	189
4.1.1	Homogeneous Nucleation .....	190
4.1.2	The Homogeneous Nucleation Rate.....	195
4.1.3	Heterogeneous Nucleation .....	196
4.1.4	Nucleation of Melting.....	200
4.2	Growth of a Pure Solid.....	201
4.2.1	Continuous Growth.....	201
4.2.2	Lateral Growth .....	202
4.2.3	Heat Flow and Interface Stability .....	205
4.3	Alloy Solidification .....	209
4.3.1	Solidification of Single-Phase Alloys .....	209
4.3.2	Eutectic Solidification.....	220
4.3.3	Off-Eutectic Alloys.....	227
4.3.4	Peritectic Solidification.....	229
4.4	Solidification of Ingots and Castings .....	230
4.4.1	Ingot Structure .....	231
4.4.2	Segregation in Ingots and Castings .....	234
4.4.3	Continuous Casting.....	236
4.5	Solidification of Fusion Welds.....	240
4.6	Solidification During Quenching from the Melt.....	244
4.7	Metallic Glasses.....	245
4.7.1	Thermodynamics and Kinetics.....	246
4.8	Case Studies of Some Practical Castings and Welds .....	248
4.8.1	Casting of Carbon and Low-Alloy Steels .....	248
4.8.2	Casting of High-Speed Steels.....	250
	References .....	256
	Further Reading .....	256
	Exercises .....	257
<b>5</b>	<b>Diffusional Transformations in Solids.....</b>	<b>261</b>
5.1	Homogeneous Nucleation in Solids .....	263
5.2	Heterogeneous Nucleation .....	269
5.2.1	Rate of Heterogeneous Nucleation.....	274
5.3	Precipitate Growth.....	276
5.3.1	Growth Behind Planar Incoherent Interfaces .....	277

5.3.2	Diffusion-Controlled Lengthening of Plates or Needles .....	281
5.3.3	Thickening of Plate-like Precipitates .....	283
5.4	Overall Transformation Kinetics—TTT Diagrams .....	285
5.5	Precipitation in Age-Hardening Alloys .....	288
5.5.1	Precipitation in Aluminum-Copper Alloys .....	288
5.5.2	Precipitation in Aluminum-Silver Alloys .....	296
5.5.3	Quenched-in Vacancies .....	297
5.5.4	Age Hardening .....	299
5.5.5	Spinodal Decomposition .....	302
5.5.6	Particle Coarsening .....	309
5.6	The Precipitation of Ferrite from Austenite .....	312
5.6.1	Case Study: Ferrite Nucleation and Growth .....	317
5.7	Cellular Precipitation .....	324
5.8	Eutectoid Transformations .....	328
5.8.1	The Pearlite Reaction in Fe–C Alloys .....	328
5.8.2	The Bainite Transformation .....	334
5.8.3	The Effect of Alloying Elements on Hardenability .....	341
5.8.4	Continuous Cooling Diagrams .....	346
5.8.5	Fibrous and Interphase Precipitation in Alloy Steels .....	348
5.8.6	Rule of Scheil .....	351
5.9	Massive Transformations .....	352
5.10	Ordering Transformations .....	358
5.11	Case Studies .....	365
5.11.1	Titanium Forging Alloys .....	365
5.11.2	The Weldability of Low-Carbon and Microalloyed Rolled Steels .....	369
5.11.3	Very Low-Carbon Bainitic Steel with High Strength and Toughness .....	372
5.11.4	Very Fine Bainite .....	374
	Exercises .....	376
	References .....	379
	Further Reading .....	381
<b>6</b>	<b>Diffusionless Transformations .....</b>	<b>383</b>
6.1	Characteristics of Diffusionless Transformations .....	384
6.1.1	The Solid Solution of Carbon in Iron .....	387
6.2	Martensite Crystallography <sup>4</sup> .....	390
6.2.1	The Bain Model of the fcc → bct Transformation .....	392
6.2.2	Comparison of Crystallographic Theory with Experimental Results .....	396
6.3	Theories of Martensite Nucleation .....	397
6.3.1	Formation of Coherent Nuclei of Martensite .....	398
6.3.2	Role of Dislocations in Martensite Nucleation .....	401
6.3.3	Dislocation Strain Energy Assisted Transformation .....	404

6.4	Martensite Growth.....	408
6.4.1	Growth of Lath Martensite.....	409
6.4.2	Plate Martensite.....	411
6.4.3	Stabilization .....	414
6.4.4	Effect of External Stresses.....	414
6.4.5	Role of Grain Size.....	415
6.5	Pre-martensite Phenomena .....	415
6.6	Tempering of Ferrous Martensites .....	416
6.7	Case Studies .....	426
6.7.1	Carbon and Low-Alloy Quenched and Tempered Steels.....	426
6.7.2	Controlled-Transformation Steels.....	427
6.7.3	The 'Shape-Memory' Metal: Nitinol .....	429
	References .....	434
	Further Reading .....	435
	Exercises .....	435
	<b>Solutions to Exercises.....</b>	<b>437</b>
	<b>Index .....</b>	<b>509</b>

# 1

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## *Thermodynamics and Phase Diagrams*

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This chapter deals with some of the basic thermodynamic concepts that are required for a more fundamental appreciation of phase diagrams and phase transformations. It is assumed that the student is already acquainted with elementary thermodynamics and only a summary of the most important results as regards phase transformations will be given here. Fuller treatment can be found in the books listed in the bibliography at the end of this chapter.

The main use of thermodynamics in physical metallurgy is to allow the prediction of whether an alloy is in equilibrium. In considering phase transformations we are always concerned with changes towards equilibrium, and thermodynamics is therefore a very powerful tool. It should be noted, however, that the rate at which equilibrium is reached cannot be determined by thermodynamics alone, as will become apparent in later chapters.

---

### 1.1 Equilibrium

It is useful to begin this chapter on thermodynamics by defining a few of the terms that will be frequently used. In the study of phase transformations we will be dealing with the changes that can occur within a given *system*, e.g. an alloy that can exist as a mixture of one or more phases. A *phase* can be defined as a portion of the system whose properties and composition are homogeneous and which is physically distinct from other parts of the system. The *components* of a given system are the different elements or chemical compounds which make up the system, and the composition of a phase or the system can be described by giving the relative amounts of each component.

The study of phase transformations, as the name suggests, is concerned with how one or more phases in an alloy (the system) change into a new phase or mixture of phases. The reason why a transformation occurs at all is because the initial state of the alloy is unstable relative to the final state. But how is phase stability measured? The answer to this question is provided by thermodynamics. For transformations that occur at constant temperature and pressure the relative stability of a system is determined by its *Gibbs free energy* ( $G$ ).

The Gibbs free energy of a system is defined by the equation

$$G = H - TS \quad (1.1)$$

where  $H$  is the enthalpy,  $T$  the absolute temperature, and  $S$  the entropy of the system. Enthalpy is a measure of the heat content of the system and is given by

$$H = E + PV \quad (1.2)$$

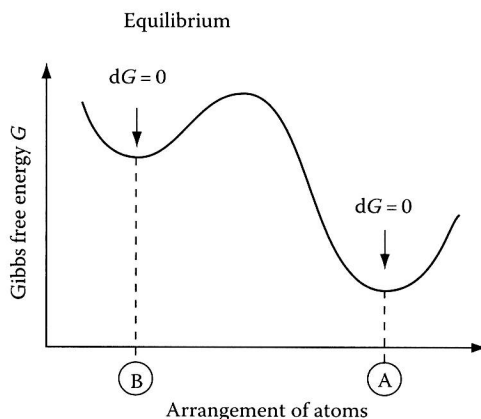
where  $E$  is the internal energy of the system,  $P$  the pressure, and  $V$  the volume. The internal energy arises from the total kinetic and potential energies of the atoms within the system. Kinetic energy can arise from atomic vibration in solids or liquids and from translational and rotational energies for the atoms and molecules within a liquid or gas; whereas potential energy arises from the interactions, or bonds, between the atoms within the system. If a transformation or reaction occurs the heat that is absorbed or evolved will depend on the change in the internal energy of the system. However it will also depend on changes in the volume of the system and the term  $PV$  takes this into account, so that at *constant pressure* the heat absorbed or evolved is given by the change in  $H$ . When dealing with condensed phases (solids and liquids) the  $PV$  term is usually very small in comparison to  $E$ , that is  $H \approx E$ . This approximation will be made frequently in the treatments given in this book. The other function that appears in the expression for  $G$  is entropy ( $S$ ) which is a measure of the randomness of the system.

A system is said to be in equilibrium when it is in the most stable state, i.e. shows no desire to change *ad infinitum*. An important consequence of the laws of classical thermodynamics is that at constant temperature and pressure a closed system (i.e. one of fixed mass and composition) will be in stable equilibrium if it has the lowest possible value of the Gibbs free energy, or in mathematical terms

$$dG = 0 \quad (1.3)$$

It can be seen from the definition of  $G$ , Equation 1.1, that the state with the highest stability will be that with the best compromise between low enthalpy and high entropy. Thus at low temperatures solid phases are most stable since they have the strongest atomic binding and therefore the lowest internal energy (enthalpy). At high temperatures however the  $TS$  term dominates and phases with more freedom of atom movement, liquids and gases, become most stable. If pressure changes are considered it can be seen from Equation 1.2 that phases with small volumes are favoured by high pressures.

The definition of equilibrium given by Equation 1.3 can be illustrated graphically as follows. If it were possible to evaluate the free energy of a given system for all conceivable configurations the stable equilibrium configuration would be found to have the lowest free energy. This is illustrated in Fig. 1.1 where it is imagined that the various atomic configurations can be represented by points along the abscissa. Configuration A would be

**FIGURE 1.1**

A schematic variation of Gibbs free energy with the arrangement of atoms. Configuration 'A' has the lowest free energy and is therefore the arrangement when the system is at stable equilibrium. Configuration 'B' is a metastable equilibrium.

the stable equilibrium state. At this point small changes in the arrangement of atoms to a first approximation produce no change in  $G$ , i.e. Equation 1.3 applies. However there will always be other configurations, e.g.  $B$ , which lie at a local minimum in free energy and therefore also satisfy Equation 1.3, but which do not have the lowest possible value of  $G$ . Such configurations are called *metastable equilibrium* states to distinguish them from the *stable equilibrium* state. The intermediate states for which  $dG \neq 0$  are *unstable* and are only ever realized momentarily in practice. If, as the result of thermal fluctuations, the atoms become arranged in an intermediate state they will rapidly rearrange into one of the free energy minima. If by a change of temperature or pressure, for example, a system is moved from a stable to a metastable state it will, given time, transform to the new stable equilibrium state.

Graphite and diamond at room temperature and pressure are examples of stable and metastable equilibrium states. Given time, therefore, all diamond under these conditions will transform to graphite.

Any transformation that results in a decrease in Gibbs free energy is possible. Therefore a necessary criterion for any phase transformation is

$$\Delta G = G_2 - G_1 < 0 \quad (1.4)$$

where  $G_1$  and  $G_2$  are the free energies of the initial and final states respectively. The transformation need not go directly to the stable equilibrium state but can pass through a whole series of intermediate metastable states.

The answer to the question "How fast does a phase transformation occur?" is not provided by classical thermodynamics. Sometimes metastable states can be very short-lived; at other times they can exist almost indefinitely as in

the case of diamond at room temperature and pressure. The reason for these differences is the presence of the free energy hump between the metastable and stable states in Fig. 1.1. The study of transformation rates in physical chemistry belongs to the realm of *kinetics*. In general, higher humps or energy barriers lead to slower transformation rates. Kinetics obviously plays a central role in the study of phase transformations and many examples of kinetic processes will be found throughout this book.

The different thermodynamic functions that have been mentioned in this section can be divided into two types called intensive and extensive properties. The *intensive* properties are those which are independent of the size of the system such as  $T$  and  $P$ , whereas the *extensive* properties are directly proportional to the quantity of material in the system, e.g.  $V$ ,  $E$ ,  $H$ ,  $S$  and  $G$ . The usual way of measuring the size of the system is by the number of moles of material it contains. The extensive properties are then molar quantities, i.e. expressed in units *per mole*. The number of moles of a given component in the system is given by the mass of the component in grams divided by its atomic or molecular weight.

The number of atoms or molecules within 1 mol of material is given by Avogadro's number ( $N_A$ ) and is  $6.023 \times 10^{23}$ .

## 1.2 Single Component Systems

Let us begin by dealing with the phase changes that can be induced in a single component by changes in temperature at a fixed pressure, say 1 atm. A single component system could be one containing a pure element or one type of molecule that does not dissociate over the range of temperature of interest. In order to predict the phases that are stable or mixtures that are in equilibrium at different temperatures it is necessary to be able to calculate the variation of  $G$  with  $T$ .

### 1.2.1 Gibbs Free Energy as a Function of Temperature

The specific heat of most substances is easily measured and readily available. In general it varies with temperature as shown in Fig. 1.2a. The specific heat is the quantity of heat (in joules) required to raise the temperature of the substance by 1 K. At constant pressure this is denoted by  $C_p$  and is given by

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad (1.5)$$

Therefore the variation of  $H$  with  $T$  can be obtained from a knowledge of the variation of  $C_p$  with  $T$ . In considering phase transformations or chemical