PHASE EQUILIBRIUM IN PROCESS DESIGN

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PREFACE

The literature on phase equilibrium is voluminous, and several excellent texts have been written on the subject. As a result, the engineer or scientist intending to specialize in the subject has at his disposal a wealth of reference material. I have found that, in spite of the vast literature, the subject is poorly understood by the engineers having responsibility for the design and development of chemical processes. This situation is especially disheartening because the success or failure of most separation processes depends on a favorable equilibrium relationship between the phases, regardless of the high efficiency of the equipment.

The lack of understanding of phase equilibrium among process engineers is due, I believe, to the tendency of authors to write primarily for the specialist, who wishes to explore the subject in depth and with mathematical rigor. The design or development engineer cannot become a specialist in phase equilibrium; too many other subjects demand his time for a disproportionate share to be allotted to this one discipline, however important it may be.

In this book I hope to provide a text and reference that meet the needs of design and development engineers. As such this volume should serve as a text on the senior or first-year-graduate level, or as a text for continuing education of practicing engineers. Although a certain amount of mathematical derivation is necessary to the understanding of the principles, I have attempted to use derivations only where they enhance the understanding of a principle. Where I have felt that a sacrifice of mathematical rigor contributes to the clarity of the presentation, I have taken that liberty. I make no apology for this, since the understanding and use of the material presented are more important than a demonstration of mathematical manipulative prowess.

It is inevitable that a book such as this should emphasize the items that are most familiar in the experience of the author. In my work in engineering research and process development, and as advisor to a number of design engineers, I have found that certain techniques are particularly valuable in expediting the quantitative representation of the phase equilibria involved. Some of these techniques are theoretically derivable, whereas others are largely empirical. I have attempted to present these as clearly as possible in the hope that they will prove as useful to the reader as they have to me.

I am indebted to many persons in the preparation of this work. The many research scientists and engineers who have published in this field are obviously contributors; I wish to state in advance that I have not attempted the impossible task of referring to them all in the text. More specifically, I am indebted to the management of the Monsanto Company—particularly R. W. Schuler, J. B. Duncan, J. R. Fair, and H. W. Martin—for encouraging this work and for releasing some of the material that was developed in the course of my work in the Monsanto laboratories. I am also indebted to several of my colleagues who have reviewed the manuscript critically. Lynn Bellamy and David Palmer have been especially helpful in this regard.

I hope the material contained herein will help to fill the gap that I feel exists between the phase-equilibrium specialist and the practicing engineer.

HAROLD R. NULL

St. Louis, Missouri
April 1970

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Chapter 1

INTRODUCTION

Equilibrium between mechanically separable phases is a part of the basis for most of the operations involved in chemical engineering. It is not much of an oversimplification to say that chemical engineering consists of the economical application of equations of balance (material, energy, and force), equations of rate (chemical kinetics, heat and mass transfer), and equations of equilibrium (chemical and phase equilibrium).

Most of the separations operations require a favorable relationship between the equilibrium states of two phases for their success. In distillation a difference in composition between a liquid and a gas phase in equilibrium is essential. The same is true of gas absorption. Liquid extraction requires a difference in composition between two liquid phases; crystallization and zone refining involve a liquid and a solid phase. Other examples are possible.

In addition to the separations, some chemical reactors involve more than one phase; the departure from phase equilibrium is just as important in these cases as the kinetics of the reactions within a single phase. The gas-sparged reactor is one of the many examples of such equipment.

Although the equipment in a plant or laboratory rarely operates at a state of equilibrium between the phases, a knowledge of the relationship between the phases at equilibrium is essential to the understanding of the process. This is true whether one adopts the convention of the equilibrium stage, in which case each compartment of equipment is assumed to attain phase equilibrium and an efficiency applied, or the concept of the transfer unit or mass-transfer coefficients, in which case the rate of change everywhere in a piece of equipment is directly proportional to the departure from equilibrium. Neither case can be analyzed without a quantitative knowledge of the compositions the phases would attain if they were allowed to reach equilibrium.

In the past the chemical engineer has usually relied on extensive and expensive laboratory data, the oversimplified *ideal-solution* concept, or the assumption of constant *distribution coefficients* as the basis for his design where phase-equilibrium data were needed. Because of the expense of the laboratory data, the less reliable assumptions have been used more extensively in industrial design. Although the theory of phase equilibrium has not yet progressed to the point where purely theoretical predictions are possible, many strides have been made in that direction in the last decade or two. It is usually possible today to arrive at a quantitative description of the phase equilibria involved in a given practical problem with a minimum of supporting experimental data. This description will be sufficiently accurate for the design engineer to proceed with confidence, expecting the resulting equipment to function to the specifications required without the use of excessive safety factors to overcome the ignorance of the equilibrium equations. Safety factors used for this purpose are extremely dangerous anyway, since no number of extra stages in a distillation column can make it possible to break an azeotrope.

This book is intended to acquaint the practicing chemical engineer with the theoretical and empirical tools required for the practical evaluation of the problems in phase equilibrium encountered in the design of chemical equipment and the development of chemical processes. This task is neither as difficult as many have assumed nor as simple as others believe. One basic assumption involved is that the phase-equilibrium problem can be solved; therefore it is unnecessary to make it a part of the scale-up problem.

In order to understand the principles developed in this book, an elementary understanding of chemical engineering thermodynamics is necessary; however, the reader need not be a thermodynamics expert. Indeed, if he is an expert, he will find much of the presentation oversimplified. A better than average mathematical ability is also required, but it is not necessary for the engineer confronted with a problem in phase equilibrium to be a mathematician. The use of computers in the solution of problems is a distinct advantage. Many of the equations encountered are cumbersome by most standards, and all attempts to linearize them through reasonable assumptions fail. Computer programming is not an essential part of the principles involved, but it must be recognized that computers will be increasingly utilized in the solution of phase-equilibrium problems. To ignore this tool is to handicap oneself unnecessarily. Several short computer programs are included within the text for illustrative purposes. They are written essentially in FORTRAN IV, although there are some variations in the language to adapt to the software for the several computers used in the course of the work (IBM 704, 7044, and 360 and G.E. remote conversational terminals).

The basic thermodynamic equations and correlations are developed in Chapters 2, 3, and 4, with the following chapters devoted to the development of the principles and techniques useful in the design and development of chemical processes. Chapters 5, 6, 7, and 8 contain many worked out numerical examples to illustrate the principles developed in the preceding chapters.

Chapter 2

BASIC THERMODYNAMICS OF PHASE EQUILIBRIUM

2.1 INTRODUCTION

The term "phase equilibrium" implies a condition of equilibrium between two or more phases. By equilibrium we mean no tendency toward change with time; the term "phase" denotes any quantity of matter that is either homogeneous throughout or contains no discontinuity of properties within the space it occupies. The term "homogeneous" is intended to include portions of material that may have been physically separated from one another but are identical in properties and composition; the alternate specification of no discontinuity of properties throughout allows us to consider as a phase a portion of matter that is undergoing a dynamic change with property gradients existing within it but having no boundary across which properties are discontinuous. In certain applications it is also convenient to consider physically separated regions of material, each of which has similar property values and gradients as a single phase.

In studies of phase equilibrium, however, the phase containing gradients is not considered. Wherever gradients exist there is a tendency for change with time; hence there is no equilibrium. On the other hand, there can be two or more phases, each of which is homogenous throughout, with no tendency for any change in properties with time, even though the phases are in intimate physical contact with one another. The latter is the condition that we denote by the term "phase equilibrium."

In a condition of phase equilibrium there are some properties that are drastically different between the phases, and others that must be identical for all phases to prevent a change of properties within individual phases from occurring.

2.2 IMPORTANT THERMODYNAMIC FUNCTIONS

The foregoing discussion outlines the conditions of phase equilibrium qualitatively; a quantitative description involves the evaluation of certain thermodynamic properties and of the mathematical relationships between them. The most basic property of a closed system is the internal energy E, whose absolute value is never known but whose change is given by the first law of thermodynamics as

$$dE = dQ - dW, \tag{2-1}$$

where Q and W represent heat added to and work done by the system, respectively. In the case of a reversible process Equation 2-1 can be written

$$dE = T\,dS - P\,dV, \tag{2-2}$$

where T represents temperature (absolute scale), P is system pressure, and V is system volume. The symbol S represents entropy, which is defined mathematically by its relationship to the heat Q and temperature T in a reversible process. In an irreversible process Equations 2-1 and 2-2 both hold, but the correspondence of dQ to $T\,dS$ and dW to $P\,dV$ is no longer valid.

Two other properties frequently used in the discussion of phase equilibrium are the enthalpy H and the free energy F. Both these properties are defined mathematically as a combination of the other basic properties. Enthalpy is defined by the equation

$$H = E + PV. \tag{2-3}$$

Its change, then, is expressed by

$$\begin{aligned} dH &= dE + d(PV) \\ &= T\,dS - P\,dV + P\,dV + V\,dP, \\ dH &= T\,dS + V\,dP. \end{aligned} \tag{2-4}$$

The free energy is defined by the expression

$$F = H - TS. \tag{2-5}$$

Equation 2-5, when differentiated, gives

$$\begin{aligned} dF &= -d(TS) + dH \\ &= -T\,dS - S\,dT + T\,dS + V\,dP, \\ dF &= -S\,dT + V\,dP. \end{aligned} \tag{2-6}$$

In the development of the mathematical relationships describing phase equilibrium the free energy receives the greatest attention of all the thermodynamic properties defined above.

2.3 THERMODYNAMIC CONDITIONS FOR PHASE EQUILIBRIUM

When two or more phases are at equilibrium in direct contact across an interface, the potentials for change must be zero. This means that there is no tendency for mass or energy to cross the boundary; thus any transport of material or energy from one phase to the other will be a reversible process. It is evident that in order for a condition of equilibrium to exist the temperatures of the phases must be the same; otherwise an irreversible flow of heat will occur. It is also evident that, if the phases are in direct contact with one another, the pressure must be the same in all phases; otherwise the force imbalance would tend to compress one phase and expand the other, with a net irreversible exchange of energy. These two conditions are not sufficient to ensure phase equilibrium, however, and the remaining conditions required are not quite so self-evident. The classic work of Willard Gibbs [1] defined the remaining conditions that ensure equilibrium between phases.

To visualize the additional conditions for equilibrium, consider three separate thermodynamic systems. Systems I and II will represent two phases in equilibrium. System III will have the same temperature and pressure as systems I and II, but it will be initially void (i.e., zero mass). Now, if an infinitesimal quantity of one of the components, dN_i, is transferred from system I to system III, the changes in certain properties are as follows:

$$dH^{\mathrm{III}} = \left(\frac{\partial H^{\mathrm{I}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i,$$

$$dS^{\mathrm{III}} = \left(\frac{\partial S^{\mathrm{I}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i,$$

$$dF^{\mathrm{III}} = \left(\frac{\partial F^{\mathrm{I}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i,$$

$$dE^{\mathrm{III}} = \left(\frac{\partial E^{\mathrm{I}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i.$$

If the properties of system III now are changed by reversible exchanges of energy with its surroundings, excluding systems I and II, until the properties become compatible for a reversible transfer to system II, infinitesimal quantities of heat and work, dQ and dW, will be involved. The changes in properties of system III are then represented by

$$dH^{\mathrm{III}} = dQ \qquad \text{(constant-pressure process),}$$

$$dS^{\mathrm{III}} = \frac{dQ}{T} \qquad \text{(reversible constant-temperature process),}$$

$$dF^{\mathrm{III}} = dH^{\mathrm{III}} - d(TS^{\mathrm{III}}) = dQ - dQ = 0,$$

$$dE^{\mathrm{III}} = dQ - dW.$$

If the quantity of material, dN_i, is now transferred to system II, the change of properties of system III is given by

$$dH^{\mathrm{III}} = -\left(\frac{\partial H^{\mathrm{II}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i,$$

$$dS^{\mathrm{III}} = -\left(\frac{\partial S^{\mathrm{II}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i,$$

$$dF^{\mathrm{III}} = -\left(\frac{\partial F^{\mathrm{II}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i,$$

$$dE^{\mathrm{III}} = -\left(\frac{\partial E^{\mathrm{II}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i.$$

The combination of processes described above represents a reversible transfer of matter from system I to system II, phases in equilibrium. Furthermore, the state of system III is the same at the end of the transfer as at the beginning. Consequently the net change in properties of system III is zero:

$$dH^{\mathrm{III}} = 0 = \left(\frac{H\partial^{\mathrm{I}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i + dQ - \left(\frac{\partial H^{\mathrm{II}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i,$$

$$dS^{\mathrm{III}} = 0 = \left(\frac{\partial S^{\mathrm{I}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i + \frac{dQ}{T} - \left(\frac{\partial S^{\mathrm{II}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i,$$

$$dF^{\mathrm{III}} = 0 = \left(\frac{\partial F^{\mathrm{I}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i - \left(\frac{\partial F^{\mathrm{II}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i,$$

$$dE^{\mathrm{III}} = 0 = \left(\frac{\partial E^{\mathrm{I}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i + dQ - dW - \left(\frac{\partial E^{\mathrm{II}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i.$$

From the foregoing equations a relationship between the properties of the two phases in equilibrium can be deduced:

$$\left(\frac{\partial H^{\mathrm{I}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial H^{\mathrm{II}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} - \frac{dQ}{dN_i},$$

$$\left(\frac{\partial S^{\mathrm{I}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial S^{\mathrm{II}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} - \frac{1}{T}\frac{dQ}{dN_i},$$

$$\left(\frac{\partial E^{\mathrm{I}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial E^{\mathrm{II}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} - \frac{d(Q-W)}{dN_i},$$

$$\left(\frac{\partial F^{\mathrm{I}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial F^{\mathrm{II}}}{\partial N_i}\right)_{T,P,N_{j\neq ii}} \tag{2-7}$$

Only Equation 2-7 defines a property that is identical in both phases. Since dQ and dW are not necessarily equal or zero, the other properties can be different in the two phases. Gibbs gave this property the name "chemical potential" and the special symbol μ. Thus the conditions for phase equilibrium are

$$T^{\text{I}} = T^{\text{II}}, \tag{2-8a}$$

$$P^{\text{I}} = P^{\text{II}}, \tag{2-8b}$$

$$\mu_i{}^{\text{I}} = \mu_i{}^{\text{II}} \qquad \text{(for all } i\text{)}, \tag{2-8c}$$

where

$$\mu_i \equiv \left(\frac{\partial F}{\partial N_i}\right)_{T,P,N_{j\neq i}} \tag{2-9}$$

2.4 THE GIBBS–DUHEM EQUATIONS

Before further considering the relationships between phases, it is advantageous to develop some of the equations relating properties within a given phase. The equation for the change of free energy for a closed system,

$$dF = -S\,dT + V\,dP,$$

implies that, at constant mass, system free energy is a function of temperature and pressure only. For an open system it also depends on the number of moles of each component. Thus the functional relationship is

$$F = f(T, P, N_1, N_2, \ldots).$$

Stated in differential form, this is

$$dF = \left(\frac{\partial F}{\partial T}\right)_{P,N_j} dT + \left(\frac{\partial F}{\partial P}\right)_{T,N_j} dP + \sum_i \left(\frac{\partial F}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i. \tag{2-10}$$

It is evident from an examination of Equation 2-10 that

$$\left(\frac{\partial F}{\partial T}\right)_{P,N_j} = -S \quad \text{and} \quad \left(\frac{\partial F}{\partial P}\right)_{T,N_j} = V, \tag{2-11}$$

giving

$$dF = -S\,dT + V\,dP + \sum_i \mu_i\,dN_i \tag{2-12}$$

as the equation describing the change in free energy in a system of variable mass.

If a system is built up from zero mass at constant temperature and pressure,

$$dF = \sum_i \mu_i \, dN_i .$$

Starting from zero mass, the initial free energy is zero; thus the integral equation becomes

$$\int_0^F dF = F = \sum_i \int_0^{N_i} \mu_i \, dN_i .$$

With the further specification that the composition expressed in terms of mole fractions x_i be constant during the process,

$$dN_i = d(x_i N_t) = x_i \, dN_t$$

and

$$F = \sum_i \int_0^{N_t} \mu_i x_i \, dN_t = \sum_i x_i \int_0^{N_t} \mu_i \, dN_t .$$

It is an experimental fact that in a system of fixed composition the molal free energy F/N_t is independent of the total number of moles in the system. Thus $F/N_t = \Sigma\,(x_i/N_t) \int_0^{N_t} \mu_i \, dN_t$ is not a function of N_t. Consequently $\int_0^{N_t} \mu_i \, dN_t \propto N_t$. This can only be true if μ_i is independent of N_t, in which case

$$\frac{F}{N_t} = \sum_i \mu_i x_i , \tag{2-13}$$

or

$$F = \sum_i \mu_i N_i . \tag{2-14}$$

The above equations, shown here for free energy, are generally true as a relationship between total and partial molal properties.

A very useful equation can be derived by differentiating Equation 2-14 and comparing the result with Equation 2-12.

$$dF = \sum_i \mu_i \, dN_i + \sum_i N_i \, d\mu_i = -S\,dT + V\,dP + \sum_i \mu_i \, dN_i ,$$

which gives

$$\sum_i N_i \, d\mu_i = -S\,dT + V\,dP, \tag{2-15a}$$

or

$$\sum_i x_i \, d\mu_i = -s\,dT + v\,dP, \tag{2-15b}$$

where $s = S/N_t$ and $v = V/N_t$.

If a specification of constant temperature and pressure is applied, the equations become

$$\sum_i N_i \, d\mu_i = 0, \tag{2-16a}$$

or

$$\sum_i x_i \, d\mu_i = 0. \tag{2-16b}$$

Equation 2-16b is known as the Gibbs–Duhem equation. Equations 2-15 and 2-16 are rigorous and are often used to test experimental data for thermodynamic consistency. Further reference will be made to these equations in subsequent chapters.

2.5 MATHEMATICAL RELATIONSHIPS BETWEEN PHASES IN EQUILIBRIUM

In order to derive further equations relating the properties of phases in equilibrium, attention must be devoted to an evaluation of the quantities μ_i, since, according to Equation 2-8c,

$$\mu_i^{\mathrm{I}} = \mu_i^{\mathrm{II}}.$$

Directing our attention initially to only one phase, the quantity μ_i for any component can be expressed as the sum of two terms:

$$\mu_i = \mu_i^\circ + \Delta\mu_i,$$

where

$$\Delta\mu_i = \mu_i - \mu_i^\circ.$$

The term μ_i° is commonly called the chemical potential of the component i in the *standard state*. In order to evaluate the quantity properly it is necessary to define the standard state. Since there is by no means a "standard" definition of the standard state, there is considerable confusion as a result. The definition of the standard state is generally taken as the state that simplifies the equations to be derived for the specific problem at hand; it is easy to see the difficulties that can arise as a result of this practice. Throughout this book the standard state is always the pure component at the system temperature and total pressure, and in the same physical state as the phase under consideration. Thus the standard state for any component in a gas mixture is the pure component in the gas phase at system temperature and pressure, whereas the standard state for the same component in a liquid mixture is the pure