Phase Equilibria

Basic Principles,
Applications,
Experimental Techniques

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PREFACE

Until the mid to late 1950's, Phase Equilibria was a topic of concern primarily to the classical metallurgist. The emphasis, naturally, was then aimed at understanding the behavior of metal alloy phenomena and, indeed, was heavily oriented to the steel industry. With the advent of the electronics, nuclear, and space ages, however, we have witnessed an increasing involvement in this field by the physicist, the physical chemist, the inorganic and organic chemist, the device oriented electrical engineer, and the interdisciplinary product of these ages, the materials scientist. Accordingly, the contributions to the literature by this grouping have increased enormously, with the emphasis shifted to nonmetallic-compound and solid-solution systems. In addition, where previously the domain of interest of the classical metallurgist was confined mainly to interactions among condensed phases, the recent entrants in the field, including the modern metallurgist, have been confronted by a need to better understand condensed-vapor phase behavior. This need exists because many systems of interest to them are volatile, or employ the vapor as a vehicle for the transport, synthesis, purification, and single crystal growth of materials.

It is because of this change in emphasis and need, as well as the fact that existing treatments are basically descriptive in nature that the present work was undertaken. Analytical treatments, for example, have in the past been provided in texts on chemical thermodynamics. These have in general focused on the phenomenological approaches involving activities and fugacities, and therefore, on the largely defensive concepts of ideal and nonideal behavior. In addition, except for advanced thermodynamic treatments, heterogeneous equilibria has been treated generally in a cursory fashion. Books devoted to phase equilibria exclusively have, for the most part, minimized analytical concepts. Instead, the subject has been developed graphically. Even a topic as widely employed by the experimentalist as the lever arm principle is almost always presented without rationalization.

The present treatment has been formulated with these and related considerations in mind. It has been organized in a fashion that affords the theoretical elements sufficient emphasis for the casual participant to understand at least the principles involved, and the serious worker may be sufficiently motivated to delve further. The method of species model systems is employed broadly following introduction of pertinent thermodynamic concepts. In a number of chapters, computer analysis of derived relationships is presented to provide graphical visualization of the consequences of species changes within coexistent phases. The chapter arrangements have been ordered so that in a course of formal instruction the presentation may include or omit the more mathematically oriented material depending upon the needs of the audience. This feature has been utilized successfully in formal presentations by the author within the IBM Research Professional Education Program.

The subject content includes the substance of classical treatments of the subjects and also more modern aspects such as concern with condensed phase–vapor phase equilibria and vapor transport reactions, zone refining techniques, nonstoichiometry, among others. Further, a fairly extensive treatment of experimental techniques is provided in the text and appendix. In addition, the appendix presents additional commentary on specialized topics,* as well as selected general and specific references to major areas treated within the body of the text. It was the intent to provide a reference work for the involved experimentalist, a step by step introductory graduate text for departments of chemistry, metallurgy, and materials science. While it would be presumptuous to assume that all these needs have been met, it is hoped that together with existing treatises, obvious voids have been reasonably filled.

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* For example, a fairly detailed discussion of the effects of vacancy concentration on the dissociation pressure of binary compounds (defect structures) is given in the appendix on p. 524 *et seq.* Other topics, e.g., phase transformations, Vegard's law, crystal growth, vapor pressure, evaporation rate, and accommodation coefficient, are also discussed in some detail with appropriate references.

ACKNOWLEDGMENTS

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Some Preliminary Remarks and Observations

The starting point for all that ensues is the body of accumulated knowledge concerned with interrelationships among work, heat, and energy for macroscopic systems existing in a state of chemical and physical equilibrium. From this body of knowledge, known as thermodynamics, a mathematical generalization called the "phase rule" was first deduced by Willard Gibbs. This equation functions usefully as a constraint on the final state of almost any conceivable macroscopic chemical or physical process. In terms of the parameters, temperature, pressure, and the number of independent chemical variables, none of which is dependent on the total quantity of material under scrutiny, one is able to predict without exception the total number of variables that must be specified in order to define uniquely the state of the system. This total number of variables is termed the degrees of freedom possessed by the system. Specifically, for a system possessing a specified number of independently variable chemical quantities (system components) present in one or more distinctly identifiable phases, all at a defined temperature and pressure, one is able to predict precisely the total number of variables that may be varied independently of the others, namely, how many may be varied simultaneously without changing the physical state of the system. Once this number of required variables is

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