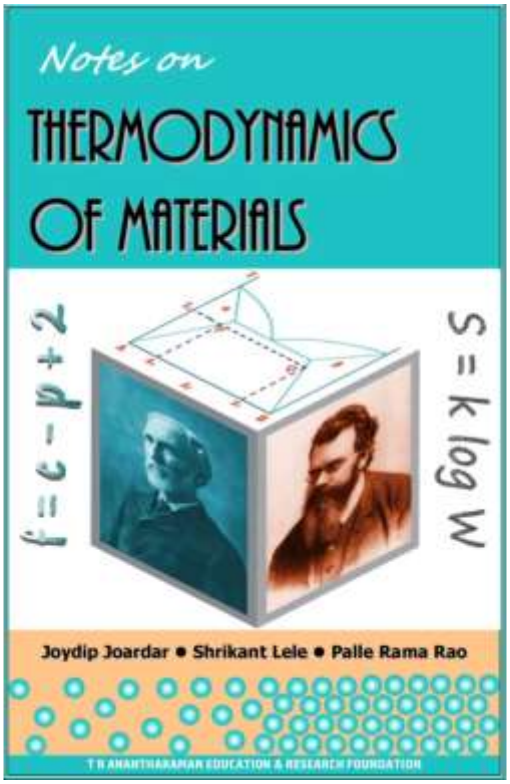

Book on "NOTES ON THERMODYNAMICS OF MATERIALS"

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Synopsis

The science of thermodynamics is the quintessential fundamental science, which every student aspires to master. Knowledge of thermodynamics helps to navigate through a wide range of phenomena in physical sciences as well as, more recently, through certain aspects of life sciences. This is also true in the case of materials science. For instance, alloy phase diagrams, encompassing structural changes in metals, are mapped and interpreted in accordance with the rules set by thermodynamics.

There are numerous books and major articles dealing with the fundamentals of thermodynamics. Further, there are texts dedicated to the subject of thermodynamics of materials. The focus in each of these excellent books is on aspects selected by the author so as to fit into his preferred approach to the study of thermodynamics. Since there are so many of these books, it becomes well-nigh impossible to read and absorb all that is documented in them. We felt therefore that a refresher text could serve as an aid to a majority of students in grasping the essentials of what the scholarly authors present in their tomes.

It is in this light that we have attempted to put together what we have called *Notes on Thermodynamics of Materials*. Many pioneers have contributed to sow the seeds of thermodynamics, which in time have taken root, grown and expanded into multifarious branches. Pictures of these stalwarts have been included with the hope that fresh students of the subject may feel inspired to get seriously acquainted with their groundbreaking contributions.

We must emphasize that we claim no originality for what has been included in these *notes;* much of it has been garnered from various sources, which have been duly credited in the text. These are indeed *notes*, because the intention is not to discuss comprehensively a whole range of topics that normally constitute the subject matter of text books on thermodynamics.

Intended as complimentary to the notes, milestones in the progress of thermodynamics as well as references to useful literature have been provided.

Historically it is application that has driven the development of the science of thermodyanamics. The classical experiment in 1798 by Benjamin Thomson in Germany demonstrated that heat was generated during the boring of cannons and Sadi Carnot of France showed in 1824 *via* Carnot's engine that heat resulted in mechanical work. These pioneering obseravations derived from typical application areas were at the heart of subsequent enunciation of the basic concepts underlying the subject of thermodynamics. Drawing inspiration in a way from this hoary past, we have, in compiling these notes, endeavoured to explain major principles of thermodynamics through the medium of their application. The idea is to use an application of a basic tenet as a tool to help the reader understand the significance of the related concept, which at first reading might seem vague. Thus, the phenomena of beta decay, adiabatic demagnetization and the allotropic modification of diamond cubic grey tin to body-centred tetragonal white tin have been used to bring out the significance respectively of the first, the second and the third law of thermodynamics (Chapters 1 & 2). Similarly the illustrative applications of phase rule show that the basis of the core and distinguishing features of metal sciences can be traced to the science of thermodynamics (Chapters 4 & 5). It is this theme that we have generally tried to maintain throughout this handy volume. We hope that this approach renders it easier to understand the concepts underlying thermodynamics of materials.

The atomistic approach to thermodynamics pioneered by Ludwig Boltzmann is outlined in Chapter 3. Boltzmann looks at the randomness of a system, i.e. the number of ways of distributing the atoms among the various allowed positions and among the various microstates. Recently, there have been interesting developments related to both configurational entropy and vibrational entropy. High entropy alloys have emerged as fascinating new materials. The basis of these multi-element alloys is that the Gibbs energy of mixing is lowered due to increase in the entropy of mixing (Sm) with the largest increase occurring for alloys of equiatomic compositions of all components. On the other hand, for infinitely dilute solutions, the entropy of mixing increases with composition of solute with infinite slope and consequently the Gibbs energy decreases sharply. Increasing purity therefore becomes increasingly difficult. However, with sufficient expenditure of energy, it is possible to achieve high purity by using techniques such as zone refining which exploit the difference in solubility in the solid and liquid state for this purpose. The vibrational entropy (Sv) increases when a material is heated. The industrially important allotropic body-centred cubic to face-centred cubic transformation, when iron is heated to 912^{o}C, is influenced by an increase in vibrational entropy. It has been revisited by resorting to *ab-initio* calculations with the help of modern fast computers and complemented by using new generation experimental techniques like nuclear resonance in-elastic X-ray scattering (NRIXS).

The phenomenon of age-hardening in aluminium alloys, which has led to the development of heavy duty aircraft structurals, and the martensitic transformation exploited extensively in the development of high strength structural steels are arguably the two most important phase transformations. The thermodynamic basis of these two transformation phenomena has been dealt with in Chapter 6.

It is useful to combine the treatments developed in classical thermodynamics and in statistical thermodynamics. The usefulness of this approach has been shown in the calculation of equilibrium concentration of vacancies (Chapter 7). The role of vacancies in atomic diffusion and in diffusion creep, which is driven by mass transport, has been briefly covered in this chapter.

Computational techniques for calculating higher order, i.e. quaternary, quinary and senary, alloy phase diagrams (CALPHAD) have been referred to in Chapter 8. These techniques have enabled design and development of new alloys, two examples of which are cited in this chapter. One of these is related to special steel which has seen application as an aircraft component. The second pertains to a lightweight magnesium alloy under development for application in automobiles.

Large scale production of a variety of nano metals, alloys and oxides achieved in recent times is spurring considerable interest in nano thermodynamics. Similarly the application of irreversible thermodynamics to the evolution of microstructures is receiving current attention. Accordingly the topics of nano thermodynamics and irreversible thermodynamics have been touched upon in Chapter 9 to bring to the attention of the reader that the subject of thermodynamics of materials continues to foray into domains not hitherto envisaged but nevertheless relevant to the emerging new materials. These developments indeed establish thermodynamics as a science of universal applicability.

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