

UNIVERSAL  
LIBRARY

**OU\_154665**

UNIVERSAL  
LIBRARY







INTERNATIONAL CHEMICAL SERIES\*

LOUIS P. HAMMETT, PH.D., *Consulting Editor*

Principles of  
Phase Equilibria

# A SELECTION OF TITLES FROM THE INTERNATIONAL CHEMICAL SERIES

LOUIS P. HAMMETT, PH.D., *Consulting Editor*

- Amsden*—  
Physical Chemistry for Premedical Students
- Arthur and Smith*—  
Semimicro Qualitative Analysis
- Bachman*—  
Organic Chemistry
- Booth and Damerell*—  
Quantitative Analysis
- Coghill and Sturtevant*—  
An Introduction to the Preparation and Identification of Organic Compounds
- Currier and Rose*—  
General and Applied Chemistry
- Daniels*—  
Mathematical Preparation for Physical Chemistry
- Daniels, Mathews, Williams, and Staff*—  
Experimental Physical Chemistry
- Desha*—  
Organic Chemistry
- Dole*—  
Experimental and Theoretical Electrochemistry
- Eastman and Rollefson*—  
Physical Chemistry
- English and Cassidy*—  
Principles of Organic Chemistry
- Gibb*—  
Optical Methods of Chemical Analysis
- Glasstone, Laidler, and Eyring*—  
The Theory of Rate Processes
- Griffin*—  
Technical Methods of Analysis
- Hamilton and Simpson*—  
Calculations of Analytical Chemistry
- Hammett*—  
Physical Organic Chemistry  
Solutions of Electrolytes
- Henderson and Fernelius*—  
Inorganic Preparations
- Huntress*—  
Problems in Organic Chemistry
- Laidler*—  
Chemical Kinetics
- Leighou*—  
Chemistry of Engineering Materials
- Long and Anderson*—  
Chemical Calculations
- Mahin*—  
Quantitative Analysis
- Millard*—  
Physical Chemistry for Colleges
- Moore*—  
History of Chemistry
- Morton*—  
Laboratory Technique in Organic Chemistry  
The Chemistry of Heterocyclic Compounds
- Norris*—  
Experimental Organic Chemistry  
The Principles of Organic Chemistry
- Parr*—  
Analysis of Fuel, Gas, Water, and Lubricants
- Paul*—  
Principles of Chemical Thermodynamics
- Reedy*—  
Elementary Qualitative Analysis  
Theoretical Qualitative Analysis
- Rieman, Neuss, and Naiman*—  
Quantitative Analysis
- Snell and Biffen*—  
Commercial Methods of Analysis
- Sterner*—  
Introduction to Chemical Thermodynamics
- Stone, Dunn, and McCullough*—  
Experiments in General Chemistry
- Thomas*—  
Colloid Chemistry
- Timm and Neal*—  
Laboratory Exercises in General Chemistry
- Wetmore and LeRoy*—  
Principles of Phase Equilibria
- Woodman*—  
Food Analysis

# Principles of Phase Equilibria

F. E. W. WETMORE and D. J. LeROY

*Department of Chemistry, University of Toronto  
Toronto, Canada*

FIRST EDITION

New York Toronto London  
McGRAW-HILL BOOK COMPANY, INC.

1951

## PRINCIPLES OF PHASE EQUILIBRIA

Copyright, 1951, by the McGraw-Hill Book Company, Inc. Printed in the United States of America. All rights reserved. This book, or parts thereof, may not be reproduced in any form without permission of the publishers.

## PREFACE

The material of this text is the result of the authors' experience in presenting to graduate and undergraduate students in arts, science, and engineering the principles of heterogeneous equilibria in terms of laboratory criteria and from a fundamental point of view, without recourse to formal thermodynamics. Because of the emphasis on fundamental principles and logical thinking, this manner of presentation has been found to serve as an ideal introduction to theoretical chemistry. While the formal mathematical treatment of heterogeneous equilibria can be derived from chemical thermodynamics, the latter is not essential for the development and application of the phase rule, since both the phase rule and the laws of thermodynamics are based on experience.

The desirability of combining the practical with the theoretical approach has been met by devoting a considerable portion of the text to such practical matters as the quantitative description of systems in equilibrium and the treatment of distillation and courses of crystallization. Systems of one, two, three, and four components are discussed. In each case the terminology and the method of treatment are exemplified by a detailed consideration of a typical system, followed by treatment of a wide variety of systems. The comprehensive nature of the phase rule and the important fact that there are only two classes of phases, pure substances and solutions, are emphasized by arranging the material to show the similarity in the behavior of gaseous, liquid, and solid solutions.

Exercises are included at the end of each chapter. Further material for exercises is available in such compendia as the "International Critical Tables," "Landolt und Börnstein Tabellen," the section on the constitution of alloys in the "Metals Handbook" of the American Society for Metals, and "Phase Diagrams for Ceramicists" by Hall and Insley, *Journal of the American Ceramic Society*, Part II, November, 1947. Articles dealing with phase equilibria appear periodically in the *Journal of Chemical Education*.

The advanced student will appreciate that many of the proofs

given in the text can be derived from thermodynamics. For his benefit the Appendixes present a thermodynamic derivation of the phase rule and a treatment of free energy-composition curves and their relation to heterogeneous equilibria.

The authors wish to acknowledge their great indebtedness to their colleagues in the Department of Chemistry, and in particular to the late Professor W. Lash Miller, and Professors Frank B. Kenrick, Andrew R. Gordon, and John B. Ferguson. Grateful acknowledgment is made to Professor Luke E. Steiner for permission to quote from his text "Introduction to Chemical Thermodynamics."

F. E. W. WETMORE  
D. J. LEROY

TORONTO, CANADA  
*December, 1950*

# CONTENTS

|              |   |
|--------------|---|
| PREFACE..... | v |
|--------------|---|

## CHAPTER 1

### CHEMICAL EQUILIBRIUM

|                                                                |    |
|----------------------------------------------------------------|----|
| 1.1 The Definition of Chemical Equilibrium.....                | 1  |
| 1.2 Conditions Affecting Equilibrium in Homogeneous Systems .. | 2  |
| 1.3 Heterogeneous versus Homogeneous Equilibria.....           | 4  |
| 1.4 Components versus Constituents.....                        | 4  |
| 1.5 Degrees of Freedom in Heterogeneous Systems ..             | 7  |
| Exercises.....                                                 | 11 |

## CHAPTER 2

### ONE-COMPONENT SYSTEMS

|                                                                    |    |
|--------------------------------------------------------------------|----|
| 2.1 Polymorphism and Isomerism.....                                | 12 |
| 2.2 The Freezing Point of Water.....                               | 13 |
| 2.3 Determination of Freezing (Melting) Points of Pure Substances. | 14 |
| 2.4 Determination of Vapor Pressures of Pure Substances.....       | 16 |
| 2.5 Critical Temperature and Pressure.....                         | 20 |
| 2.6 Boiling Points of Pure Substances ..                           | 22 |
| 2.7 Sublimation Temperature.....                                   | 22 |
| 2.8 Triple Points for the System Water ..                          | 22 |
| 2.9 The System Sulfur.....                                         | 23 |
| 2.10 The System Phosphorus ..                                      | 25 |
| 2.11 The System Menthol ..                                         | 27 |
| 2.12 The System Tin.....                                           | 28 |
| 2.13 The System Silica ..                                          | 28 |
| Exercises.....                                                     | 30 |

## CHAPTER 3

### TWO-COMPONENT SYSTEMS

|                                                                 |    |
|-----------------------------------------------------------------|----|
| 3.1 The Solubility of Glauber's Salt.....                       | 31 |
| 3.2 The Solubility of Sodium Sulfate.....                       | 33 |
| 3.3 The Effect of Temperature and Pressure on Solubility.....   | 34 |
| 3.4 Freezing Points of Aqueous Sodium Sulfate Solutions.....    | 35 |
| 3.5 Boiling Points of Aqueous Sodium Sulfate Solutions.....     | 36 |
| 3.6 The Phase Diagram for the System Sodium Sulfate-Water ..    | 38 |
| 3.7 The Description of a System and the Proportioning Rule..... | 41 |

|      |                                                                                               |    |
|------|-----------------------------------------------------------------------------------------------|----|
| 3.8  | Courses of Crystallization.....                                                               | 44 |
| 3.9  | Temperature-Time Curves. Thermal Analysis.....                                                | 47 |
| 3.10 | The Isothermal Phase Diagram for the System $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ ..... | 49 |
| 3.11 | Dissociation Pressures of Hydrates.....                                                       | 51 |
| 3.12 | The Metastability of the Heptahydrate of Sodium Sulfate.....                                  | 52 |
| 3.13 | Pressure-Temperature Curves and Quadruple Points.....                                         | 54 |
|      | Exercises.....                                                                                | 56 |

## CHAPTER 4

## TWO-COMPONENT SYSTEMS. TYPES OF EQUILIBRIA INVOLVING ONLY ONE PHASE OF VARIABLE COMPOSITION

|     |                                                              |    |
|-----|--------------------------------------------------------------|----|
| 4.1 | The Binary Eutectic.....                                     | 57 |
| 4.2 | Equilibria Involving a Vapor and Two Immiscible Liquids..... | 60 |
| 4.3 | Binary Compounds, Melting Congruently.....                   | 62 |
| 4.4 | Binary Compounds, Melting Incongruently.....                 | 63 |
|     | Exercises.....                                               | 64 |

## CHAPTER 5

## TWO-COMPONENT SYSTEMS. TYPES OF EQUILIBRIA INVOLVING MORE THAN ONE PHASE OF VARIABLE COMPOSITION

|     |                                                             |    |
|-----|-------------------------------------------------------------|----|
| 5.1 | Classification.....                                         | 66 |
| 5.2 | Liquid Solution-Liquid Solution.....                        | 67 |
| 5.3 | Solid Solution-Solid Solution.....                          | 70 |
| 5.4 | Liquid Solution-Solid Solution.....                         | 73 |
| 5.5 | Liquid Solution-Gaseous Solution. Constant Pressure.....    | 78 |
| 5.6 | Liquid Solution-Gaseous Solution. Constant Temperature..... | 85 |
| 5.7 | Combined $L$ - $V$ and $L$ - $L$ Equilibria.....            | 88 |
| 5.8 | Combined $L$ - $S$ and $S$ - $S$ Equilibria.....            | 91 |
| 5.9 | The System Silver-Tin.....                                  | 93 |
|     | Exercises.....                                              | 96 |

## CHAPTER 6

## THREE-COMPONENT SYSTEMS

|     |                                                                            |     |
|-----|----------------------------------------------------------------------------|-----|
| 6.1 | Methods of Representing Ternary Composition.....                           | 97  |
| 6.2 | Degrees of Freedom in Three-component Systems.....                         | 101 |
| 6.3 | The System $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ ..... | 101 |
|     | Exercises.....                                                             | 113 |

## CHAPTER 7

## THREE-COMPONENT SYSTEMS AT FIXED TEMPERATURE AND PRESSURE

|     |                                                                                                                         |     |
|-----|-------------------------------------------------------------------------------------------------------------------------|-----|
| 7.1 | One Phase of Variable Composition. The System $\text{Na}_2\text{SO}_4\text{-NaCl-Na}_2\text{SO}_4\cdot\text{NaF}$ ..... | 115 |
| 7.2 | Two Phases of Variable Composition. The System Diethyl Ether-Ethyl Alcohol-Water.....                                   | 119 |

|     |                                                                                                                                |     |
|-----|--------------------------------------------------------------------------------------------------------------------------------|-----|
| 7.3 | Two Phases of Variable Composition. The System $(\text{NH}_4)_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$ . . . . . | 122 |
| 7.4 | Two Phases of Variable Composition. The System Phenol-Water-Aniline . . . . .                                                  | 124 |
| 7.5 | Two Phases of Variable Composition. Systems Showing More than One Binodal Curve . . . . .                                      | 126 |
|     | Exercises . . . . .                                                                                                            | 128 |

## CHAPTER 8

## THREE-COMPONENT SYSTEMS. SOLID DIAGRAMS AND THEIR PLANE PROJECTIONS

|     |                                                                                                                                |     |
|-----|--------------------------------------------------------------------------------------------------------------------------------|-----|
| 8.1 | The System $\text{Na}_2\text{SO}_4\text{-NaCl-Na}_2\text{SO}_4\cdot\text{NaF}$ . . . . .                                       | 129 |
| 8.2 | Courses of Crystallization in a System Having a Single Ternary Invariant Point . . . . .                                       | 131 |
| 8.3 | Systems Having a Single Binary Compound Which Melts Congruently. The System $\text{Na}_2\text{SO}_4\text{-NaCl-NaF}$ . . . . . | 133 |
| 8.4 | Systems Having a Single Binary Compound Which Melts Incongruently . . . . .                                                    | 136 |
| 8.5 | Systems Having a Ternary Compound Which Melts Congruently . . . . .                                                            | 144 |
| 8.6 | Systems Exhibiting a Binary Compound Which Has a Ternary Field, but Not a Binary Field . . . . .                               | 145 |
| 8.7 | The Quadrilateral Diagram, Required to Represent Certain Types of Three-component Systems . . . . .                            | 148 |
| 8.8 | The Division of a Complicated Diagram into Simpler Independent Parts . . . . .                                                 | 149 |
|     | Exercises . . . . .                                                                                                            | 151 |

## CHAPTER 9

## FOUR-COMPONENT SYSTEMS

|     |                                                                                                                                                                       |     |
|-----|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 9.1 | Considerations Bearing on the Choice of Components . . . . .                                                                                                          | 153 |
| 9.2 | Components in Systems Showing Reciprocal Salt Pair Transformations . . . . .                                                                                          | 155 |
| 9.3 | Graphical Representation of a Four-component System of Water and Three Salts Having a Common Ion, by a Regular Tetrahedron . . . . .                                  | 158 |
| 9.4 | Graphical Representation of a Four-component System of Water and Three Salts Having a Common Ion, by a Triangular Prism (Jänecke's Method). . . . .                   | 163 |
| 9.5 | The Use of Jänecke's Projection to Predict Courses of Crystallization during Isothermal Evaporation of a Quaternary Solution $A\text{-}B\text{-}C\text{-}W$ . . . . . | 165 |
| 9.6 | Poly-component Compounds in the System $A\text{-}B\text{-}C\text{-}W$ . . . . .                                                                                       | 167 |
| 9.7 | Graphical Representation of the Anhydrous Composition of a System Consisting of Water and Two Reciprocal Salt Pairs . . . . .                                         | 170 |
| 9.8 | Aqueous Reciprocal Salt Pair Systems. The Pyramidal Solid Diagram and Its Projection . . . . .                                                                        | 171 |

|                                                                                                       |     |
|-------------------------------------------------------------------------------------------------------|-----|
| 9.9 Aqueous Reciprocal Salt Pair Systems. The Prismatic Solid<br>Diagram and Its Projection . . . . . | 173 |
| 9.10 The System $\text{NaCl-NH}_4\text{HCO}_3\text{-H}_2\text{O}$ . . . . .                           | 176 |
| Exercises . . . . .                                                                                   | 179 |

## APPENDIX I

|                                                           |     |
|-----------------------------------------------------------|-----|
| THE THERMODYNAMICS DERIVATION OF THE PHASE RULE . . . . . | 183 |
|-----------------------------------------------------------|-----|

## APPENDIX II

|                                                                                                         |     |
|---------------------------------------------------------------------------------------------------------|-----|
| FREE ENERGY-COMPOSITION CURVES FOR TWO-COMPONENT SYSTEMS .                                              | 187 |
| II.1 Free Energy Changes for Spontaneous Processes .                                                    | 187 |
| II.2 The Free Energy-Composition Curve for a Mixture at Constant<br>Temperature and Pressure . . . . .  | 187 |
| II.3 The Free Energy-Composition Curve for a Solution at Constant<br>Temperature and Pressure . . . . . | 189 |
| II.4 Partial Molal Free Energies . . . . .                                                              | 190 |
| II.5 Free Energy Curves and Solubility . . . . .                                                        | 191 |
| II.6 Free Energy-Composition Curves for Systems Having Conjugate<br>Solutions . . . . .                 | 194 |
| INDEX . . . . .                                                                                         | 197 |

## CHAPTER 1

### CHEMICAL EQUILIBRIUM

#### 1.1 The Definition of Chemical Equilibrium

In any discussion of scientific principles there must be no doubt as to the meaning and usage of the terms employed. This is particularly important for chemical equilibrium, a concept which is too frequently treated by intuition rather than logic. Every equilibrium has to do with a *process*. In *chemical* equilibria the processes involved are changes in chemical composition or in physical state or in both; the materials which can undergo these changes constitute the *system*. Furthermore these processes must be *reversible*. An example of a reversible process is afforded by a system consisting of nitrogen, hydrogen, and ammonia.

It is a well-known fact that gaseous nitrogen and hydrogen can react, at least partially, to form ammonia and that ammonia gas can decompose, at least partially, to form nitrogen and hydrogen, according to the stoichiometric relation  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ . Although a gaseous solution of nitrogen, hydrogen, and ammonia may be homogeneous, its properties may change progressively with time.<sup>1</sup> Some of the nitrogen and hydrogen may react to form ammonia, or the reverse process may occur, but in either event the rate of the reaction will steadily decrease and eventually vanish, as far as any laboratory experiments of reasonable duration can show. There is no assurance, however, that a great lapse of time would show no further reaction and hence there is no assurance that equilibrium with respect to this process has been reached.

An unambiguous test for equilibrium can be made by *changing the conditions* slightly. If a small increase in the *temperature* of the system results in the formation of a little more nitrogen and hydrogen, and a small decrease in the temperature of the system results in the formation of a little more ammonia, then, within the

<sup>1</sup> The presence of a catalyst may accelerate this change.

accuracy of the measurements, it can be said that the system must have been in equilibrium with respect to the process of nitrogen and hydrogen forming ammonia, and ammonia forming nitrogen and hydrogen. Similarly a small increase and decrease in the *pressure* on the system or small changes in the *proportions* of the three gases could be used as alternative criteria for equilibrium.

It should be noted that the decision as to whether or not a system is in equilibrium with respect to a certain process rests on a purely *experimental* basis and in order to show that equilibrium obtains, the state of equilibrium must be upset by changing the conditions which determine it. *A system is said to be in equilibrium with respect to a particular process if it can be shown that the process is reversible for small opposite changes of conditions.* This definition is a general one, applicable to the mechanical equilibrium of physical systems as well as to chemical equilibrium. The factors which must be taken into consideration in dealing with any specific case are (1) the process involved (always including the reverse process) and (2) the conditions affecting the equilibrium.

## 1.2 Conditions Affecting Equilibrium in Homogeneous Systems

In chemical systems the processes with respect to which there can be equilibrium are both numerous and varied, but the conditions affecting equilibrium are small in number. Only because of this fact is it possible to discuss equilibria in general terms. In the equilibrium discussed above, temperature, pressure, and composition were the variables considered as affecting equilibrium. Additional conditions would be gravitational, electrical, and magnetic fields, and radiation; these factors can all be taken into account thermodynamically. In most cases, however, these conditions are either maintained constant or are completely absent; under such circumstances they need not be considered. Although surface-to-volume ratio may be important in some heterogeneous equilibria, this effect belongs properly to the field of surface and colloid chemistry. In an elementary treatise, therefore, the only conditions given consideration are temperature, pressure, and composition. The comprehensive treatment of equilibria in chemical systems was first put on a precise basis by J. Willard Gibbs,<sup>1</sup> who showed that all chemical equilibria are controlled by the first and second laws of thermodynamics.

<sup>1</sup> *Trans. Conn. Acad. Sci.*, **3**, 228 (1876).

In discussing the equilibrium among nitrogen, hydrogen, and ammonia it was pointed out that a small change of any one of the conditions resulted in a small change in the proportions of the three substances. The direction in which the reversible process will proceed depends on the direction in which the condition is changed. If no reaction were to occur when heat is added to a system, its temperature would rise. If an endothermic reaction were to occur, the temperature rise would be less. But if an exothermic reaction were to occur, more heat would be produced, which would result in further exothermic reaction until one or more of the reagents was consumed. This last possibility is contrary to all experience with systems initially in equilibrium.

The reaction between nitrogen and hydrogen to form ammonia is exothermic; the reverse process is therefore endothermic. Consequently, if heat is added to a gaseous solution of nitrogen, hydrogen, and ammonia in equilibrium, the proportion of ammonia can decrease but cannot increase. Since an increase in the temperature of the system requires the addition of heat, an increase in temperature is associated with a decrease in the proportion of ammonia. Conversely, a decrease in temperature is associated with an increase in the proportion of ammonia. It follows, therefore, that if a system is in equilibrium with respect to a process, an increase of temperature can only result in that change of proportions required by the endothermic direction of the process, while a decrease of temperature can only result in that change of proportions required by the exothermic direction of the process.

By similar reasoning it can be shown that an increase of pressure on a system at equilibrium can only result in that change of proportions required by the process which diminishes the volume of the system, while a decrease of pressure can only result in that change of proportions required by the process which leads to an increase of volume.

Likewise it can be shown that an increase in the proportion of one of the substances in a homogeneous system at equilibrium can only result in the change of proportions required by the process which diminishes the proportion of that substance. For example, an increase in the proportion of nitrogen will result in the formation of more ammonia. It is always the relative amount of a substance (proportion or concentration), rather than its absolute amount, which affects the equilibrium.

The ability to predict the direction in which changes can take

place in a system initially at equilibrium was recognized by several workers in the latter half of the nineteenth century. Robin (1879) stated the rule for changes of pressure, van't Hoff (1884) for changes of temperature, and in 1888, Le Châtelier stated the rule in general terms.

### 1.3 Heterogeneous versus Homogeneous Equilibria

*Phases* are bodies of matter differing in properties, such as chemical composition, density, refractive index, optical rotation, crystalline form, and physical state (solid, liquid, or gas). Thus homogeneous equilibria pertain to a single phase in which the properties are uniform throughout the system and the substances involved constitute a solution.

Under certain conditions ice and water can exist in equilibrium with respect to the process of ice turning into water and water turning into ice. The properties of ice obviously differ from those of water, and hence the system consists of two phases, water and ice. It may contain many lumps of ice, but since they all have the same properties, they constitute a single phase. The relative amounts of the phases have no bearing on the equilibrium. Systems consisting of more than one phase are said to be heterogeneous; equilibria involving more than one phase are thus heterogeneous equilibria.

Another example of a two-phase equilibrium is that between ice and an aqueous solution of sodium sulfate. Here the equilibrium is with respect to the process of ice dissolving in and crystallizing from the solution. There is an important difference, however, between this case and the ice-water system. While the two phases, ice and water, have the same composition, this is not true for the salt solution and ice. The consequences of this difference will be made apparent in a subsequent portion of this chapter.

### 1.4 Components versus Constituents

The composition of a substance can be expressed in terms of any set of constituents from which it can be quantitatively synthesized or into which it can be quantitatively decomposed. For example, hydrogen and oxygen are an obvious set of constituents of water or ice; hydrogen peroxide and hydrogen are a less obvious choice. Among the possible sets of constituents of sodium sulfate are so-

dium, sulfur, and oxygen; sodium, sulfur dioxide, and oxygen; sodium oxide and sulfur trioxide; sodium sulfide and oxygen. Similarly, possible sets of constituents of an aqueous sodium sulfate solution are sodium, sulfur, oxygen, and hydrogen; sodium sulfate and water; aqueous sodium hydroxide solution and aqueous sulfuric acid of suitable concentrations.

The *elementary composition*, stated in terms of the elements as constituents, is commonly used for pure substances. In describing heterogeneous systems, such as ice and sodium sulfate solution, the *phase constituents*, i.e., the mechanically mixed phases themselves, constitute a set of considerable importance. The chemist can choose any set of constituents appropriate to his particular needs.

To assess properly the conditions affecting a heterogeneous equilibrium the chemist uses a particular set of constituents, namely the set having the least number necessary to describe the composition of every phase present. The constituents in such a set are termed *components*. Ice and water have the same composition and therefore constitute a one-component system. Ice and an aqueous solution of sodium sulfate constitute a two-component system. For the heterogeneous system ice-sodium sulfate solution, a possible set of constituents is sodium, sulfur, hydrogen, and oxygen. However, in the ice phase the relative proportions of hydrogen and oxygen are always the same (in accordance with the law of reacting weights), and hence one constituent, water, is sufficient to describe the composition of this phase. Two constituents, water and sodium sulfate, are sufficient to describe the composition of the solution. The constituents sodium, sulfur, hydrogen, and oxygen are clearly not a set of components since they are four in number. Moreover, if the proportions of any pair (except the pair sodium and sulfur) are specified, the composition of the solution is established. The proportions of the two remaining constituents are known by virtue of the two relations

$$\text{Weight of sulfur} = \text{weight of sodium} \times \frac{32}{2 \times 23} \quad (a)$$

$$\begin{aligned} \text{Weight of oxygen} = \text{weight of sulfur} \times \frac{4 \times 16}{32} \\ + \text{weight of hydrogen} \times \frac{16}{2 \times 1} \quad (b) \end{aligned}$$

It should be noted that equation (b) applies to the ice phase as well as to the solution. For any set of constituents greater in number than the components there will always be interrelating stoichiometric equations of this type. The number of such relations will be equal to the difference between the number of constituents and the number of components. Thus by broader definition, applicable to homogeneous as well as heterogeneous systems, a set of components is a set of composition variables (constituents) among which there exist no interrelating equations. A gaseous solution of nitrogen, hydrogen, and ammonia in general requires three components; however, if equilibrium exists, so that the mass law serves as one relation among the three constituents, then only two components are necessary; the proportion of the third constituent is fixed by the mass law.

The number of components may be less than the number of phases. For example, sodium sulfate, steam, and an aqueous solution of sodium sulfate can coexist at the boiling point of a solution saturated with respect to sodium sulfate. In this instance the solution can be in equilibrium with steam with respect to the process of steam dissolving in and being liberated from the solution, and in equilibrium with sodium sulfate with respect to the process of sodium sulfate dissolving in and crystallizing from the solution. Although three phases are present the system is two-component.

The *number* of components is more important than the *choice* of components. At 760 mm pressure and 32.384°C the three phases, sodium sulfate, Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), and a solution (33.2% sodium sulfate, 66.8% water)<sup>1</sup> can coexist in equilibrium with respect to three processes. (These processes will be discussed at some length in Chapter 3.) Although three phases are present, two constituents are sufficient to describe their compositions. Three choices of components for this two-component system are shown in Table 1.1.

Although the composition of sodium sulfate expressed in *B* may appear artificial, it simply records the fact that 100 g of sodium sulfate can be obtained by removing 127 g of water from 227 g of Glauber's salt. Whether a substance can be made by adding various things together or by removing one substance from another

<sup>1</sup> Throughout this book percentages are to be interpreted as percentages by weight unless otherwise stated.

is unimportant. It will be found necessary in later portions of this book to use choices such as *B* or *C*.

TABLE 1.1 CHOICE OF COMPONENTS FOR A SYSTEM HAVING THE PHASE CONSTITUENTS SODIUM SULFATE, GLAUBER'S SALT, AND SATURATED SOLUTION

| A. Components: Sodium Sulfate-Water |                  |         |
|-------------------------------------|------------------|---------|
| PHASE                               | COMPOSITION      |         |
|                                     | % sodium sulfate | % water |
| Sodium sulfate.....                 | 100              | 0       |
| Glauber's salt.....                 | 44.1             | 55.9    |
| Solution.....                       | 33.2             | 66.8    |

| B. Components: Glauber's Salt-Water |                  |         |
|-------------------------------------|------------------|---------|
|                                     | % Glauber's salt | % water |
| Sodium sulfate.. . . . .            | 227              | -127    |
| Glauber's salt.. . . . .            | 100              | 0       |
| Solution.....                       | 75.3             | 24.7    |

| C. Components: Sodium Sulfate-Glauber's Salt |                  |                  |
|----------------------------------------------|------------------|------------------|
|                                              | % sodium sulfate | % Glauber's salt |
| Sodium sulfate.... . . . .                   | 100              | 0                |
| Glauber's salt.. . . . .                     | 0                | 100              |
| Solution . . . . .                           | -19.5            | 119.5            |

## 1.5 Degrees of Freedom in Heterogeneous Systems

Just as in the case of homogeneous systems, the conditions affecting equilibrium in heterogeneous systems are temperature, pressure, and the compositions of the phases.<sup>1</sup>

The properties of water are defined once the temperature and pressure are fixed, since they are single-valued functions of these variables. Liquid water can exist over a wide range of temperature and pressure, either of which can be varied independently. A system consisting of water and steam can also exist over a wide

<sup>1</sup> Phases of variable composition are of necessity solutions, since the composition of a pure substance (element or compound) is invariant.

range of temperature and pressure and yet be in equilibrium with respect to the process  $\text{water} \rightleftharpoons \text{steam}$ . Only one of these variables can be independent, however. If the temperature is arbitrarily fixed at  $25^{\circ}\text{C}$  water can exist in equilibrium with steam only at the pressure fixed by nature, 23.756 mm. If the pressure were fixed at 17.535 mm this equilibrium could obtain only at the temperature  $20^{\circ}\text{C}$ . Equilibrium is also possible between ice and water or between ice and steam, but if one of the variables (either temperature or pressure) is chosen, the other is fixed by nature. The three phases, water, steam, and ice, can coexist in equilibrium simultaneously with respect to the three processes  $\text{water} \rightleftharpoons \text{steam}$ ,  $\text{ice} \rightleftharpoons \text{water}$ , and  $\text{ice} \rightleftharpoons \text{steam}$ , but only at  $0.0098^{\circ}\text{C}$  and 4.576 mm pressure, *i.e.*, neither the temperature nor the pressure can be chosen at will.

In a one-component system composition is clearly not one of the conditions affecting equilibrium. The only variables to be considered are temperature and pressure; whether both, only one, or neither of them be independently variable depends on the number of phases involved. The independent variables are usually referred to as the degrees of freedom of the system, *i.e.*, the quantities which must be stated in order to define the system. The terms invariant, univariant, bivariant, etc., are used to indicate the number of degrees of freedom. The relation between the number of phases and the variance of a one-component system is summarized in Table 1.2.

TABLE 1.2 DEGREES OF FREEDOM IN ONE-COMPONENT SYSTEMS

|                                   |   |   |   |
|-----------------------------------|---|---|---|
| Number of phases . . . . .        | 1 | 2 | 3 |
| Number of independent variables.. | 2 | 1 | 0 |

The properties of an aqueous solution of sodium sulfate are uniquely defined only when the temperature, the pressure, and the composition of the solution are stated. As long as the solution is the only phase involved these conditions can be varied independently. Three numbers are sufficient to define the state of this system: the temperature, the pressure, and the proportion of *one* of the components. In Table 1.1 composition was expressed in terms of two percentages, but once the components are stated only one need be specified, since the two must always total 100. In general, the number of composition variables requiring speci-

fication is *one less* than the number of components. In a system having  $C$  components, composition can be expressed in terms of  $C - 1$  of the components; for once the components are stated, the proportion of the unspecified one can be obtained by subtraction.

For the two-component system consisting of ice and an aqueous solution of sodium sulfate in equilibrium, only two of the three variables, temperature, pressure, and composition, are independent. At a pressure of 1 atm the freezing point of a 3% sodium sulfate solution (97% water) is fixed by nature at  $-0.84^{\circ}\text{C}$ . Similarly, the particular solution having the freezing point  $-1.0^{\circ}\text{C}$  at 1 atm has a composition fixed by nature at 3.5% sodium sulfate (96.5% water); and if one should wish to have an equilibrium between ice and a 1.00% sodium sulfate solution (99.00% water) at  $-0.29^{\circ}\text{C}$ , it would be possible at a pressure of 1 atm, but not at 2 atm. For a two-phase equilibrium in a two-component system there are, then, only two degrees of freedom. Any two of the variables may be chosen at will,<sup>1</sup> but the value of the third is dependent on the other two; it is, in fact, a *dependent* variable in the mathematical sense.

At a pressure of 1 atm, ice, Glauber's salt, and an aqueous solution of sodium sulfate can coexist in equilibrium with respect to the process of ice dissolving in and crystallizing from the solution, as well as with respect to the process of Glauber's salt dissolving in and crystallizing from the solution. However, at 1 atm this equilibrium can obtain only when the temperature is  $-1.10^{\circ}\text{C}$  and the composition of the solution is 3.85% sodium sulfate (96.15% water). If some other pressure were chosen, equilibrium among the three phases would still be possible; the temperature and the composition of the solution would be somewhat different, but their numerical values would be determined once the pressure was chosen. In this example the pressure is the only degree of freedom. It should be clear, however, that any one of the variables (temperature, pressure, or composition of the solution) can be made the independent one; but once the independent variable has been selected, the other two become dependent. For a three-phase equilibrium in a two-component system there is, therefore, only one degree of freedom.

<sup>1</sup> It should be clear that equilibrium between any number of specified phases will be possible only over a *range* of conditions. The fact that this range is finite in no way invalidates the arguments set forth here.

In addition to the three phases, ice, Glauber's salt, and solution, which can exist in equilibrium with respect to the processes enumerated above, it is possible to have a fourth phase involved, namely water vapor. The additional processes would be water vapor dissolving in and being liberated from the solution and  $\text{ice} \rightleftharpoons \text{water vapor}$ . There would be no degrees of freedom in this four-phase equilibrium, however, since the pressure exerted by the water vapor (the common vapor pressure of the solution and the ice) would be fixed by nature. The dependence of the variance of a two-component system on the number of phases is given in Table 1.3.

TABLE 1.3 DEGREES OF FREEDOM IN TWO-COMPONENT SYSTEMS

|                                      |   |   |   |   |
|--------------------------------------|---|---|---|---|
| Number of phases.... .               | 1 | 2 | 3 | 4 |
| Number of independent variables. . . | 3 | 2 | 1 | 0 |

It can be seen from Table 1.2 that for a one-component system the sum of the number of phases  $\mathcal{P}$  and the number of degrees of freedom  $\mathcal{F}$  is always equal to 3. For a two-component system it can be seen from Table 1.3 that  $\mathcal{P} + \mathcal{F}$  is always equal to 4. In both cases it is seen that  $\mathcal{P} + \mathcal{F} = \mathcal{C} + 2$ , an equation that has been shown to be valid for systems at equilibrium having any number of components; it is usually written in the form  $\mathcal{F} = \mathcal{C} + 2 - \mathcal{P}$ . This expression is the *phase rule*. The number 2 arises from the two variables, temperature and pressure.

While the form of the phase rule has been developed here with reference to only two systems, its applicability is perfectly general for any case of heterogeneous equilibrium. Since the phase rule has never been found to be in disagreement with experiment, it can be accepted as one of those laws of nature which, by the scientific method, are established through inductive reasoning. The first and second laws of thermodynamics have been established in the same way. Because of their comprehensive nature Gibbs was able to deduce the phase rule from them.<sup>1</sup> In the chapters that follow, the phase rule will be used as a basis for the discussion of heterogeneous equilibria in a wide variety of systems. It not only predicts the number of degrees of freedom in any given system, but also the maximum number of phases which can participate in

<sup>1</sup> A derivation is given in Appendix I.

equilibrium; since  $\mathfrak{F}$  cannot be less than zero, the maximum number of phases which can participate in equilibrium will be  $\mathfrak{C} + 2$ .

### EXERCISES

1. State whether or not equilibrium could exist among the phases in the following sets:

- a. Water and solid sodium chloride
- b. Solid sodium chloride and an aqueous solution of sodium chloride
- c. Solid sodium chloride and a liquid solution consisting of sodium chloride, copper sulfate, and water
- d. Water vapor and an aqueous solution of sodium chloride
- e. Water vapor and Glauber's salt
- f. Water vapor, Glauber's salt, and anhydrous sodium sulfate
- g. Glauber's salt and anhydrous sodium sulfate

For those sets in which equilibrium is possible, state the process or processes with respect to which there could be equilibrium.

2. Ammonium chloride vaporizes on being heated. State the number of components in a system consisting of solid ammonium chloride and its vapor. Would the number of components be changed by admitting ammonia gas from a cylinder? Would the number of phases be altered? Would an equilibrium still be possible?

3. At elevated temperatures calcium carbonate can exist in equilibrium with its dissociation products:  $\text{CaCO}_3(\text{solid}) \rightleftharpoons \text{CaO}(\text{solid}) + \text{CO}_2(\text{gas})$ . State the number of phases and the number of components in this system. Would the number of components be changed by admitting carbon dioxide from a cylinder? Would the number of phases be altered?

## CHAPTER 2

### ONE-COMPONENT SYSTEMS

#### 2.1 Polymorphism and Isomerism

Pure substances of the same elementary composition can be classed as polymorphs<sup>1</sup> or as isomers.<sup>2</sup> They are classed as polymorphs of one another if they give rise to the same solid, liquid, or gas by simple phase transitions. For example, there are several crystalline modifications of ice known, but all of these are convertible, one to the other, by simple phase transitions; they all give rise to the same liquid, water, and to the same vapor, steam. These various forms of ice are therefore polymorphs of the pure substance water. Solid polymorphs are distinguished by difference in crystalline form, density, refractive index, solubility, and other properties. Since all vapors and most liquids are amorphous,<sup>3</sup> the term polymorphs is not always extended to include them. No pure substance is known to exist in more than one vapor phase. A few pure substances are known to exist in more than one liquid phase; those which show some regularity of structure are referred to as "liquid crystals."

Pure substances of the same elementary composition which do *not* give rise to a common phase by simple phase transition are classed as isomers, *e.g.*, the structural isomers butane and isobutane, ethanol and dimethyl ether; the geometrical isomers *cis*- and *trans*-butene-2; the optical isomers *d*- and *l*-tartaric acid. This class also includes those polymeric<sup>4</sup> forms which cannot be classed as polymorphs, *e.g.*, acetylene and benzene, styrene and polystyrene, formaldehyde and trioxane. Polymerism is a special case of isomerism arising from the concept of molecular weight, a concept which plays no part in distinguishing isomers from polymorphs.

<sup>1</sup> From *polys*, many, and *morphe*, form.

<sup>2</sup> From *isos*, equal, and *meros*, parts.

<sup>3</sup> From *a*, negative, and *morphe*, form.

<sup>4</sup> From *polys*, many, and *meros*, parts.

In the case of elements the term allotropes<sup>1</sup> is applied to both polymorphs and isomers, regardless of whether one form can be turned into another by simple phase transition. The allotropes rhombic and monoclinic sulfur are polymorphic; the allotropes oxygen and ozone are not. For compounds the term "allotropes" is synonymous with "polymorphs."

The treatment of one-component systems concerns the simple phase transitions among polymorphs. The only conditions affecting equilibrium among polymorphs are temperature and pressure. These two parameters are conventionally represented as the coordinates of a diagram with mutually perpendicular axes. Such a diagram is used to present, in graphical form, information about freezing points, boiling points, vapor pressures, and transition temperatures of pure substances (elements or compounds).

## 2.2 The Freezing Point of Water

The freezing point of water is the temperature at which ice and water can exist in equilibrium with respect to the process of ice turning into water and water turning into ice. The effect of pressure on the freezing point is shown in Table 2.1. It should

TABLE 2.1 FREEZING POINTS OF WATER ( $\rightleftharpoons$  ICE I)

| Pressure           | Freezing point, °C |
|--------------------|--------------------|
| 5 mm. . . . .      | + 0.0098           |
| 760 mm . . . . .   | + 0.0023           |
| 590 atm . . . . .  | - 5.00             |
| 1090 atm. . . . .  | - 10.00            |
| 1540 atm . . . . . | - 15.00            |
| 1910 atm . . . . . | - 20.00            |

be noted that the freezing point of water at 1 atm is *not* zero on the centigrade scale; on this scale zero has been defined as the temperature at which ice can exist in equilibrium with water saturated with air at 1 atm pressure. The liquid is then not pure water, but a solution, and its freezing point has been found to be 0.0023° lower than that of pure water. The accuracy of most freezing-point determinations is such that the effect of dissolved air can be neglected.

It is seen from Table 2.1 that increase of pressure lowers the

<sup>1</sup> From *allos*, another, and *tropos*, condition.

freezing point of water; this is true for any liquid which *expands* on freezing. If the specific volume of the solid is *less* than that of the liquid (*e.g.*, benzene), the freezing point is raised with increase of pressure.

That the foregoing statements are correct can be made clear by considering the following cases. At 0°C and 1 atm pressure a mixture of ice and water will be at equilibrium. If this temperature is maintained constant while the pressure is increased to, say, 10 atm, the ice will all melt, in keeping with the fact that an increase in pressure on a system in equilibrium can only result in the process which leads to a decrease of volume. However, if at this new pressure the temperature is lowered, ice can be made to form again (an exothermic process) and to participate in a new equilibrium with water at the lower temperature. Clearly an increase of pressure lowers the freezing point of water. On the other hand, if the pressure on a system consisting of liquid and solid benzene in equilibrium is increased, the liquid benzene will solidify (with a consequent decrease in the volume of the system) and at this new pressure liquid can only be made to form again (an endothermic process) by increasing the temperature. Thus it is seen that the freezing point of benzene is raised by an increase in pressure.

### 2.3 Determination of Freezing (Melting) Points of Pure Substances

From the phase rule it is clear that at a specified pressure the solid and liquid forms of a pure substance (one component) can exist in equilibrium only at a definite temperature fixed by nature. Since this is true regardless of the amounts of the two phases present, it is clear that pure substances must have “*sharp*” freezing or melting points, *i.e.*, the temperature of the system must remain constant throughout the freezing or melting process, under equilibrium conditions. The “sharpness” of the freezing or melting temperature is frequently taken as a criterion of purity; if the temperature of a system varies continuously throughout the process of phase transition, the system is obviously not one-component.<sup>1</sup> This criterion must be applied with caution, first since

<sup>1</sup> Variation of temperature during phase transitions in two-component systems will be treated in Chapter 3.

the effect of impurities may be small, and secondly since poly-component systems of certain compositions are known to have sharp melting points. Melting points of compounds at atmospheric pressure are frequently used for purposes of identification, particularly by the organic chemist. Melting and freezing points are also widely used as fixed points in thermometry.

While in general liquids can be cooled below their freezing points (undercooled), it is a peculiarity of solids that almost without exception they cannot be heated above their melting points (superheated). For one-component systems the temperature obtained from a freezing-point determination must obviously be the same as that obtained from a melting-point determination. Freezing points are commonly determined by cooling the liquid and following the temperature of the system through its phase transition. A typical cooling curve for a pure substance is shown in Figure 2.1. Solidification starts in the undercooled liquid at *a*; with the liberation of latent heat the temperature rises to *b*, remains constant until solidification is complete at *c*, and then falls. The temperature corresponding to the interval *bc* is the freezing point. If the system is not one-component, *i.e.*, if impurities are present, cooling will give rise to a curve such as that shown in Figure 2.2. Here the portion *bc* is not horizontal and hence the solidification of the main constituent is seen to occur over a "freezing range." The length of the time interval *bc* in both figures depends on the rate of heat removal and the latent heat of solidification. Pronounced undercooling, *e.g.*, to *a'*, may shorten this interval to such an extent that an accurate determination is not possible. Freezing-point determinations are difficult in the case of substances which have small latent heats of solidification or which show pronounced undercooling, or if the amount of sample is small.

In determining *melting points*, curves such as shown in Figures 2.3 and 2.4, respectively, are found for pure substances and those containing small amounts of impurities. The latter shows a "melting range." The interpretation of Figures 2.2 and 2.4 rests on the consideration of two-component systems, to be treated in Chapter 3.

If the specific latent heat of solidification is small or if the chemist has a limited amount of material for the determination, it is preferable to place the substance in a bath having a relatively high heat capacity. The bath is slowly cooled or heated and the bath

temperature noted during the phase transition. Solidification or liquefaction is usually accompanied by a marked change of such properties as volume, electrical resistance, optical transmission, etc. The choice of a property to indicate phase change will depend on the particular nature of the system. The organic chemist frequently makes use of an apparatus such as that shown in Figure 2.5. A small portion of material is placed in a thin-walled capil-

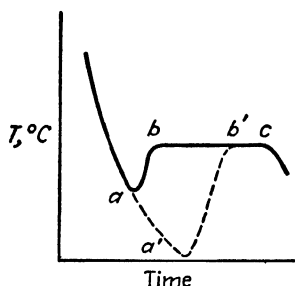


FIG. 2.1 Freezing curve for a pure substance.

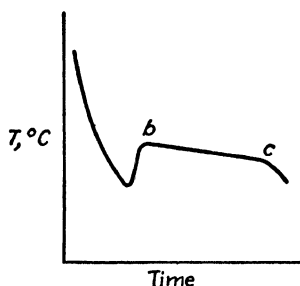


FIG. 2.2 Freezing curve for an impure substance.

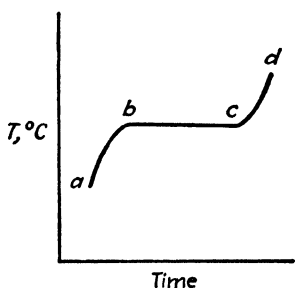


FIG. 2.3 Melting curve for a pure substance.

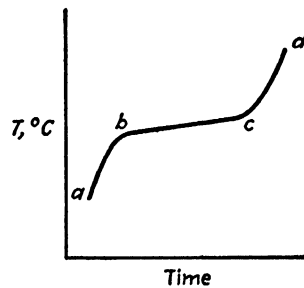


FIG. 2.4 Melting curve for an impure substance.

lary tube which is attached to a thermometer and immersed in a bath as shown. The bath is heated *slowly* and its temperature noted when melting occurs. If the bath is heated too rapidly an *apparent* melting range will be obtained even for a pure substance. Reducing the rate of heating will not diminish a *true* melting range.

## 2.4 Determination of Vapor Pressures of Pure Substances

The vapor pressure of a substance is the pressure of its vapor at which there can be equilibrium with respect to the process of

the substance vaporizing and condensing from the vapor. To ensure that equilibrium obtains, measurements can be made with an apparatus similar to that shown in Figure 2.6. The closed limb  $T$  of the manometer is first evacuated by lowering the mercury-leveling bulb  $L$  and exhausting through  $S$ . The leveling bulb is then raised to the position shown (leaving a Torricellian vacuum in  $T$ ). The pump is temporarily disconnected from  $S$  and the liquid or solid substance introduced into  $B$ . The system is

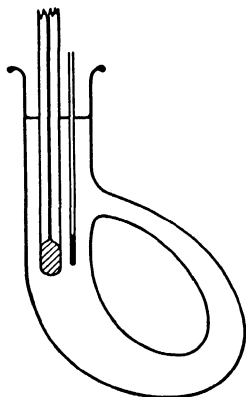


FIG. 2.5 Thiele-Dennis melting-point apparatus.

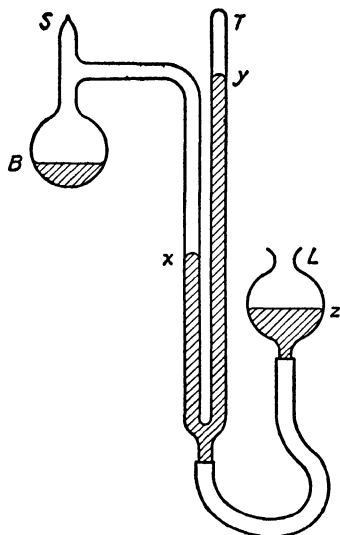


FIG. 2.6 Apparatus for determining the vapor pressure of a pure substance.

again pumped down to remove air and sealed off at  $S$ . For precise determinations it is necessary to remove all dissolved or trapped gases from the substance as well as from the manometer. The bulb  $B$  is maintained at the desired temperature; to avoid distillation the manometer must be maintained at a temperature higher than that of the bulb. The pressure of the vapor is given by the difference in levels  $y - x$ , regardless of changes in atmospheric pressure,  $y - z$ . If the substance and its vapor were in equilibrium,  $y - x$  would be its vapor pressure and should be independent of the volume of the system. On raising the leveling bulb  $L$  the volume of the system is decreased and vapor will condense;

on lowering the leveling bulb the substance will vaporize. If after each of these operations the value of  $y - x$  is unchanged, it is clear that this is the pressure at which there is equilibrium with respect to the process of vaporization and condensation.

Vapor-pressure determinations are sometimes made by the "flow" method, in which dry air is passed very slowly over the surface of the substance. The vapor content of the effluent gas is determined by analysis. If equilibrium were reached during the passage of air over the material the vapor pressure could be calculated from the volume of the effluent gas and its vapor content (partial pressure). However, the vapor content may be lower than that corresponding to equilibrium, or higher if spray is present.

The rate of evaporation is sometimes used to estimate the vapor pressure of relatively nonvolatile substances such as tungsten and platinum. It is assumed that under equilibrium conditions the rate at which molecules evaporate from a unit surface is equal to the rate at which vapor molecules strike this surface. From kinetic theory the latter quantity can be calculated in terms of the pressure of the vapor. In practice the rate of evaporation is calculated from the decrease in weight of the material when evaporated at constant temperature. Clearly the rate of evaporation is not measured under equilibrium conditions. Nevertheless vapor pressures have been estimated by equating the measured rate of evaporation with the theoretical expression for the rate of collision and solving the resulting equation for the pressure of the vapor.

It has been emphasized that equilibrium must refer to a particular process. Although water cooled below its freezing point is unstable with respect to the process of water turning into ice and ice turning into water, the undercooled water can exist in equilibrium with water vapor with respect to the process of water forming vapor and vapor forming water. Stability and instability, as well as equilibrium, must be stated with respect to a particular process. The term "metastable" is applied to a phase which is unstable with respect to the formation of another (more stable) phase, although it may be stable with respect to other processes.

The vapor pressure of a metastable phase must be greater than that of the more stable phase of the same composition. This can be demonstrated by the following experiment. The phases are placed in separate bulbs joined by a stopcock. All residual air is

removed and the bulbs are maintained at the same temperature. With the stopcock closed, the equilibrium pressures of the vapor will be different in the two bulbs. On opening the stopcock, vapor will pass from the region of high pressure to that of low pressure. The phase having the higher vapor pressure will evaporate and that having the lower vapor pressure will condense, until the phase of higher vapor pressure has vanished. The spontaneous process is the formation of the more stable phase, *i.e.*, the one with the lower vapor pressure. It is seen from Table 2.2 that the vapor pressure of undercooled water is always greater than that of ice at the same temperature.

TABLE 2.2 VAPOR PRESSURES

| TEMPERATURE,<br>°C | VAPOR PRESSURE,<br>mm | DENSITY OF SATURATED<br>VAPOR, g/cc. |
|--------------------|-----------------------|--------------------------------------|
| Ice                |                       |                                      |
| -15                | 1.241                 | $1.39 \times 10^{-6}$                |
| -10                | 1.950                 | $2.14 \times 10^{-6}$                |
| -5                 | 3.013                 | $3.25 \times 10^{-6}$                |
| Water              |                       |                                      |
| -15                | 1.436                 | $1.61 \times 10^{-6}$                |
| -10                | 2.149                 | $2.36 \times 10^{-6}$                |
| -5                 | 3.163                 | $3.42 \times 10^{-6}$                |
| 0                  | 4.579                 | $4.85 \times 10^{-6}$                |
| 20                 | 17.535                | $1.73 \times 10^{-5}$                |
| 25                 | 23.756                | $2.30 \times 10^{-5}$                |
| 50                 | 92.51                 | $8.32 \times 10^{-5}$                |
| 100                | 760.00                | $5.98 \times 10^{-4}$                |
| 200                | 11,659                | $7.84 \times 10^{-3}$                |
| 300                | 64,433                |                                      |
| 374                | 165,467               | $4.0 \times 10^{-1}$                 |

The familiar fact that vapor pressures of both solids and liquids increase with rise of temperature is in keeping with the general principles of equilibrium. An increase in the temperature of a system consisting of a condensed phase and its vapor initially in equilibrium will result in the complete vaporization of the condensed phase (an endothermic process). At the higher temperature the condensed phase can be restored only by increasing the pressure, since the formation of the condensed phase corresponds

to a reduction in the volume of the system. Thus equilibrium at the higher temperature can be maintained only at increased pressure.

Vapor-pressure and freezing-point data for the water system are shown graphically in Figure 2.7.

## 2.5 Critical Temperature and Pressure

When a vessel containing only water and its vapor is heated, the pressure within the vessel rises very markedly, as indicated by the vapor-pressure data for water shown in Table 2.2. The properties of the water and of the steam are modified by the increase of temperature and pressure. The density of the water is lowered more

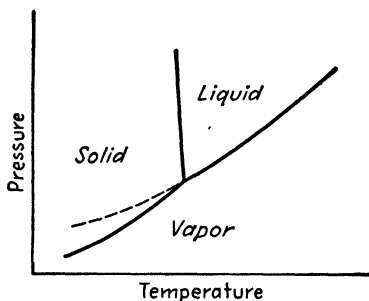


FIG. 2.7 Phase diagram for the system water. Both the temperature and pressure scales have been distorted.

by the increase of temperature than it is raised by the corresponding increase of pressure. The density of the *saturated* steam rises very rapidly with increase of temperature, as shown in Table 2.2, and approaches that of the water; in the same way other properties of the two phases approach one another. Since phases are distinguished by differences in their properties, it is conceivable that at sufficiently high temperatures (and pressures) the separate phases could not be distinguished and the system would become homogeneous. This is strikingly demonstrated by the *appearance* of the system in the vessel. The meniscus between the two phases, which is apparent only because of the difference in their refractive indices, gradually disappears as the temperature is raised and above  $360^{\circ}\text{C}$  is no longer visible. At  $374.0^{\circ}\text{C}$  the system becomes homogeneous in all its properties. This temperature, above which no distinction can be made between the properties of vapor

and liquid, is called the *critical temperature*. The corresponding vapor pressure, 217.7 atm in this case, is called the *critical pressure*. The critical point for a substance represents a termination of its vapor-pressure curve.

The peculiar nature of a fluid above its critical temperature and pressure can be illustrated by reference to the following operations. At 400°C and 1 atm pressure water exists as an unsaturated vapor. On removing heat at constant pressure<sup>1</sup> the temperature will decrease and at 100°C the vapor will become saturated. If equi-

TABLE 2.3 CRITICAL-POINT DATA

| SUBSTANCE                | CRITICAL TEMPERATURE, °C | CRITICAL PRESSURE, atm | DENSITY, g/cc |
|--------------------------|--------------------------|------------------------|---------------|
| Hydrogen.....            | -239.9                   | 12.8                   | 0.031         |
| Oxygen ...               | -118.8                   | 39.7                   | 0.430         |
| Water.. . . . .          | 374.0                    | 217.7                  | 0.4           |
| Ammonia .. . . . .       | 132.4                    | 111.5                  | 0.235         |
| Carbon dioxide.....      | 31.1                     | 73.0                   | 0.460         |
| Carbon monoxide.....     | -139                     | 35                     | 0.311         |
| Methane .. . . . .       | - 82.5                   | 45.8                   | 0.162         |
| Ethyl alcohol .. . . . . | 243.1                    | 63.1                   | 0.275         |
| Acetone .. . . . .       | 235.0                    | 47                     | 0.268         |
| Benzene .. . . . .       | 288.5                    | 47.7                   | 0.304         |
| Stannic chloride ...     | 318.7                    | 37.0                   | 0.742         |

librium obtains, further removal of heat will produce liquid water, resulting in a two-phase system. The temperature will remain constant at 100°C until all the vapor is liquefied. At this temperature the properties of the system undergo a marked change (discontinuity). Continued removal of heat will now lower the temperature and at, say, 50°C the system will consist of liquid water at 1 atm pressure. This same final state can be reached by an entirely different operation. Let the unsaturated vapor at 400°C and 1 atm be compressed isothermally to 300 atm, cooled to 50°C at this pressure, and then let the pressure be reduced isothermally to 1 atm. The final state of the system will be the same in both cases, yet in the second operation the system was at all times homogeneous (only one phase present) and at no time would there have occurred any discontinuity in its properties. It is obvious

<sup>1</sup> Constant pressure can be maintained by confining the system in a cylinder under a loaded piston, the weight of which determines the pressure.

that compression of a gas above its critical temperature cannot produce a saturated vapor and therefore cannot cause liquefaction. The critical temperatures, pressures, and densities of a number of substances are given in Table 2.3.

## 2.6 Boiling Points of Pure Substances

The boiling point of a substance is the temperature at which there can be equilibrium with respect to the process of the substance vaporizing from its liquid and liquefying from its vapor. The equilibrium process is precisely the same as that involved in the definition of vapor pressure. A one-component system consisting of two phases in equilibrium has but one degree of freedom, either the temperature or the pressure. If the former is the chosen parameter, the other is called the vapor pressure; if the pressure is chosen, the corresponding temperature is called the boiling point. The *normal* boiling point is the boiling point at a pressure of 760 mm.

Boiling points of pure substances are usually determined by observing the temperature at which liquid condenses on the bulb of a thermometer suspended above the gently boiling liquid. While the temperature observed may not correspond exactly with equilibrium conditions, it is usually precise enough to identify the substance or to indicate its purity. That the boiling point rises with increase of pressure is a corollary of the fact that the vapor pressure increases with temperature.

## 2.7 Sublimation Temperature

Sublimation is the process by which a solid changes directly into its vapor without the intermediate formation of liquid. The sublimation point is the temperature at which there can be equilibrium with respect to the process of the solid subliming to form vapor and the vapor condensing to form the solid. The sublimation point bears the same relationship to the vapor pressure of a solid as the boiling point bears to the vapor pressure of a liquid. Thus the sublimation point of ice at 1.95 mm pressure is  $-10^{\circ}\text{C}$  (see Table 2.2).

## 2.8 Triple Points for the System Water

So far there have been discussed three different processes with respect to which the system water can exist in equilibrium, *viz.*,

ice  $\rightleftharpoons$  water, water  $\rightleftharpoons$  steam, and ice  $\rightleftharpoons$  steam. In each case only two phases were involved. Either the temperature or the pressure can be chosen as the independent variable and the relations between them shown graphically as lines on a  $T$ - $P$  diagram. The maximum number of phases which can exist in equilibrium in this system is three ( $C + 2 = 3$ ). Neither the temperature nor the pressure at which such an equilibrium can exist admits of choice. Ice, water, and steam can coexist in equilibrium with respect to the three processes mentioned above at  $0.0098^\circ\text{C}$  and  $4.58$  mm pressure. This is a *triple point*; it is the intersection of the fusion, boiling, and sublimation curves of Figure 2.7. At high pressures ice can exist in several different crystalline forms. Equilibria involving these phases give rise to transition curves and the triple points listed in Table 2.4.

TABLE 2.4 TRIPLE POINTS FOR THE SYSTEM WATER

| PHASES               | TEMPERATURE, $^\circ\text{C}$ | PRESSURE, atm |
|----------------------|-------------------------------|---------------|
| Steam-water-ice I*   | 0.0098                        | 0.00602       |
| Water-ice I-ice III  | -22.0                         | 2045          |
| Water-ice III-ice V  | -17.0                         | 3420          |
| Water-ice V-ice VI   | 0.16                          | 6175          |
| Ice I-ice II-ice III | -34.7                         | 2100          |
| Ice II-ice III-ice V | -24.3                         | 3400          |

\* Ice I is ordinary ice.

## 2.9 The System Sulfur

Sulfur can exist in several polymorphic forms. The equilibrium relationships among the vapor, liquid, and the rhombic and monoclinic crystalline forms are shown in Figure 2.8. The pressure scale has been purposely distorted to avoid loss of detail at the lower pressure. The  $L$ - $V$  curve is the vapor-pressure curve for liquid sulfur; the  $M$ - $V$  curve is the vapor-pressure curve for the monoclinic form of solid sulfur; the  $M$ - $L$  curve shows the effect of pressure on the melting point of the monoclinic form. The  $M$ - $L$  curve has a positive slope since the density of the solid is greater than that of the liquid. The three curves intersect at the triple point 1 ( $119.3^\circ\text{C}$ ,  $0.04$  mm). This portion of the diagram is analogous to that for the system water (Figure 2.7). As in the case of ice, the normal melting point (at atmospheric pressure) differs only slightly from the temperature of the triple point. The

dotted extension of the  $L$ - $V$  curve represents the vapor pressure of the liquid in the metastable (undercooled) condition.

The  $R$ - $V$  curve represents the vapor pressure of solid sulfur in the rhombic form and intersects the  $M$ - $V$  curve at point 2. To the left of point 2, the extension of the  $M$ - $V$  curve lies above the  $R$ - $V$  curve, indicating that at temperatures below point 2 the  $M$ - $V$  equilibrium is metastable as compared with the  $R$ - $V$  equilibrium (cf. Section 2.4). At the triple point 2 (95.6°C, 0.01 mm) the rhombic and monoclinic forms and the vapor can coexist in equilibrium. The effect of pressure on the rhombic-monoclinic transition temperature is shown by the curve  $R$ - $M$ . The slope of this curve is in agreement with the facts that the density of the rhombic

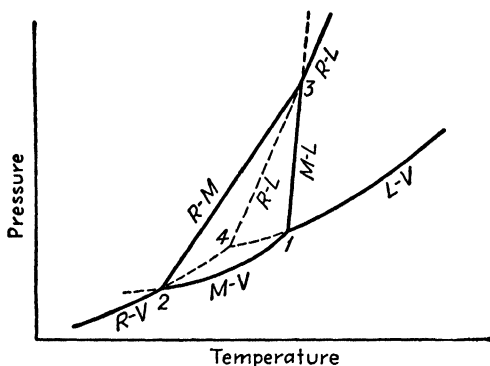


FIG. 2.8 Phase diagram for the system sulfur.

form is greater than that of the monoclinic and that the transition of rhombic to monoclinic is endothermic. The  $R$ - $M$  and  $M$ - $L$  curves intersect at the point 3 (151°C, 1288 atm); this is a triple point since at this temperature and pressure the rhombic and monoclinic forms and the liquid can coexist in equilibrium. The point 3 is common not only to the  $R$ - $M$  and  $M$ - $L$  curves, but also to a third curve  $R$ - $L$ , which shows the effect of pressure on the melting point of the rhombic solid.

In addition to the three triple points  $L$ - $V$ - $M$ ,  $V$ - $M$ - $R$ , and  $M$ - $R$ - $L$  it might be expected that with four polymorphic forms ( $L$ ,  $V$ ,  $M$ ,  $R$ ) chosen three at a time there would be a fourth triple point,  $R$ - $L$ - $V$ . This is shown as point 4 (114.5°C, 0.03 mm); it is the intersection of the metastable extensions of the  $L$ - $V$  and  $R$ - $V$  curves. Point 4 must also be common to the  $R$ - $L$  curve. At

point 4 the three phases vapor, liquid, and rhombic sulfur are all metastable with respect to the formation of the monoclinic form; point 4 is therefore a *metastable triple point*.

In Figure 2.8 certain curves are shown as solid lines to indicate that the equilibria concern stable phases. The dotted extensions of these solid lines beyond triple points indicate equilibria between metastable phases. It is evident that some extensions have been omitted. These omissions are consonant with the experiences that (1) in general, solids cannot be superheated with respect to the formation of liquid or vapor and (2) equilibria involving liquids or solids cannot be investigated unambiguously at pressures below their vapor pressures. Therefore the curve  $M-L$  is not extended below 1;  $M-V$  not above 1;  $R-M$  not below 2 nor above 3;  $R-L$  not below 4;  $R-V$  not above 4.

It has already been shown that at any particular temperature the vapor pressure of a metastable phase is greater than that of a more stable phase. It can also be shown that at any particular pressure the melting point of a metastable solid is less than that of a more stable solid. For example, if rhombic sulfur (m.p.  $114.5^{\circ}\text{C}$ ) is added to liquid sulfur maintained at, say,  $117^{\circ}\text{C}$  and 1 atm, it will melt. Since the resulting liquid would be undercooled with respect to the formation of monoclinic sulfur (m.p.  $119.3^{\circ}\text{C}$ ), the addition of even a small crystal of this latter form can bring about complete transformation to the monoclinic solid. The over-all result of these processes would be the spontaneous conversion of rhombic to monoclinic sulfur. Clearly under these conditions the rhombic is the metastable form. In general it can be seen that, at any pressure, the solid having the lower melting point must be the metastable form at that pressure. Above 1288 atm the melting point of monoclinic sulfur is lower than that of the rhombic and hence monoclinic is the metastable form. Thus the portion of the  $M-L$  curve above point 3 is dotted.

## 2.10 The System Phosphorus

The known polymorphic forms of solid phosphorus include a red ( $R$ ), a black, and two white varieties ( $\alpha$  and  $\beta$ ); the red form and the white form of higher melting point ( $\alpha$ ) are the most familiar. The equilibrium relationships for phosphorus are indicated in Figure 2.9. As in the case of the diagrams for sulfur and water, the temperature and pressure scales have been distorted.

The  $R$ - $L$ - $V$  triple point, 1 (589°C, 43.1 atm), is analogous to the  $M$ - $L$ - $V$  triple point of Figure 2.8. The liquid is pale yellow in color; its vapor pressure has been investigated in the undercooled state as low as 504°C (23.2 atm). The solid  $\alpha$  melts to a pale-yellow liquid; its vapor pressure has been investigated up to 409°C (7.36 atm); at higher temperatures vapor-pressure determinations are complicated by the formation of the red solid, which occurs with great rapidity. However, extrapolation of the two liquid-vapor curves over the range 409 to 504°C yields a common  $L$ - $V$  curve without discontinuity. Thus molten red and molten  $\alpha$  phosphorus are not different liquids, but comprise a single form.

The determination of the vapor pressure of red phosphorus is difficult, for while it can be vaporized readily, the vapor on being cooled generally forms the  $\alpha$  solid. At first sight this might appear to indicate that the  $\alpha$  form is the more stable solid. However, the process concerned here is not the direct conversion of solid red to solid  $\alpha$ , but rather the vaporization of the solid red, followed by the metastable formation of solid  $\alpha$  from the vapor. If the direct conversion of solid red to solid  $\alpha$  were to occur spontaneously, it would indicate the  $\alpha$  to be the more stable solid; actually a mixture of red and  $\alpha$  solids will ultimately change completely to the red form, although the process is extremely slow. This is in agreement with the facts that the vapor pressure of the red solid is less than that of the  $\alpha$  form at the same temperature and that the melting point of the  $\alpha$  form (44.1°C) is considerably lower than that of the red.

The  $R$ - $V$  and  $\alpha$ - $V$  curves do not intersect below the  $L$ - $V$  curve, and thus cannot give rise to a triple point  $R$ - $\alpha$ - $V$  below the  $L$ - $V$  curve. Extrapolation of the  $R$ - $V$  and  $\alpha$ - $V$  curves above the points 1 and 2 might give rise to an intersection, but the conditions necessary for a triple point are not realizable, since this would entail the existence of solids above their melting points. Solid polymorphs are said to be "monotropic" if their vapor-pressure curves do not intersect, *i.e.*, if they cannot exist in equilibrium with a common vapor. The term "monotropic"<sup>1</sup> is unfortunate since it might be taken to indicate that one form is always stable with respect to the other. This is not necessarily the case, for there may exist a triple point involving the two solids and the liquid form. For

<sup>1</sup> From *monos*, single, and *tropos*, condition.

example, there is no a priori reason why the  $R$ - $L$  and  $\alpha$ - $L$  curves of phosphorus should not intersect at very high pressures, in which case the monotropic forms  $R$  and  $\alpha$  could coexist in stable equilibrium. Equilibrium between monotropic forms has indeed been observed at high pressures in several cases, *e.g.*, in the systems carbon dioxide and tertiary butyl alcohol.

The monotropic relationship between  $\alpha$  and red phosphorus is in contrast to the relationship between the  $\alpha$  and  $\beta$  forms. Here the vapor-pressure curves  $\alpha$ - $V$  and  $\beta$ - $V$  intersect at a realizable triple point 3 and hence the  $\alpha$  and  $\beta$  forms are said to be *enantiotropic*<sup>1</sup> with respect to one another, although they are both monotropic

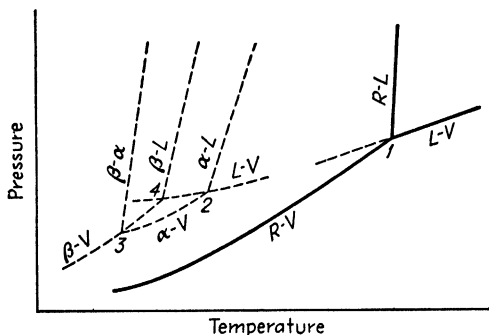


FIG. 2.9 Phase diagram for the system phosphorus.

with respect to the red form. Point 3 is also the origin of an  $\alpha$ - $\beta$  transition curve which has been determined experimentally.

In the sulfur system (Figure 2.8) the liquid, the vapor, and the two enantiotropes, rhombic and monoclinic sulfur, give rise to four triple points. In the case of the phosphorus system, the liquid, the vapor, and the enantiotropic forms  $\alpha$  and  $\beta$  give rise to only three realizable triple points, 2 ( $\alpha$ - $V$ - $L$ ), 3 ( $\alpha$ - $\beta$ - $V$ ), and 4 ( $\beta$ - $V$ - $L$ ). The  $\beta$ - $\alpha$ ,  $\beta$ - $L$ , and  $\alpha$ - $L$  curves appear to converge only at pressures lower than the vapor pressures of the phases concerned and hence the fourth conceivable triple point ( $\alpha$ - $\beta$ - $L$ ) is not realizable.

## 2.11 The System Menthol

This system provides an interesting example of the general rule that the melting points of metastable polymorphs are lower than

<sup>1</sup> From *enantios*, opposite, and *tropos*, condition.

the melting point of the stable form. Four solid polymorphic modifications of menthol have been studied:  $\alpha$  (m.p. 42.5°),  $\beta$  (m.p. 35.5°),  $\gamma$  (m.p. 33.5 to 34.0°),  $\delta$  (m.p. 31.5°C). The spontaneous transitions  $\beta \rightarrow \alpha$ ,  $\gamma \rightarrow \alpha$ , and  $\delta \rightarrow \alpha$  have been observed; this indicates that  $\alpha$  is the most stable form. The spontaneous transition of  $\delta$  to  $\beta$  has also been observed, which indicates that the  $\beta$  is more stable than the  $\delta$  form. While the spontaneous transitions  $\delta \rightarrow \gamma$  and  $\gamma \rightarrow \beta$  were not observed, it would be predicted from the melting-point rule that the reverse processes,  $\gamma \rightarrow \delta$  and  $\beta \rightarrow \gamma$ , would *not* occur spontaneously.

## 2.12 The System Tin

At room temperature and pressure the stable form of tin is the ordinary white variety,  $\beta$ , tetragonal crystals of specific gravity 7.2. Below 19°C the stable form is "gray tin,"  $\alpha$ , cubic crystals of specific gravity 5.8. It is fortunate that the transition from the  $\beta$  to the  $\alpha$  form is extremely slow, otherwise the magnitude of the accompanying expansion would preclude the use of tin as a protective coating. If white tin is maintained below 19°C for a long time, however, the transition to gray tin can be effected; this phenomenon is sometimes referred to as the "tin plague." There is a third polymorph of tin,  $\gamma$ , having a rhombic structure and a specific gravity of 6.5; this is the stable form of tin between 161°C and the melting point, 232°C. The transitions  $\alpha \rightleftharpoons \beta$  and  $\beta \rightleftharpoons \gamma$  are reversible and hence  $\alpha$ ,  $\beta$  and  $\beta$ ,  $\gamma$  are enantiotropic pairs.

## 2.13 The System Silica

Silica exists in a variety of polymorphic forms. The stable form at room temperature is called *low*, or  $\alpha$ , quartz; this undergoes a transition to *high*, or  $\beta$ , quartz at 573°C. High quartz is the stable form from 573 to 870°C, at which temperature it can undergo a transition to upper high tridymite. This is the stable form between 870 and 1470°C; at this latter temperature the upper high tridymite can undergo a transition to high cristobalite, which is stable up to its melting point, 1710°C. The transitions quartz  $\rightleftharpoons$  upper high tridymite and upper high tridymite  $\rightleftharpoons$  high cristobalite usually occur very slowly, so that both high quartz and upper high tridymite can be heated above their range of stability. As would be predicted from the relation of melting point to stability, high

quartz and upper high tridymite have melting points below that of cristobalite; 1670°C is the melting point of upper high tridymite, while that of high quartz has been reported as less than 1470°C.

While certain of the polymorphic transitions are sluggish, as pointed out above, others are relatively rapid. The former are associated with major changes in crystalline form, the latter with slight modifications of structure. The transition low quartz  $\rightleftharpoons$  high quartz is relatively rapid; on this account the high quartz is not known at ordinary temperatures. If upper high tridymite is undercooled with respect to the formation of quartz, it will undergo a relatively rapid inversion at 163°C to form lower high tridymite, which in turn will undergo a relatively rapid inversion to low tridy-

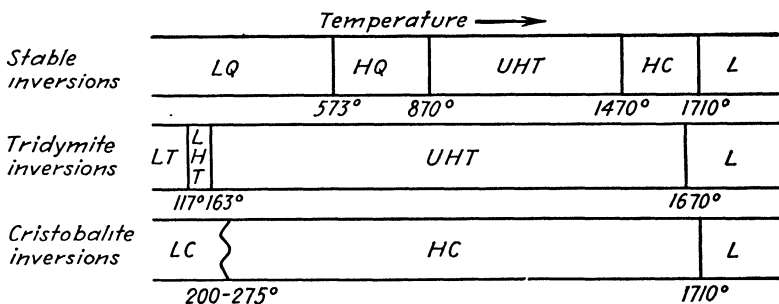


FIG. 2.10 Inversion (transition) temperatures in the system silica.

mite at 117°C. This last form is found at ordinary temperatures, but the high tridymites are not. Although the low tridymite is metastable with respect to the formation of low quartz at ordinary temperatures, it is commonly found in nature because the spontaneous transition is so slow. High cristobalite undergoes a relatively rapid inversion to low cristobalite in the temperature range 200 to 275°C; as with low tridymite, the low cristobalite is metastable with respect to the formation of low quartz at ordinary temperatures. The inversion temperature of the cristobalite depends quite markedly on the particular sample and its history. This is true within narrower ranges for the other high-low inversions.

During high-low inversions the properties of the system change *continuously* over small ranges of temperature, very small for the quartz inversion, a few degrees for the tridymite inversions, and as much as 75° for the high-low cristobalite inversion. The fur-

ther fact that the properties at a given temperature differ, depending on whether the system had been heated or cooled, makes suspect the classification of these forms as enantiotropes. It may be that isomeric forms exist and that these can participate in homogeneous equilibrium. If such were the case the system would be poly-component in the range of hysteresis.

A form of silica commonly encountered at ordinary temperatures is vitreous silica, which is widely used in optical equipment and for high-temperature ware. It is actually undercooled liquid silica, but its very high viscosity makes it appear solid. In Figure 2.10 the inversion temperatures in the system silica are shown schematically.

### EXERCISES

1. Classify the following pairs of substances as polymorphs or isomers:
  - a. Benzene and acetylene
  - b. Red and  $\alpha$  phosphorus
  - c.  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$
  - d. Oxygen and ozone
2. The density of white ( $\beta$ ) tin is 7.2, that of gray ( $\alpha$ ) tin is 5.8. The former is stable above  $19^\circ\text{C}$ , the latter below  $19^\circ\text{C}$ . Will the  $\alpha \rightleftharpoons \beta$  transition temperature be raised or lowered by an increase in pressure? Give your reasons.
3. At atmospheric pressure the melting point of  $\alpha$  menthol is  $42.5^\circ\text{C}$  and that of  $\beta$  menthol is  $33.5^\circ\text{C}$ . From fundamental principles prove which is the stable form of the solid at  $33.5^\circ\text{C}$  and which solid would have the higher vapor pressure at this temperature.
4. Red phosphorus has a higher melting point than yellow ( $\alpha$ ) phosphorus and the reversible transition  $\text{red} \rightleftharpoons \alpha$  does not occur. Show by argument that this information is sufficient to predict a higher solubility for the  $\alpha$  form in any given solvent.

## CHAPTER 3

### TWO-COMPONENT SYSTEMS

A two-component system is one for which two constituents are necessary and sufficient to describe the compositions of all phases involved. Once the components are selected only three numbers are required to specify the state of any phase, namely the temperature, the pressure, and the proportion of either of the components. The state of any phase can be represented on a diagram having three mutually perpendicular axes. Three-dimensional diagrams are, however, difficult to represent on a plane surface such as the page of a book. It is more convenient to fix one of the three quantities, specify its value, and represent the state of the phases on a two-dimensional diagram. Inasmuch as systems of fixed composition belong to the class of one-component systems, the parameter fixed is either the temperature (isothermal diagram) or the pressure (isobaric diagram). Such a diagram is used to present in graphical form information about solubilities, freezing points, boiling points, vapor pressures, transition temperatures, and the like. Although there is a great variety of two-component systems, the pattern of treatment is similar, and will be exemplified in this chapter with particular reference to the system sodium sulfate-water.

#### 3.1 The Solubility of Glauber's Salt

To determine the solubility of Glauber's salt in water at, say, 25°C and 1 atm, the chemist carries out two experiments. In the one experiment, *A*, a mixture of Glauber's salt and water is agitated in a thermostat at 25°C. Periodically samples of the liquid phase are withdrawn and analyzed. In the other experiment, *B*, a solution is prepared by agitating Glauber's salt and water for some time at a higher temperature, say, 30°C. At intervals a small sample of this liquid is cooled to 25°C and seeded with a small

crystal of Glauber's salt. If crystallization occurs, the mixture is transferred to the thermostat at 25°C and agitated at this temperature. Again samples of the liquid are periodically withdrawn and analyzed. Typical sets of analyses from such experiments are shown in Figure 3.1.

For both *A* and *B* the compositions of the solutions approach a common value, that of the saturated solution. It is a matter of experience that experiments of type *A* never yield supersaturated solutions and those of type *B* never yield unsaturated solutions, provided that the temperature control is satisfactory. Solutions from *A* can be either unsaturated or saturated and solutions from *B* either supersaturated or saturated. When solutions from *A* and *B* have the same composition, they must be saturated. An ex-

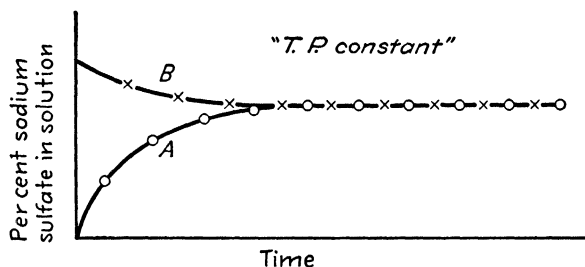


FIG. 3.1 Determination of the solubility of Glauber's salt.

periment of type *A* alone or of type *B* alone is insufficient to settle the composition of a saturated solution.

It is too frequently stated that a saturated solution is one for which the rate of solution is equal to the rate of crystallization. The *measurable* rate of solution is the tangent to curve *A* and the *measurable* rate of crystallization is the negative of the tangent to curve *B*. At saturation both these rates are zero. While possibly adequate as an *interpretation*, such a concept is clearly inadequate as a *criterion* of saturation.

In expressing solubility it is necessary to state not only the composition of the saturated solution, but also the composition of the phase with respect to which the solution is saturated. At 25°C and 1 atm the composition of the solid phase is Glauber's salt (44.1% sodium sulfate, 55.9% water) and the composition of the solution saturated with respect to it is 21.8% sodium sulfate, 78.2% water. The composition of this saturated solution might equally

well be stated as 49.4% Glauber's salt, 50.6% water. Either composition expresses the solubility of Glauber's salt and both are used in Table 3.1. It should be made clear that in the study of

TABLE 3.1 SOLUBILITY OF GLAUBER'S SALT

| TEMPERATURE, °C | % SODIUM SULFATE | % WATER | % GLAUBER'S SALT | % WATER |
|-----------------|------------------|---------|------------------|---------|
| 0               | 4.6              | 95.4    | 10.4             | 89.6    |
| 5               | 5.7              | 94.3    | 12.9             | 87.1    |
| 10              | 8.2              | 91.8    | 18.6             | 81.4    |
| 15              | 11.5             | 88.5    | 26.1             | 73.9    |
| 20              | 15.9             | 84.1    | 36.1             | 63.9    |
| 25              | 21.8             | 78.2    | 49.4             | 50.6    |
| 30              | 29.0             | 71.0    | 65.8             | 34.2    |

the phase rule the particular choice of components for a solution is not in any way intended to suggest the molecular constitution of the solution.

### 3.2 The Solubility of Sodium Sulfate

If solubility determinations are carried out in the temperature range 35 to 100°C, it will be found that the solid phase in excess is sodium sulfate, regardless of whether sodium sulfate (anhydrous) or Glauber's salt is used as the solute. In contrast to that of Glauber's salt, the solubility of sodium sulfate decreases with increasing temperature. Consequently, to obtain solutions supersaturated at, say, 40°C it will be necessary to agitate the mixture at a *lower* temperature before placing it in the thermostat at 40°C.

TABLE 3.2 SOLUBILITY OF SODIUM SULFATE

| Temperature, °C | % Sodium sulfate |
|-----------------|------------------|
| 35              | 32.9             |
| 40              | 32.6             |
| 50              | 31.8             |
| 60              | 31.2             |
| 70..            | 30.6             |
| 80..            | 30.2             |
| 90 ..           | 29.9             |
| 100...          | 29.7             |

In other respects the determination is the same as for the solubility of Glauber's salt. In Table 3.2 are given solubility data for sodium sulfate. While the compositions of the saturated solutions could

be expressed in terms of Glauber's salt and water, this is not usually done.

### 3.3 The Effect of Temperature and Pressure on Solubility

It was pointed out in Chapter 1 that the conditions affecting equilibrium in a heterogeneous system are temperature, pressure, and phase composition. The equilibrium concerned in the expression of solubility involves two phases; for a two-component system there are therefore two degrees of freedom ( $\mathcal{F} = 2 + 2 - 2 = 2$ ). Since solubility is an expression of phase composition, the two parameters affecting equilibrium are temperature and pressure. At constant pressure the solubility is dependent only on the temperature; at constant temperature the solubility depends only on the pressure.

A mixture of Glauber's salt and its saturated solution is in equilibrium with respect to the process of Glauber's salt dissolving in and crystallizing from the saturated solution. If the temperature is increased (at constant pressure) the saturated solution can undergo only that change of composition required by the endothermic direction of the process (see Sections 1.2 and 1.5). The *dissolving* of Glauber's salt is endothermic and hence its solubility increases with rising temperature. In the case of sodium sulfate the *crystallization* is endothermic and hence its solubility decreases with rising temperature. In both cases the determining factor is the *differential* heat of solution for the saturated solution. This quantity should be distinguished from the *integral* heat of solution. The *integral heat of solution* for a saturated sodium sulfate solution is the heat liberated when sodium sulfate is dissolved in *water* to form the saturated solution. The *differential heat of solution* for a saturated sodium sulfate solution is the heat liberated when sodium sulfate is dissolved in an almost saturated solution to form the saturated solution. Heats of solution may be either positive or negative. Thus for aqueous solutions sodium sulfate has a positive differential heat of solution (heat is liberated in the process of solution, absorbed in the process of crystallization), while Glauber's salt has a negative differential heat of solution (heat is absorbed in the process of solution, liberated in the process of crystallization). Whether the solubility of a substance increases or decreases with rising temperature depends, then, on the sign of the differential heat of solution.

When sodium sulfate dissolves in an almost saturated solution the volume of the system as a whole decreases. Since an increase in pressure on a system in equilibrium can result only in the process which leads to a decrease in volume, it is clear that the solubility of sodium sulfate is greater at higher pressures.

### 3.4 Freezing Points of Aqueous Sodium Sulfate Solutions

The freezing point of an aqueous solution is the temperature at which that solution can exist in equilibrium with ice with respect to the process of ice dissolving in and crystallizing from the solution. It is important to note that there is no essential difference between this case and that of the solubility of Glauber's salt or of sodium sulfate; all three phenomena concern an equilibrium between a phase of invariable composition and a phase of variable composition. To state the freezing point of an aqueous sodium sulfate solution is equivalent to stating the solubility of ice in sodium sulfate at a certain temperature (the freezing point of the solution).

The usual method of measuring the freezing point of a solution of specified concentration is to undercool it until ice crystals can be made to form on agitation. The mixture is immediately removed from the cooling bath and its temperature observed as it warms up. If the mixture is well stirred during this process, a plot of temperature against time similar to that of Figure 2.4 is obtained. The curve shows three distinct portions: a rapid rise *ab*, due to the sudden release of the latent heat of crystallization of the ice; a gently sloping almost linear portion *bc*, when the ice is gradually melting (dissolving) and diluting the solution; a more steeply sloping almost linear portion *cd*, when the ice has disappeared completely and the solution is warming to room temperature. Due to the heat capacity of the thermometer its temperature lags behind that of the system to a small extent; this, together with possibly inadequate stirring, causes the three portions to merge into a continuous smooth curve. The experimenter wishes to obtain the temperature at which the last ice crystal disappears, since only at this temperature has the solution reached its original concentration. This temperature is never an observed number if the above procedure is followed, but is obtained by drawing tangents to the portions *bc* and *cd*. The temperature corresponding to the inter-

section of the two tangents is taken to be the freezing point of the original solution.

While this method of determining the freezing point is simple experimentally, there might be some doubt whether the temperature obtained is the true equilibrium value. Whereas in a solubility determination the temperature is kept constant and the composition of the solution determined by analysis, here both the temperature and the composition of the solution vary and the estimation of the temperature at which the last ice crystal disappears is subject to possible error. Only by taking elaborate precautions to ensure adequate stirring and a slow influx of heat to the system can the chemist obtain reproducible values. The determination involves the assumption that along the portion *bc* the solution is in equilibrium with ice at all times, even though the temperature of the system is changing continuously.

To determine the composition of a solution saturated with respect to ice at, say,  $-2^{\circ}\text{C}$  by a method similar to that described for the solubility of Glauber's salt would require two experiments at  $-2^{\circ}\text{C}$ , one with a solution unsaturated with respect to ice, the other with a solution supersaturated with respect to ice. These could be obtained by agitating ice and solution at  $-3^{\circ}\text{C}$  and at  $-1^{\circ}\text{C}$ , respectively. These mixtures would then be agitated in a thermostat at  $-2^{\circ}\text{C}$  and samples of the solutions periodically withdrawn and analyzed. When the compositions of the solutions have become the same they will both be saturated with respect to ice at  $-2^{\circ}\text{C}$ , *i.e.*,  $-2^{\circ}\text{C}$  is the freezing point of a solution of this composition. Freezing points of aqueous solutions of sodium sulfate are given in Table 3.3.

TABLE 3.3 FREEZING POINTS OF AQUEOUS SOLUTIONS OF SODIUM SULFATE

| <i>% Sodium sulfate</i> | <i>Freezing point, °C</i> |
|-------------------------|---------------------------|
| 0.56                    | -0.187                    |
| 1.40                    | -0.434                    |
| 2.76                    | -0.812                    |
| 3.43                    | -0.986                    |

### 3.5 Boiling Points of Aqueous Sodium Sulfate Solutions

The boiling point of a solution is the temperature at which that solution can exist in equilibrium with its vapor, with respect to the process of the vapor dissolving in and being liberated from the

solution. To state the boiling point of an aqueous solution of sodium sulfate of specified concentration is equivalent to stating the solubility of steam in sodium sulfate solution at a certain temperature (the boiling point of the solution). Since the phases involved do not comprise a condensed system, the pressure is of great importance; unless stated otherwise, a pressure of 760 mm is understood. The boiling point of an aqueous solution of sodium sulfate can be obtained by observing the temperature of the gently boiling solution and using a reflux condenser to return the condensate to the solution. If the volume of the solution is sufficiently large, its concentration will not be changed appreciably by the small amount of steam and returning condensate present. If necessary, allowance can be made for this and the true concentration of the boiling solution computed. It is obvious that a boiling solution may be either saturated or supersaturated with respect to steam. The equilibrium can be approached from the opposite direction by bubbling steam at 760 mm pressure into the solution at a temperature  $T - \delta T$  slightly lower than its boiling point  $T$ . If the solution at this lower temperature  $T - \delta T$  is unsaturated with steam, its temperature will be raised by the heat liberated as the steam dissolves. The solution will be diluted by this process, to a small extent if  $\delta T$  is small. The heat required to raise the temperature of the solution to its boiling point is  $C \delta T$ , where  $C$  is the heat capacity of the solution. The weight of steam  $\delta y$ , which must dissolve to supply this heat, is given by  $C \delta T / Q_s$ , where  $Q_s$  is the heat of solution per gram of steam dissolved, approximately 540 cal. The solution becomes diluted in the process and its boiling point consequently lowered. The boiling-point elevation of a solution,  $\Delta T = T_{\text{solution}} - T_{\text{water}}$ , is approximately proportional to the molality,  $m$ , which is defined as  $1000x/fy$ , where  $x$  = grams of solute,  $y$  = grams of water, and  $f$  = formula weight (molecular weight) of the solute. If the weight of the solute is fixed, as it is for the case under consideration,  $\delta(\Delta T)/\Delta T = \delta m/m = -\delta y/y$ . Therefore the error in the measured boiling point,  $\delta(\Delta T)$ , due to the dilution  $\delta y$ , is given by

$$\delta(\Delta T) = - \Delta T \frac{\delta y}{y} = - \Delta T \frac{C \delta T}{y Q_s}$$

For aqueous solutions the heat capacity,  $C$ , is approximately equal to the weight of water present,  $y$ , whence  $\delta(\Delta T) \cong -\Delta T \delta T / Q_s$ .

A 22.1% solution of sodium sulfate has a boiling-point elevation of  $2.08^{\circ}$ . If steam is introduced into this solution at  $101^{\circ}\text{C}$  the relation above shows that the temperature can rise to a value  $0.004^{\circ}$  below  $102.08^{\circ}\text{C}$ . If the original solution had been at  $102.0^{\circ}\text{C}$ , this error would have been only  $0.0004^{\circ}$ . Thus the equilibrium between steam and aqueous solution can be approached from both directions and the boiling point determined within narrow limits of experimental error. Boiling points of aqueous solutions of sodium sulfate are given in Table 3.4.

TABLE 3.4 BOILING POINTS OF AQUEOUS SOLUTIONS OF SODIUM SULFATE

| % Sodium sulfate | Boiling point, $^{\circ}\text{C}$ |
|------------------|-----------------------------------|
| 1.4.....         | 100.105                           |
| 6.6.....         | 100.527                           |
| 12.4.....        | 101.07                            |
| 17.6.....        | 101.61                            |
| 22.1.....        | 102.08                            |
| 29.2.....        | 102.87                            |

### 3.6 The Phase Diagram for the System Sodium Sulfate-Water

Tables 3.1 to 3.4 give the compositions and temperatures of phases which can exist in equilibrium at atmospheric pressure. This information can be expressed in the form of a diagram on which the compositions are plotted as abscissas and the temperatures as ordinates. Referring to Table 3.1, one would plot on the  $25^{\circ}$  isotherm two points, one at 44.1% sodium sulfate (the composition of Glauber's salt), the other at 21.8% (the composition of the solution saturated with Glauber's salt). These two points, designated as *a* and *b* in Figure 3.2, are joined by a *tie line* to indicate that they represent the compositions of *conjugate* phases which can exist in equilibrium; tie lines must obviously be isotherms since equality of temperature is a prime requisite for equilibrium. A similar construction is shown for the other data of Table 3.1. It is customary to plot the results of laboratory experiments in this way and then to interpolate by drawing smooth curves through the points. This has been done in Figure 3.3; the tie lines may be omitted, provided there is no doubt about the phases which can exist in equilibrium. When extrapolated, the various solubility curves intersect at the points *x*, *y*, and *z*.

The *eutectic* point *x* (3.85%,  $-1.10^{\circ}\text{C}$ ) represents the composition and temperature of a solution which can exist in equilibrium with

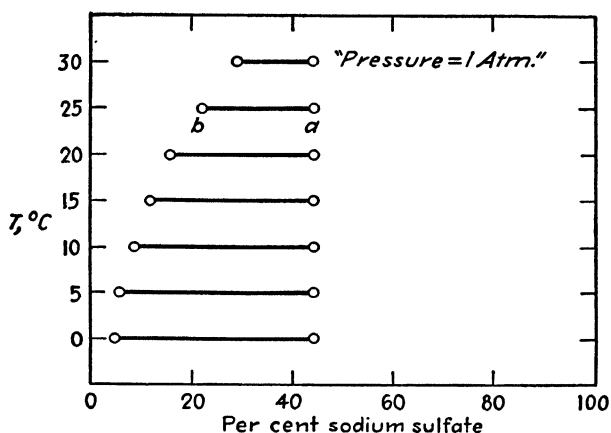


FIG. 3.2 Conjugate phases in the system sodium sulfate-water.

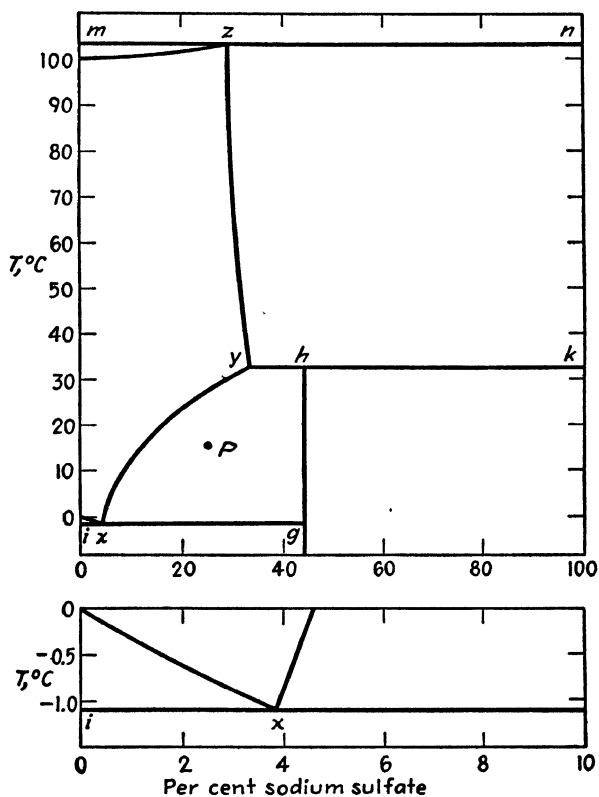


FIG. 3.3 Phase diagram for the system sodium sulfate-water at 1 atm.

ice and with Glauber's salt simultaneously. This eutectic temperature is the lowest temperature at which a sodium sulfate solution can exist, provided that the solution is not supersaturated with Glauber's salt or ice. With the same provision, the eutectic composition is the composition of the solution having the lowest freezing point. The term *eutectic* literally means *easy melting*. It is customary to draw in the tie lines *ix* and *gx* since they serve as boundary lines for the two fields, ice-solution and Glauber's salt-solution. At temperatures below these lines ice and Glauber's salt can exist as a mechanical mixture; there is no chemical process, however, with respect to which these two phases can exist in equilibrium with one another.

The point *y* (33.2%, 32.384°C) represents the composition of a solution which can exist in equilibrium with Glauber's salt and sodium sulfate simultaneously. On being heated Glauber's salt decomposes at the temperature *y* to give sodium sulfate and a solution of composition *y*. This temperature can be called the melting point of Glauber's salt, but since the composition of the resulting liquid, *y*, differs from that of Glauber's salt, *h*, it is said to be an *incongruent* melting point; Glauber's salt is said to melt incongruently. Solids which melt to give liquids of the same composition are said to melt *congruently* and to have congruent melting points, *e.g.*, ice; a mixture of ice and Glauber's salt of composition *x*. The temperature *y* is also called the *transition point* of Glauber's salt, with reference to the change from the hydrate to the anhydrous form; this term is used in connection with transitions from one hydrate to another as well as transitions from one polymorphic form of a substance to another. The tie lines *hy* and *ky* are included in the diagram as boundaries of the fields Glauber's salt-solution and sodium sulfate-solution. At temperatures below *y* Glauber's salt and sodium sulfate can exist as a mechanical mixture not in equilibrium. The transition temperature of Glauber's salt is easily reproduced and has been determined with great accuracy; it is widely used as a fixed point in thermometry.

The point *z* (29.6%, 103.03°C) represents the composition and temperature of a solution which can exist in equilibrium with steam and sodium sulfate simultaneously. This temperature is called the *maximum boiling point* since it is the highest temperature at which a solution of sodium sulfate can exist in equilibrium with steam provided, of course, that it is not supersaturated with sodium sul

fate. Above the tie lines  $mz$  and  $nz$  steam and sodium sulfate exist as a mechanical mixture not in equilibrium.

It is clear that if the system sodium sulfate-water were investigated at a pressure other than 1 atm, the corresponding phase diagram would differ from Figure 3.3. The solubility curves of ice, Glauber's salt, and sodium sulfate, the eutectic point  $x$ , the transition point  $y$ , and the melting point of ice would not be markedly changed; the boiling-point curve, the maximum boiling point  $z$ , and the boiling point of water would show considerable change. In many diagrams no consideration is given to equilibria involving the vapor phase and the boiling-point curve is omitted from the diagram. The solubility curve for sodium sulfate at high temperatures can be investigated by subjecting the system to a pressure not less than the vapor pressure of the solution.

### 3.7 The Description of a System and the Proportioning Rule

So far, the phase diagram has been used to indicate the *compositions* of phases participating in equilibrium. It can also be used to indicate the *proportions* of phases participating in equilibrium. The procedure can be illustrated by reference to a system  $P$  (Figure 3.3), made up of 25 g of sodium sulfate and 75 g of water at 15°C and 1 atm. This point lies in the field of Glauber's salt and hence, if equilibrium obtains, the solid phase will be Glauber's salt and the liquid phase a solution saturated with Glauber's salt. In order to describe this system completely under equilibrium conditions it will be necessary to state the temperature, the pressure, and the over-all composition of the system; the phase constituents and the process or processes with respect to which equilibrium obtains; the compositions and the proportions of the phase constituents. The temperature, the pressure, and the phase constituents of the system  $P$  have been stated above; the over-all composition of the system is clearly 25% sodium sulfate, 75% water. The equilibrium process is that of Glauber's salt dissolving in and crystallizing from the solution. The composition of Glauber's salt can be expressed in terms of the components (44.1% sodium sulfate, 55.9% water or by the formula  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ). The composition of the solution can be expressed most conveniently in terms of a set of *solution constituents*; these are the substances which aptly suggest the properties of the solution and from which the solution can be formed

spontaneously. In this case there are two obvious sets of solution constituents: sodium sulfate and water; Glauber's salt and water. Table 3.1 gives the composition of the saturated solution in terms of the first set as 11.5% sodium sulfate, 88.5% water and in terms of the second set as 26.1% Glauber's salt, 73.9% water.

To state the proportions of the phases present is equivalent to stating the composition  $P$  in terms of the phase constituents, *i.e.*, the percentage of Glauber's salt and the percentage of saturated solution. In Figure 3.4a the composition  $P$  is given in terms of the components, water,  $W$ , and anhydrous sodium sulfate,  $A$ , on a linear scale running from 0 for water to 100 for sodium sulfate. On this scale  $P$  has the composition 25% sodium sulfate, 75% water, *i.e.*,  $(P - W)/(A - W) \times 100\%$  sodium sulfate,  $(A - P)/(A - W)$

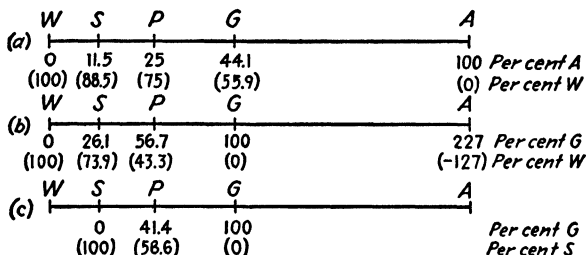


FIG. 3.4 Composition of a heterogeneous system in terms of the phase constituents.

$\times 100\%$  water. In Figure 3.4b the composition  $P$  is given in terms of the components water,  $W$ , and Glauber's salt,  $G$ , on a linear scale running from 0 for water to 100 for Glauber's salt. Clearly, any numbers on the scale  $b$  must be  $100/44.1$  times the corresponding numbers on the scale  $a$ . For example, the system  $P$  could equally well have been made up from 56.7 g of Glauber's salt and 43.3 g of water, *i.e.*,  $(P - W)/(G - W) \times 100\%$  Glauber's salt and  $(G - P)/(G - W) \times 100\%$  water. In Figure 3.4c the composition of  $P$  is given in terms of the phase constituents, saturated solution,  $S$ , and Glauber's salt,  $G$ , on a linear scale running from 0 for saturated solution to 100 for Glauber's salt. Scale  $c$  can be derived from  $b$  by foreshortening from a common value for  $G$  ( $= 100$ ). Since 100 to 0 on scale  $c$  is equal to 100 to 26.1 on scale  $b$ , the scales stand in the ratio 100:73.9. Point  $P$  on scale  $b$  is  $100 - 56.7 = 43.3$  divisions below 100; on scale  $c$  it will lie  $43.3 \times 100/73.9 = 58.6$  divisions below 100, *i.e.*, at  $100 - 58.6 = 41.4$ .

This can be shown in another way. It is apparent from Figure 3.4*b* that the system can be made from 56.7 g of Glauber's salt and 43.3 g of water. It was shown that 100 g of solution consists of 26.1 g of Glauber's salt and 73.9 g of water. Therefore 43.3 g of water will be contained in  $43.3 \times 100/73.9 = 58.6$  g of solution. The weight of Glauber's salt dissolved in the 58.6 g of solution will be  $58.6 \times 26.1/100 = 15.3$  g. The weight of undissolved Glauber's salt will then be  $56.7 - 15.3 = 41.4$  g, as shown by Figure 3.4*c*. The portions of the phase constituents are  $(P - S)/(G - S) \times 100\%$  Glauber's salt,  $(G - P)/(G - S) \times 100\%$  solution, measured on a percentage scale running from 0 at *S* to 100 at *G*. It is an interesting fact that the addition of any quantity *x* to all the scale numbers will not alter the algebraic expression for the proportion of the phase constituents, for example,

$$(P + x) - (S + x) = P - S$$

and

$$(G + x) - (S + x) = G - S$$

Moreover, if the size of the scale divisions is changed, *i.e.*, if all the scale numbers are multiplied by a factor *k*, the expression is still unchanged, for example,

$$\frac{kP - kS}{kG - kS} = \frac{k(P - S)}{k(G - S)} = \frac{P - S}{G - S}$$

Furthermore, no change is produced by utilizing a scale in which *both* the position of zero and the size of the divisions differ from the percentage scale, for example,

$$\begin{aligned} k(P + x) - k(S + x) &= k(P - S) \\ k(G + x) - k(S + x) &= k(G - S) \\ \frac{k(P - S)}{k(G - S)} &= \frac{P - S}{G - S} \end{aligned}$$

Thus *any* linear scale (*i.e.*, one in which all divisions are of identical size) can be used to determine the proportions of the constituents represented by *S* and *G*. For example, the scales *a* and *b* could be used,

$$\frac{25 - 11.5}{44.1 - 11.5} \times 100\% = 41.4\%; \quad \frac{56.7 - 26.1}{100 - 26.1} \times 100\% = 41.4\%$$

The proportioning rule can now be stated in its general form: The composition of any system  $P$  in terms of any set of constituents  $X$  and  $Y$  can be given as  $(P - X)/(Y - X) \times 100\%$  of  $Y$  and  $(Y - P)/(Y - X) \times 100\%$  of  $X$ , in which  $X$ ,  $Y$ , and  $P$  lie on any linear scale. It should be emphasized that the proportioning rule is valid only if the compositions are expressed in terms of conservative weight units, such as grams, pounds, or tons; it is not valid if the compositions are expressed in terms of nonconservative quantities such as volume; in certain cases moles or equivalents can be used (see Chapter 9). In the absence of scale divisions the differences  $P - X$ ,  $Y - X$ , and  $Y - P$  may be conveniently determined with an ordinary scale ruler. In the example cited above,  $P$  was intermediate in composition between  $X$  and  $Y$ , that is, the system  $P$  could be made from *positive* quantities of  $X$  and  $Y$ . The proportioning rule is equally valid in cases in which the system  $P$  can be made by subtracting some  $X$ , say, from some  $Y$ , for example, on scale  $a$  let  $X = W$ ,  $Y = G$ , and  $P = A$ ; the composition of the anhydrous sodium sulfate can then be given as  $(100 - 0)/(44.1 - 0) \times 100\% = 227\%$  of Glauber's salt and  $(44.1 - 100)/(44.1 - 0) \times 100\% = -127\%$  of water, a result consonant with the data shown by scale  $b$ .

### 3.8 Courses of Crystallization

Isobaric phase diagrams can be used to predict phase changes which occur under equilibrium conditions when the temperature of a system is changed. The course of crystallization during the cooling of the system  $P$  of composition 40% sodium sulfate, 60% water, from 50 to  $-10^\circ\text{C}$  is illustrated in Figure 3.5. The over-all composition of the system will remain fixed at 40% sodium sulfate and the path of the representative point of the whole system will follow the line  $Ps$  during this cooling. The initial composition of the system in terms of its phase constituents is 12.0% sodium sulfate, 88.0% of the solution saturated with respect to sodium sulfate. As the system is cooled, the point representing the composition of the solution will follow the path  $Ay$ , while that for the solid will follow the path  $Bk$ . During this process the proportion of solution will increase until, when the temperature of the system reaches  $q$ , the proportions become 89.9% solution and 10.1% sodium sulfate.

At this temperature the solution will be saturated with Glauber's salt as well as sodium sulfate. Under equilibrium conditions

further removal of heat will cause crystallization of Glauber's salt. The system will then consist of three phases and according to the phase rule will be univariant. Under isobaric conditions the temperature of the system and the compositions of the phases will remain fixed until such time as the number of phases is reduced.

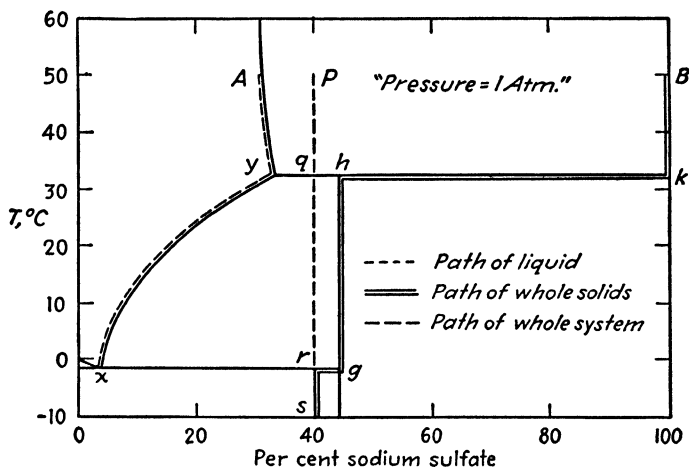
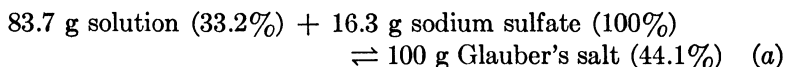


FIG. 3 5 Paths of the representative points of the liquid and of the whole solids during the cooling of the system *P*.

The formation of Glauber's salt from the phase constituents, solution and sodium sulfate, can be expressed quantitatively,



in accordance with the proportioning rule. The weight ratio solution/sodium sulfate in the system just before crystallization of Glauber's salt is 89.9/10.1; the stoichiometric requirement in equation (a) is only 83.7/16.3. Hence some solution will still remain when all the sodium sulfate has been used up in the formation of Glauber's salt. This can also be shown from a consideration of the relative positions of *y*, *q*, *h*, and *k* on the diagram. Glauber's salt is formed at the expense of both solution and sodium sulfate until one of the latter phases is completely used up. There must be *positive* quantities of the two remaining phases. The composition *q*, of the over-all system, can be made up of positive quantities of *h* and *y*

but not of  $h$  and  $k$ . Thus the two remaining phases will be Glauber's salt and solution, not Glauber's salt and sodium sulfate.

So long as the three phases are present the system can be in equilibrium with respect to process (a). The formation of Glauber's salt from sodium sulfate and solution is exothermic and hence removal of heat will cause an increase in the proportion of Glauber's salt; the amount of Glauber's salt so formed will be directly proportional to the amount of heat removed. During this isothermal change the point representing the composition of the *total solids* will move along the path  $kh$ , indicating the change from pure sodium sulfate to a mixture of it and Glauber's salt, and ultimately to pure Glauber's salt. At any point between  $k$  and  $h$  the relative proportions of the two salts can be obtained with the aid of the proportioning rule. When the composition of the total solids has reached  $h$ , the system will consist of 37.6% of the solution, 62.4% Glauber's salt.

Since the system now consists of only two phases it is again bi-variant and further removal of heat will lower the temperature. The point representing the composition of the solution will follow the solubility curve of Glauber's salt,  $yx$ , while that for the solid will follow the path  $hg$ . At any temperature the composition of the system in terms of the phase constituents, Glauber's salt and saturated solution, can be found by applying the proportioning rule to the appropriate tie line. When the temperature of the system reaches the eutectic temperature  $r$ , the proportions will be 89.8% Glauber's salt, 10.2% of the eutectic solution.

Under equilibrium conditions further removal of heat will cause crystallization of both ice and Glauber's salt. With three phases present the system will again be univariant; the temperature of the system and the compositions of the phases will remain fixed until one of the phases has been used up. The decomposition of the solution into ice and Glauber's salt is expressed by the relation



The crystallization of ice and Glauber's salt is an exothermic process; hence the removal of heat will ultimately cause complete crystallization of the solution. The final phase constituents, ice and Glauber's salt, must have the over-all composition  $r$ , corresponding to 9.3% ice, 90.7% Glauber's salt. During the isothermal crystallization the point representing the composition of the total

solids will follow the path *gr*, indicating the change from Glauber's salt alone to the mixture of ice and Glauber's salt. When the composition of the total solids has become equal to the over-all composition of the system, *r*, crystallization will be complete. The cooling of the mixture of ice and Glauber's salt is indicated by the path *rs*. There is, of course, no equilibrium possible between the ice and the Glauber's salt.

It should be clearly understood that a phase diagram is an *equilibrium* diagram and that courses of crystallization predicted from it presuppose the absence of such nonequilibrium conditions as

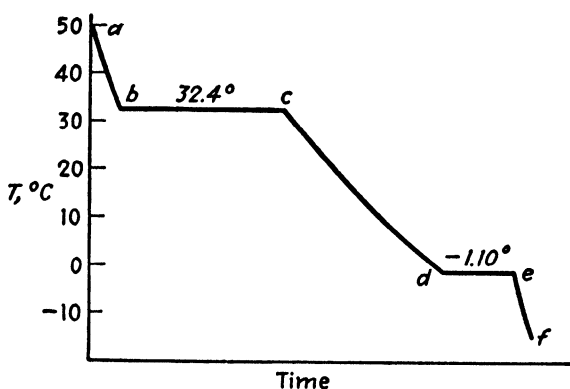


FIG. 3.6 Temperature-time curve for the cooling of the system represented by the point *P* of Figure 3.5.

supersaturation and undercooling. In practice such conditions do arise, particularly in systems of high viscosity where diffusion is slow, frequently encountered in the fields of geology, metallurgy, and ceramics. Nevertheless the phase diagram indicates the phases and proportions which can ultimately obtain.

### 3.9 Temperature-Time Curves. Thermal Analysis

If, in the course of crystallization described above, heat had been removed at a constant rate (calories per unit time) then, in the absence of nonequilibrium conditions, a plot of the temperature of the system as a function of time would appear as in Figure 3.6. The line *ab* corresponds to the cooling of the system from 50 to 32.4°C. If no changes of phase composition had occurred, the slope of this line would have been determined solely by the heat

capacity of the system and the rate of removal of heat. However, sodium sulfate dissolves during this cooling and liberates its heat of solution. For the same rate of removal of heat, the cooling curve then has a more gentle slope. The line *bc* corresponds to the isothermal reaction (*a*). The line *cd* is related to the cooling of the system from 32.4 to  $-1.1^{\circ}\text{C}$ , during which Glauber's salt crystallizes with the liberation of heat. The slope of the line *cd* is therefore more gentle than if no change of phase composition had occurred. The line *de* has reference to the isothermal reaction (*b*). The slope of the line *ef*, corresponding to the cooling of the mixture of ice and Glauber's salt, is determined only by the heat capacity of the mixture and the rate of heat removal.

The duration of the temperature arrest *bc* depends both on the rate of removal of heat and on the amount of heat liberated by the

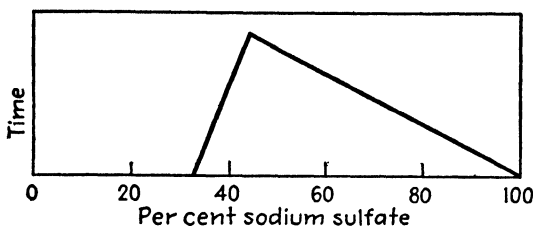


FIG. 3.7 Duration of the temperature arrest at the transition temperature.

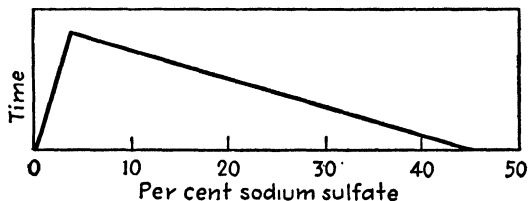


FIG. 3.8 Duration of the temperature arrest at the eutectic temperature.

formation of the Glauber's salt; the latter is directly proportional to the amount of Glauber's salt formed. The amount of Glauber's salt formed during the isothermal process depends on the over-all composition of the system as well as on its weight. For any given weight of system the amount of Glauber's salt formed will be a maximum for the system having the same over-all composition as Glauber's salt (44.1% sodium sulfate). In the case of a system of composition *q* (Figure 3.5), the weight of Glauber's salt formed is

$yq/yh$  of the total weight of the system. It follows that the duration of the temperature arrest is  $yq/yh$  times the maximum arrest time. A plot of the duration of this arrest against the composition of the system is shown in Figure 3.7.

Figure 3.8 is obtained for the arrest at the eutectic temperature and shows a maximum time at the eutectic composition. If the eutectic composition were unknown, it could be estimated from a series of temperature-time cooling curves by plotting the time of arrest against the composition of the system and extrapolating the two lines to their point of intersection.

### 3.10 The Isothermal Phase Diagram for the System $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$

While isobaric diagrams such as Figure 3.3 are convenient for showing solubilities, freezing points, boiling points, and transition points, it is necessary to show vapor pressures on isothermal diagrams, such as Figure 3.9.

At  $40^\circ\text{C}$  the vapor pressure of water is 55.3 mm. The addition of sodium sulfate to form a solution will result in a lowering of the vapor pressure of the liquid, as shown by the falling curve of the isotherm at  $40^\circ\text{C}$ . In the case of a volatile solute the total vapor pressure of the solution may either increase or decrease with increasing concentration of solute, but for a nonvolatile solute such as sodium sulfate the vapor pressure of the solution invariably decreases with increasing concentration. The addition of sodium sulfate to its saturated solution does not change the composition of the solution, and hence the vapor pressure of the mixture of sodium sulfate and its saturated solution is identical with that of the saturated solution (47.4 mm). This is shown by the horizontal portion of the isotherm at  $40^\circ\text{C}$ , extending from the composition of the saturated solution to 100% sodium sulfate. At this latter point the curve is discontinuous; the vapor pressure of pure sodium sulfate is negligibly small.

The vapor pressures of solutions supersaturated with respect to sodium sulfate lie on the dotted extension of the vapor-pressure curve for the unsaturated solutions. It is interesting to note that the vapor pressure of a metastable solution supersaturated with respect to sodium sulfate is *less* than that of the more stable mechanical mixture of sodium sulfate and its saturated solution. This is in contrast to the behavior discussed in the treatment of one-component systems, for which the metastable phase invariably has

a higher vapor pressure than the stable phase. Actually no anomaly exists here, as can be shown by consideration of the process involved in the statement of metastability. The supersaturated solution would be metastable with respect to the formation of sodium sulfate but stable with respect to the formation and condensation

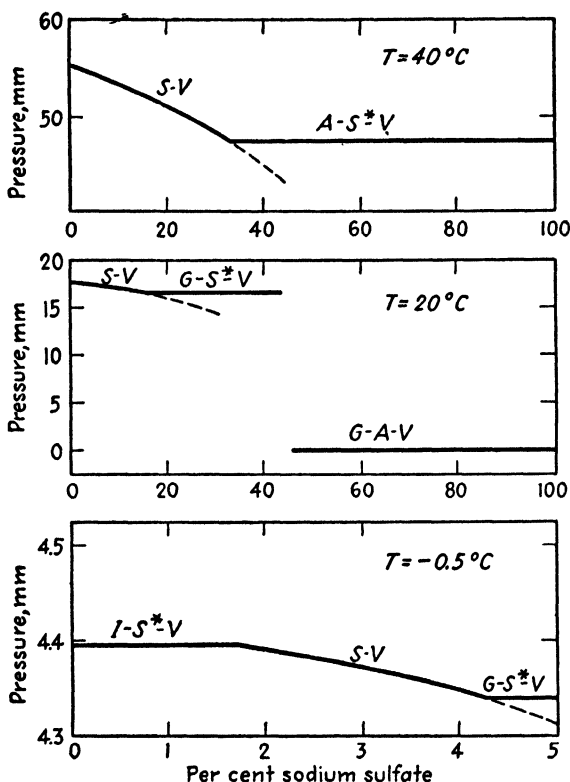


FIG. 3.9 Equilibrium pressures in the system sodium sulfate-water.  $S$  = unsaturated solution;  $S^*$  = saturated solution;  $G$  = Glauber's salt;  $V$  = vapor;  $A$  = anhydrous sodium sulfate.

of vapor. The lower vapor pressure of the supersaturated solution is due to the increased proportion of solute.

In the isotherm at 20°C the vapor-pressure curve for the unsaturated solutions is analogous to that in the isotherm at 40°C, extending from 17.5 mm for pure water to 16.5 mm for the solution saturated with respect to Glauber's salt. The vapor pressure of

any mechanical mixture of Glauber's salt and its saturated solution is identical with that of the saturated solution. As before, the curve is discontinuous at the composition of a nonvolatile pure substance, in this case Glauber's salt. Again, the vapor pressures of solutions supersaturated with respect to Glauber's salt are shown by the dotted extension. At 20°C condensed systems with a proportion of sodium sulfate greater than 44.1% are, in the most stable condition, mixtures of Glauber's salt and sodium sulfate (see Figure 3.3). These two phases can participate in an equilibrium process involving water vapor, namely



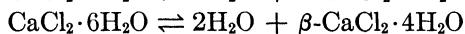
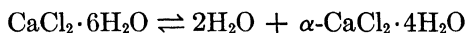
Under isothermal conditions equilibrium with respect to this process can obtain at only one pressure, *e.g.*, 0.017 mm at 20°C. The horizontal portion of the isotherm from 44.1 to 100% sodium sulfate shows this pressure; the curve is, of course, discontinuous at both ends.

The isotherm at -0.5°C is similar to that at 20°C with the exception of the portion at the extreme left, where the equilibrium pressure of any mixture of ice and solution saturated with respect to ice (1.6% sodium sulfate) is identical with that of the saturated solution. This is analogous to the equilibrium pressure of mixtures of Glauber's salt and its saturated solution; however, the vapor pressure of a solution saturated with respect to ice is identical with the vapor pressure of ice, whereas the same cannot be said of Glauber's salt and its saturated solution.

### 3.11 Dissociation Pressures of Hydrates

The pressure at which there can be equilibrium with respect to process (c) at any particular temperature is called the "dissociation pressure" of Glauber's salt at that temperature. It is clear that this pressure cannot be referred to as the vapor pressure of Glauber's salt, inasmuch as the vapor does not have the same composition as the pure substance Glauber's salt. Even the term "dissociation pressure" is not sufficiently definitive, for it takes no account of the solid formed in the decomposition. This is readily apparent from a consideration of the dissociation of the hexahydrate of calcium chloride. There are two polymorphic forms of the tetrahydrate,  $\alpha$  and  $\beta$ , and as might be expected there are at any

given temperature two dissociation pressures, corresponding to the processes



At 25°C the corresponding values are 0.508 mm and 0.432 mm, respectively. Hence a dissociation pressure should be stated with reference to a particular process, unless the process is obvious.

The process referred to in stating a dissociation pressure involves only phases of invariant composition, *i.e.*, pure substances. It is convenient, then, to plot dissociation pressures against tempera-

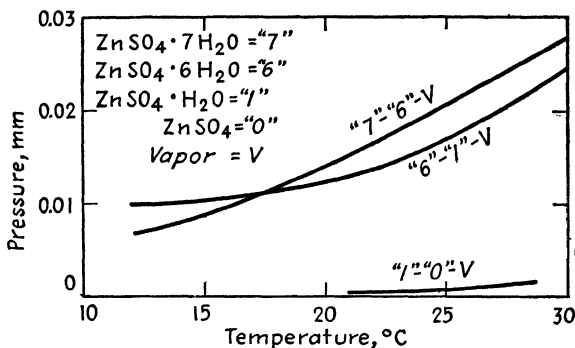


FIG. 3.10 Dissociation pressures of hydrates of zinc sulfate.

ture. Figure 3.10 shows the effect of temperature on the dissociation pressures of hydrates of zinc sulfate.

### 3.12 The Metastability of the Heptahydrate of Sodium Sulfate

If a solution containing about 33% sodium sulfate is cooled below 17°C without formation of solid Glauber's salt, crystals of the hydrate  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  are commonly formed. If a crystal of Glauber's salt is added to a mixture of the heptahydrate and its saturated solution, more Glauber's salt is spontaneously formed at the expense of the solution and the heptahydrate until the latter is completely used up. The heptahydrate is therefore metastable with respect to this process. Its solubility is greater than that of Glauber's salt, as shown in Figure 3.11.

The equilibrium relationships involving the heptahydrate are analogous to those for Glauber's salt. There is a eutectic point with ice at  $-3.55^{\circ}\text{C}$ , 12.7% sodium sulfate, and a transition point at  $24.4^{\circ}\text{C}$ , 34.1% sodium sulfate. This latter point is the junction of the metastable solubility curves of the heptahydrate and of the anhydrous salt; the temperature  $24.4^{\circ}\text{C}$  is the incongruent melting point of the heptahydrate. Below  $24.4^{\circ}\text{C}$  the equilibrium between the anhydrous salt and its saturated solution is metastable

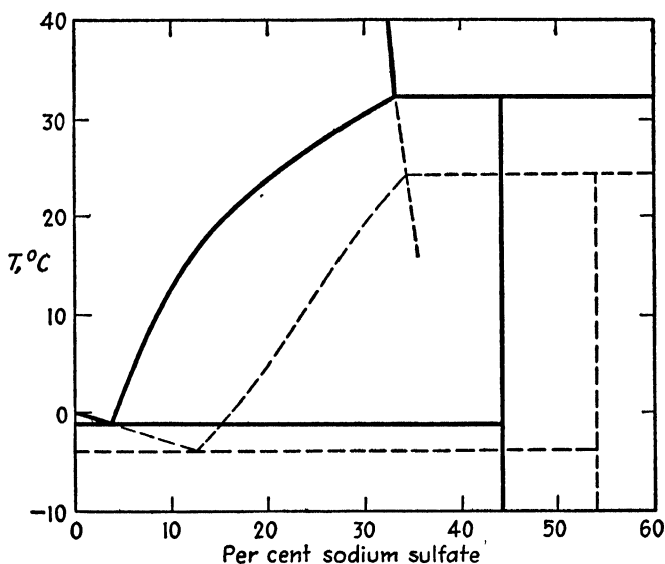


FIG. 3 11 Part of the phase diagram for the system sodium sulfate-water, including data for the heptahydrate.

with respect to the equilibrium between the heptahydrate and its saturated solution; both of these equilibria are, of course, metastable with respect to the equilibrium between Glauber's salt and its saturated solution. As before, the saturating phase of the less stable equilibrium has the higher solubility. This is true in general for metastable solubility. If heptahydrate is to disappear and Glauber's salt to be formed spontaneously, when in contact with a solution, that solution must be unsaturated with respect to the heptahydrate and supersaturated with respect to Glauber's salt, *i.e.*, the former must have the greater solubility. Similar behavior

is shown by the red and white polymorphic forms of phosphorus. The metastable  $\alpha$  variety is extremely soluble in carbon disulfide, while the stable red form is practically insoluble.

### 3.13 Pressure-Temperature Curves and Quadruple Points

In Section 3.11 reference was made to the use of pressure-temperature curves to represent dissociation pressures. Such curves are also useful in representing the vapor pressures of saturated solutions, because a two-component system consisting of a solute, its saturated solution, and vapor in equilibrium has but one degree of freedom, conveniently chosen as the temperature. Figure 3.12 shows vapor pressures and dissociation pressures for the system  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ . The scales on the diagram have been distorted.

Values of the vapor pressure for solutions saturated with respect to Glauber's salt have been shown in Figure 3.9 for two temperatures,  $20^\circ\text{C}$  and  $-0.5^\circ\text{C}$ . The  $G\text{-}S^*\text{-}V$  curve of Figure 3.12 extends these data over a range of temperature. Similarly, the  $A\text{-}S^*\text{-}V$  curve shows the effect of temperature on the vapor pressure of a solution saturated with respect to anhydrous sodium sulfate and the  $G\text{-}A\text{-}V$  curve the effect on the dissociation pressure of Glauber's salt.

The  $G\text{-}S^*\text{-}V$  and the  $A\text{-}S^*\text{-}V$  curves must intersect at  $32.4^\circ\text{C}$  (point 1), inasmuch as the saturated solutions have the same composition at this temperature and hence the same vapor pressure. Point 1 is a *quadruple point* at which the four phases  $G$ ,  $A$ ,  $S^*$ , and  $V$  can coexist in equilibrium. This point must therefore lie on the  $G\text{-}A\text{-}V$  curve and hence at this transition temperature the dissociation pressure of Glauber's salt is identical with the vapor pressure of its saturated solution. Because of the small effect of pressure on the equilibrium  $G \rightleftharpoons A + S^*$ , point 1 is practically coincident with the transition point at 1 atm shown in Figure 3.3.

Although the  $G\text{-}S^*\text{-}V$  and  $G\text{-}A\text{-}V$  curves cannot be extended above  $32.4^\circ\text{C}$ , since this would entail the superheating of  $G$ , the  $A\text{-}S^*\text{-}V$  curve has been extended below the quadruple point 1 to show the existence of the metastable  $A\text{-}S^*\text{-}V$  equilibrium. The  $H\text{-}A\text{-}S^*\text{-}V$  quadruple point 2 is analogous to point 1, but represents an equilibrium which is metastable with respect to the formation of Glauber's salt from both the anhydrous salt and the heptahydrate (and the saturated solution). The  $H\text{-}S^*\text{-}V$  curve represents the vapor pressures of solutions saturated with respect to the meta-

stable heptahydrate; since the vapor pressure of a solution decreases with increasing proportion of salt, the greater solubility of the heptahydrate demands that the  $H-S^*-V$  curve lie below the  $G-S^*-V$  curve. The  $H-A-V$  curve shows the effect of temperature on the dissociation pressure of the heptahydrate; it becomes

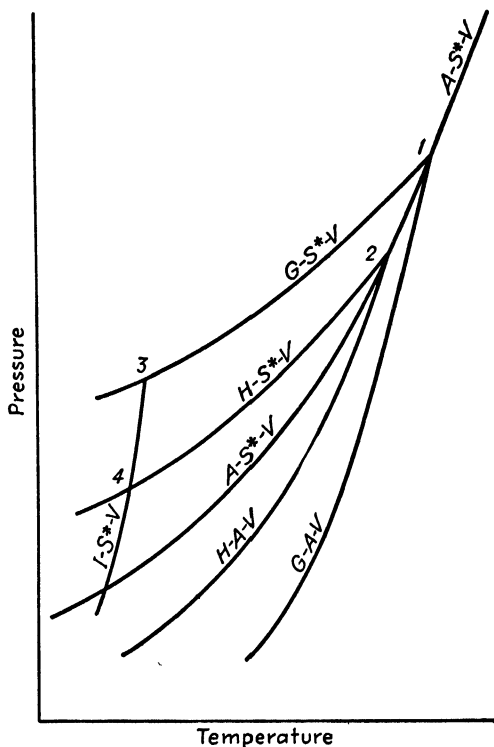


FIG. 3.12 Dissociation pressures and vapor pressures of saturated solutions in the system sodium sulfate-water.

identical with the vapor pressure of the solution saturated with heptahydrate at the intersection point 2.

As shown on the diagram, the dissociation pressure of the heptahydrate is greater than that of Glauber's salt. This follows from the metastability of the former, as can be shown by an experiment with two bulbs (*cf.* Section 2.4). Let one bulb contain heptahydrate, anhydrous salt, and water vapor in equilibrium ( $H-A-V$ ) and the other Glauber's salt, anhydrous salt, and water vapor in

equilibrium ( $G-A-V$ ). In order that Glauber's salt can form at the expense of the heptahydrate on connecting the two bulbs, the pressure in the first bulb must be the greater.

At sufficiently low temperatures dilute solutions of sodium sulfate can exist in equilibrium with ice, which gives rise to an  $I-S^*-V$  curve. Inasmuch as the vapor pressure of the solution saturated with respect to ice is identical with that of ice, the  $I-S^*-V$  curve is identical with the vapor-pressure curve of ice. The quadruple point 3 arises when the solution is simultaneously saturated with ice, Glauber's salt, and steam. Similarly, a quadruple point 4 arises at the intersection of the  $I-S^*-V$  and  $H-S^*-V$  curves. The temperatures for these quadruple points are, of course, very close to the corresponding eutectic temperatures at atmospheric pressure.

### EXERCISES

1. Assuming equilibrium, describe completely the following systems:
  - a. 1.0% sodium sulfate, 99% water at  $-0.5^{\circ}\text{C}$
  - b. 20% sodium sulfate, 80% water at  $50^{\circ}\text{C}$
  - c. 20% sodium sulfate, 80% water at  $10^{\circ}\text{C}$
  - d. 20% sodium sulfate, 80% water at  $-10^{\circ}\text{C}$
2. Is it possible to describe completely a system containing 60% sodium sulfate, 40% water at  $32.384^{\circ}\text{C}$  and 1 atm? Give your reasons.
3. Draw representative temperature-time curves for the cooling of the following systems from  $60^{\circ}$  to  $-10^{\circ}\text{C}$ , assuming equilibrium conditions:
  - a. Pure water
  - b. 2% sodium sulfate, 98% water
  - c. 3.85% sodium sulfate, 96.5% water
  - d. 20% sodium sulfate, 80% water
  - e. 44.1% sodium sulfate, 55.9% water
  - f. 70% sodium sulfate, 30% water
4. Trace the paths of the representative points of the liquid and of the whole solids during the cooling of the systems listed in Exercise 3.
5. Describe how thermal analysis could be used to determine the composition of the eutectic solution in the system sodium sulfate-water, without resorting to actual chemical analysis of this solution.
6. At atmospheric pressure and at any temperature below  $32.4^{\circ}\text{C}$ , an aqueous solution saturated with respect to anhydrous sodium sulfate is metastable with respect to the formation of Glauber's salt and its saturated solution. From this statement show which of these solids must have the greater solubility in water below  $32.4^{\circ}\text{C}$ .
7. From the data in Section 3.11 prove which of the tetrahydrates of calcium chloride is the more stable under the conditions stated.

## CHAPTER 4

### TWO-COMPONENT SYSTEMS. TYPES OF EQUILIBRIA INVOLVING ONLY ONE PHASE OF VARIABLE COMPOSITION

#### 4.1 The Binary Eutectic

One of the simplest types of phase diagrams is illustrated by Figures 4.1 to 4.4. The components of these systems form neither intermediate binary compounds nor solid solutions and their diagrams consist simply of the solubility curves of the components intersecting at a eutectic point.

Figure 4.1 shows the melting point of the component bismuth to be  $273^{\circ}\text{C}$  and that of the component cadmium to be  $323^{\circ}\text{C}$ . Both melting points are lowered by the addition of the other component. The solubility curve of bismuth in cadmium, shown on the left, and the solubility curve of cadmium in bismuth, shown on the right, intersect at the eutectic point,  $140^{\circ}\text{C}$ , 40% cadmium. The two solubility curves, taken together, are referred to as the *liquidus curve*; systems represented by points lying above the liquidus curve are wholly liquid. Systems represented by points below  $140^{\circ}\text{C}$  are wholly solid; the horizontal line at the eutectic temperature is therefore referred to as the *solidus curve*. The area between the liquidus and solidus curves is divided into two parts, the field of bismuth, of which the solubility curve of bismuth forms one boundary, and the field of cadmium, of which the solubility curve of cadmium forms one boundary. Systems represented by points within the field of a pure substance consist, under equilibrium conditions, of mixtures of the pure substance and solution saturated with respect to the pure substance.

In the absence of undercooling, a solution containing less than 40% by weight of cadmium will deposit bismuth on being cooled to a temperature below the liquidus curve. The liquid will then become enriched in cadmium as its composition follows the liquidus

curve down to the eutectic temperature. Further removal of heat will cause precipitation of cadmium as well as bismuth without further alteration in the composition of the liquid; moreover, the temperature of the system will remain fixed at  $140^{\circ}\text{C}$  until the last of the liquid has solidified. It should be noted that two types of precipitation occur during this cooling; first, the precipitation of

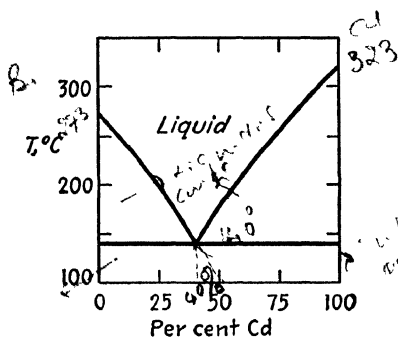


FIG. 4.1 Cd-Bi.

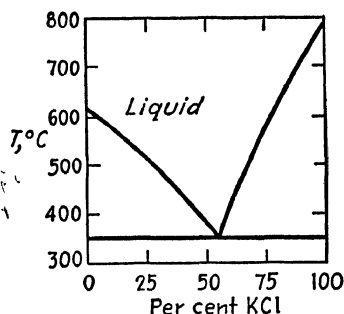


FIG. 4.2 KCl-LiCl.

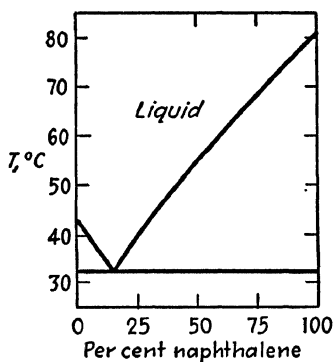
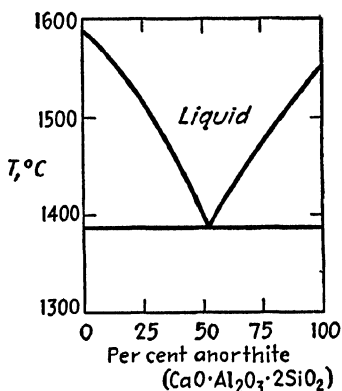


FIG. 4.3 Naphthalene-menthol.

FIG. 4.4  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ - $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ .

pure bismuth, followed, at the eutectic temperature, by the coprecipitation of bismuth and cadmium in the constant ratio 60:40 by weight.

The determination of the eutectic temperature in metallic systems is sometimes made by using a technique based on the great difference between the tensile strengths of solids and liquids. For

example, if a wire prepared from a solid alloy of cadmium and bismuth is slowly heated while under a slight tension, it will break at the temperature at which liquefaction occurs, *i.e.*, at the eutectic temperature.

Figure 4.2 gives information of interest to the chemist concerned with electrolysis in the molten state. While lithium chloride melts at 614°C and potassium chloride at 770°C, a mixture of the two salts in the proportions 45 and 55%, respectively, melts completely at the conveniently low temperature of 355°C. In many industrial electrolyses the operating temperature of the molten electrolyte can be lowered by the addition of a second component without appreciably affecting the electrochemical efficiency of the process.

Data such as those shown in Figures 4.1 and 4.2 are frequently useful in the selection of media for constant-temperature baths operated between 150 and 400°C, a range in which neither organic liquids nor common single-salt melts are suitable.

The type of phase diagram showing simply a binary eutectic is also common among two-component organic systems, as shown for the system naphthalene-menthol in Figure 4.3. It was pointed out earlier that melting points are used extensively, particularly by organic chemists, for the identification of pure substances. It was also shown that the occurrence of a melting range rather than a sharp melting point is an indication of the presence of impurity. A sample of menthol with 10% by weight of naphthalene would begin to melt at 31.7°C and would become completely liquid at 35°C, showing a melting range of 3.3°. From the diagram one might expect a sample containing only 0.1% of naphthalene to show a melting range of almost 10.3°. However, the proportion of liquid would not become appreciable until the temperature was raised considerably above the eutectic, and the apparent melting range would be small. The temperature of complete fusion would be slightly less than that for pure menthol. As will be seen in the treatment of poly-component systems, the simultaneous presence of several impurities would be expected to show a similar effect.

The technique of "mixed melting points" is based on the fact that the melting point of a mixture of two pure substances is in general different from that of either. For example, if a material melting sharply at 42°C is thought to be menthol, it is mixed with

pure menthol and the melting point then determined. If the "mixed melting point" is sharp and at 42°C, this is taken to indicate that the substance is indeed menthol.

Figure 4.4 represents a portion of a much more complicated diagram (discussed in Chapter 8) for which the components are lime, alumina, and silica. Although the components of Figure 4.4 are both ternary compounds in a three-component system, any system made up of these two compounds alone can be discussed in terms of this simple diagram.

## 4.2 Equilibria Involving a Vapor and Two Immiscible Liquids

In the equilibria treated so far in this chapter the phases concerned were solid pure substances and liquid solutions. A wholly similar treatment can be applied to the case of liquid pure substances in equilibrium with gaseous solutions. The formal thermodynamic treatments are identical, since only one phase of variable composition (liquid solution or gaseous solution) is involved.

If two immiscible pure substances, such as water and decane,  $C_{10}H_{22}$ , are shaken together in a closed vessel in the absence of air, the ultimate pressure of the vapor will be the sum of the vapor pressures of the two liquids at the particular temperature. Both the composition and the total pressure of the vapor are independent of the relative amounts of the two liquids and depend only on the temperature. A knowledge of the vapor-pressure curve of each liquid makes it possible to calculate the temperature at which the total pressure would have any particular value, say 1 atm. This temperature is necessarily below the normal boiling point of either liquid. Advantage is taken of this fact in the technique of steam distillation, whereby impurities can be removed by distillation at reduced temperature. This is particularly advantageous for compounds which decompose readily at the normal boiling point. The immiscibility of the two liquids in the distillate renders separation easy. The process can be performed by distilling an emulsion of the substance in water, but is commonly effected by introducing steam from a separate source. While the process does not necessarily occur under equilibrium conditions, the assumption of equilibrium leads to the prediction that the composition of the distillate in terms of mole ratio is identical with the corresponding ratio of the partial pressures.

At 96.8°C the vapor pressure of an intimate mixture of decane

and water is 760 mm, the respective partial pressures being 83 and 677 mm. At atmospheric pressure the mixture will boil at 96.8°C giving a distillate with a mole ratio (decane/water) of  $\frac{83}{677} = 0.123$ . This corresponds to 49% by weight of decane. This information is shown in Figure 4.5; the tie lines  $PW$  and  $PD$  indicate that a vapor of composition  $P$ , 49% decane, can exist in equilibrium simultaneously with water,  $W$ , and with decane,  $D$ , at 96.8°C and 1 atm. Since the liquids are immiscible, the line  $WD$  is *not* a tie line and there are no tie lines below this temperature.

If a vapor of composition  $P$  is cooled, it will yield a mixture of the two liquids having the same composition; at 1 atm pressure the condensation will take place, under equilibrium conditions, at 96.8°C.

If the composition of the vapor is different from  $P$ , the condensation will begin at a temperature higher than 96.8°C. Furthermore, the composition of the first condensate will be one or the other of the pure liquids. For example, if a vapor having the composition and temperature

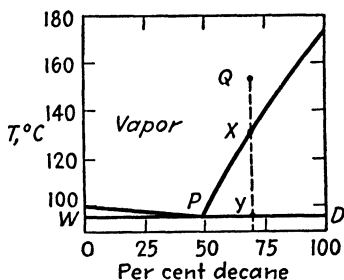


FIG. 4.5 Phase diagram for the system decane-water at 1 atm.

$Q$  is cooled, it will become saturated with respect to liquid decane at the temperature  $x$ ; at this temperature the partial pressure of decane in the vapor coincides with the vapor pressure of liquid decane. If the temperature is reduced below  $x$ , the vapor pressure of liquid decane will become less than the partial pressure of decane in the vapor and under equilibrium conditions liquid decane will therefore condense from the vapor. The partial pressure of decane in the vapor is therefore reduced until it again coincides with the vapor pressure of liquid decane. As the temperature of the system is lowered from  $x$  to  $y$  (and the vapor pressure of liquid decane is lowered correspondingly), the composition of the vapor will follow the path  $xP$ . On reaching the temperature  $y$ , the weights of decane and vapor will be in the ratio  $Py/yD$ . The vapor  $P$  is saturated also with liquid water. Further removal of heat will, under equilibrium conditions, cause the simultaneous condensation of water and decane. The system will then consist of three phases and be invariant at fixed pressure. The temperature will remain at 96.8°C and

the composition of the vapor at 49% decane until condensation is complete. The cooling of a vapor containing less than 49% decane will result in the condensation of water at temperatures lying below the saturation curve, followed by simultaneous condensation of both liquids at 96.8°C.

The close similarity of the behavior of this system to those showing a simple binary eutectic is quite apparent. The physical states (solid, liquid, gas) of the phases involved are not important in determining the form of the phase diagram or the types of phase changes encountered. This comprehensive character of the principles of heterogeneous equilibrium will become increasingly apparent as more examples are discussed.

### 4.3 Binary Compounds, Melting Congruently

Systems having congruently melting binary compounds can be illustrated by reference to Figure 4.6 for the system magnesium-copper. In addition to the components magnesium (m.p. 648°C) and copper (m.p. 1085°C), two other pure substances, the intermetallic compounds  $\text{MgCu}_2$  and  $\text{Mg}_2\text{Cu}$ , are encountered. These binary compounds melt congruently at 800 and 580°C, respectively; the melting points are maxima in the liquidus curve. Points on the liquidus curve between 0 and 9.4% magnesium represent the compositions of liquid solutions which can exist in equilibrium with solid copper; between 9.4 and 34% magnesium, in equilibrium with the solid compound  $\text{MgCu}_2$ ; between 34 and 65% magnesium, in equilibrium with the solid compound  $\text{Mg}_2\text{Cu}$ ; between 65 and 100% magnesium, in equilibrium with solid magnesium.

It is evident that at any temperature between 680 and 800°C, the compound  $\text{MgCu}_2$  can exist in equilibrium with either of two solutions of different composition, one containing less than 16%, the other more than 16% magnesium. The three phases cannot, however, coexist in equilibrium simultaneously, since, according to the phase rule, a three-phase equilibrium in a two-component system at fixed pressure can occur only at a unique temperature. Thus the compound can be involved in equilibria with solutions containing less than 16% *or* with solutions containing more than 16% magnesium; solutions containing less than 16% magnesium cannot be involved in equilibria with solutions containing more than 16%. Since systems containing less than 16% magnesium

do not involve phases containing more than 16%, the diagram can be divided at this composition without loss of generality. Similar reasoning would suggest a second division at the composition of the compound  $\text{Mg}_2\text{Cu}$ . The complex diagram is thus resolved into three portions, each of which is similar to those shown in Figures 4.1 to 4.4.

If a binary compound melts incongruently, as in the case of Glauber's salt (Figure 3.3), the phase diagram cannot be divided at that composition. This is evident, for the composition of the compound which melts incongruently must lie between the composi-

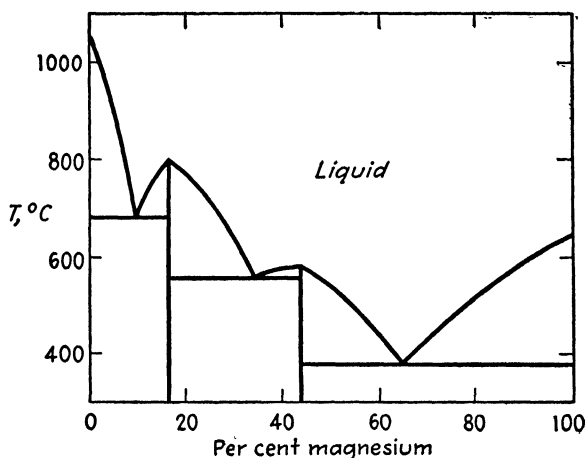


FIG. 4.6 Phase diagram for the system magnesium-copper.

tions of the decomposition products with which the compound can coexist in equilibrium. In general, then, division of a diagram is permissible only at a composition corresponding to a compound (as shown by agreement with the law of reacting weights) and at which a maximum occurs in the solubility curve of the compound.

#### 4.4 Binary Compounds, Melting Incongruently

A system having an incongruently melting compound has already been exemplified in the treatment of the system sodium sulfate-water in Chapter 3; the binary compound Glauber's salt melts incongruently at  $32.4^\circ\text{C}$ . Compounds which melt incongruently occur commonly in both inorganic and organic systems.

The system benzhydrol-benzene, Figure 4.7, shows an equimolecular binary compound which melts incongruently at  $29.5^{\circ}\text{C}$  to give solid benzhydrol and a liquid solution containing 55% benzhydrol (45% benzene). There is a eutectic point at  $1.5^{\circ}\text{C}$ , 20% benzhydrol; a liquid of this composition can exist in equilibrium with benzene and the binary compound simultaneously at this temperature. The similarity between Figures 3.3 and 4.7 is quite apparent.

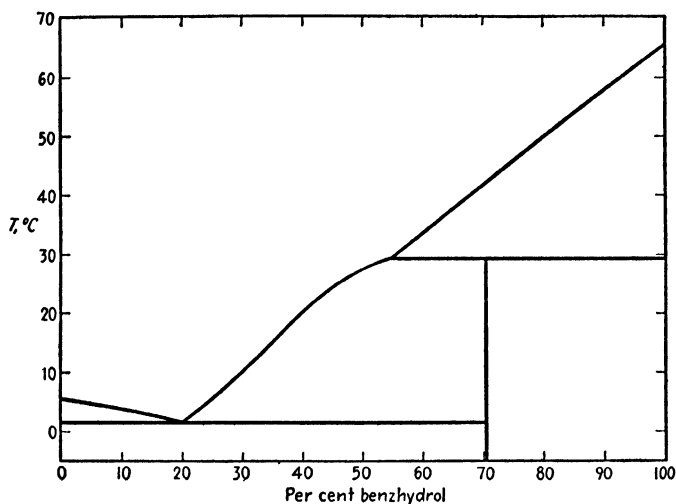


FIG. 4.7 Phase diagram for the system benzhydrol-benzene.

### EXERCISES

1. Assuming equilibrium conditions, describe completely the system 50% naphthalene, 50% menthol at  $40^{\circ}\text{C}$ .
2. Assuming stable conditions, describe the composition of the system consisting of 80% cadmium, 20% bismuth at  $100^{\circ}\text{C}$  in terms of (a) the phase constituents and (b) the eutectic solid and one of the pure metals.
3. Draw a representative temperature-time curve for the cooling, under equilibrium conditions, of a melt composed of 30% bismuth, 70% cadmium from  $325$  down to  $125^{\circ}\text{C}$ . Trace the paths of the representative points of the liquid and the whole solids during this cooling.
4. With reference to Figure 4.6, justify the classification of the solids having the compositions 16% magnesium, 84% copper, and 43% magnesium, 57% copper as compounds.
5. Trace the paths of the representative points of the liquid and the

whole solids during the equilibrium cooling of a melt consisting of 25% magnesium, 75% copper to complete solidification.

6. Draw a temperature-time curve for the cooling from 800 to 300°C of a melt containing 75% potassium chloride, 25% lithium chloride, (a) assuming some undercooling to take place, (b) assuming no undercooling.

7. Over the range 90 to 100°C the vapor pressure of water (in millimeters) can be represented with sufficient accuracy by the equation  $\log p = 8.688 - (2167/T)$  and that of *n*-nonane over the range 90 to 180°C by the equation  $\log p = 6.9351 - [1428.8/(T - 71.54)]$ . Construct the phase diagram for the system nonane-water at 1 atm over the range of temperature from 90 to 180°C. *T* is the Kelvin temperature.

## CHAPTER 5

### TWO-COMPONENT SYSTEMS. TYPES OF EQUILIBRIA INVOLVING MORE THAN ONE PHASE OF VARIABLE COMPOSITION

#### 5.1 Classification

In the equilibria discussed in Chapters 3 and 4, only *one* of the phases was a solution. In the present chapter consideration will be given to systems in which more than one solution phase can participate in an equilibrium. Such systems can be conveniently classified according to the physical states of the solutions. The complete miscibility of gases excludes the possibility of more than one gaseous solution participating in an equilibrium. The five possible classes of equilibria involving two solution phases are:

|                                  |                |
|----------------------------------|----------------|
| Liquid solution-liquid solution  | ( <i>L-L</i> ) |
| Solid solution-solid solution    | ( <i>S-S</i> ) |
| Liquid solution-solid solution   | ( <i>L-S</i> ) |
| Liquid solution-gaseous solution | ( <i>L-V</i> ) |
| Solid solution-gaseous solution  | ( <i>S-V</i> ) |

Since the first three classes concern only condensed phases, the treatment of these equilibria will be restricted to isobaric conditions, *i.e.*, the variables will then be temperature and composition. Equilibria of the *S-V* type will not be discussed in the present treatment since they are relatively unimportant and have not been extensively investigated. Their interpretation will be apparent from consideration of the *L-V* equilibria, which will be discussed in terms of both fixed pressure and fixed temperature. Following this, consideration will be given to more general types of two-component systems, the interpretation of which can be resolved in terms of simpler diagrams.

## 5.2 Liquid Solution-Liquid Solution

The system phenol-water (Figure 5.1) affords an example of this type of equilibrium. At temperatures above 66°C phenol (m.p. 41°C) and water are miscible in all proportions. At temperatures between 41 and 66°C the liquid components are only partially miscible. For example, if phenol is added to water at 50°C in successive small amounts, it will dissolve to form a homogeneous liquid solution, until the composition of the system as a whole exceeds 11.8% phenol. If more phenol is added the system will be found

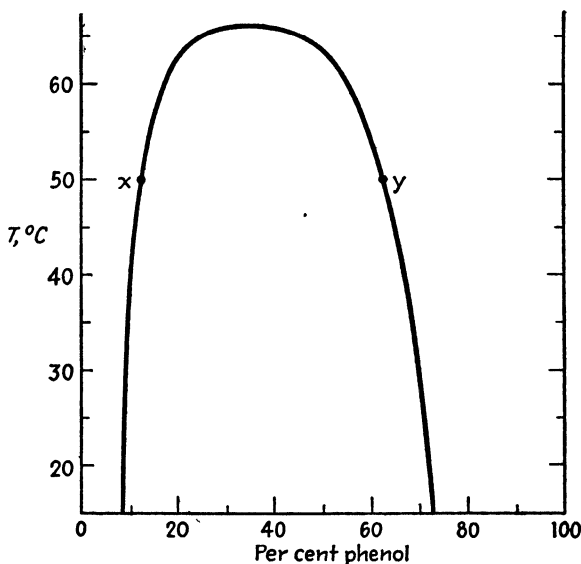


FIG. 5.1 Conjugate liquid solutions in the system phenol-water at 1 atm.

to consist of two liquid phases which readily form an opalescent emulsion on being stirred. Under equilibrium conditions one phase will be a solution of composition 11.8% phenol, 88.2% water; the other phase will be a solution of composition 62.6% phenol, 37.4% water. If sufficient phenol is added to make the over-all composition of the system greater than 62.6% phenol, the system will again consist of a single liquid phase. Alternatively, the same range of immiscibility can be demonstrated by the addition of water to phenol. In the range of over-all composition between 11.8 and 62.6% phenol, the compositions of the two phases will remain fixed

at 11.8 and 62.6% phenol, respectively; the relative amounts of the phases will depend on the over-all composition of the system and can be computed with the aid of the proportioning rule. The compositions of these phases are designated as  $x$  and  $y$  in Figure 5.1. It can be shown that phases having these compositions can exist in equilibrium at 50°C by applying the usual criteria; the corresponding equilibrium process is the simultaneous transfer of both phenol and water between the phases. Solutions such as  $x$  and  $y$ ,

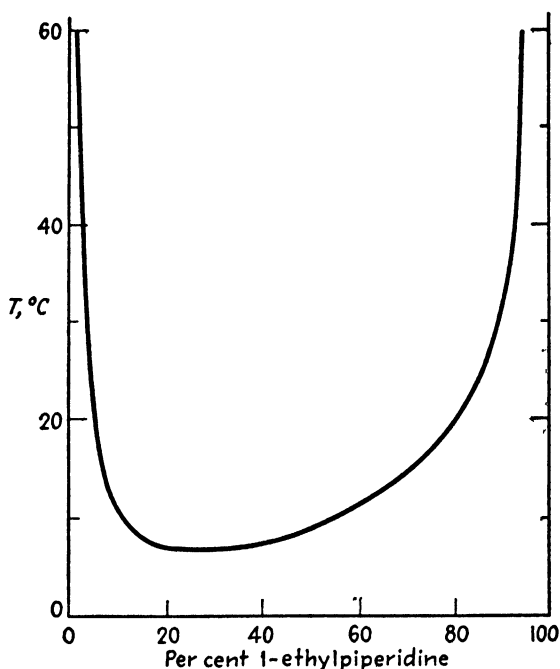


FIG. 5.2 The system 1-ethylpiperidine-water.

which can coexist in equilibrium, are said to be *conjugate solutions*; their representative points can be joined by a tie line.

As shown in Figure 5.1 the range of coexistence of conjugate solutions extends below the melting point of phenol. This diagram is incomplete in that it does not indicate known equilibria involving such additional phases as ice, solid phenol, and the hydrate of phenol,  $2\text{C}_6\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ . It is apparent that the compositions of the conjugate solutions approach one another as the temperature

is raised and become identical (34% phenol) at the *critical solution temperature* or *consolute temperature*, 66°C.

The phase diagram can be conveniently determined in the laboratory by thermal analysis. Weighed samples of phenol and water are mixed to give a system of desired over-all composition. The system is stirred and the temperatures noted at which opalescence disappears on heating and appears on cooling. If the rates of heating and cooling are sufficiently slow, the two temperatures will be

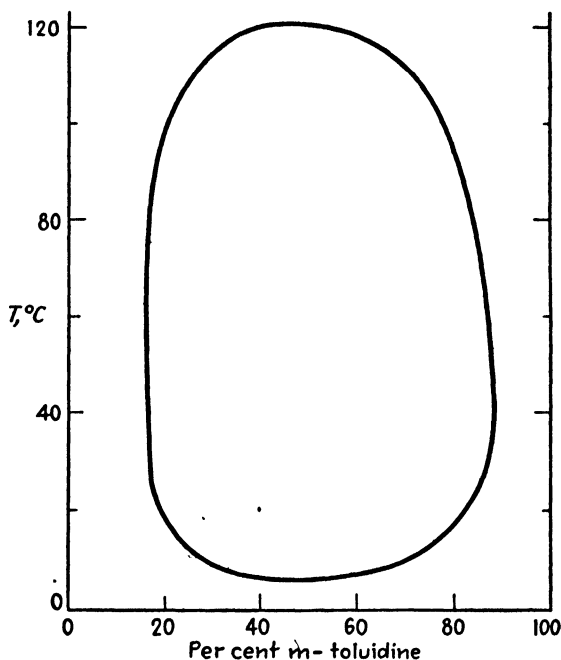


FIG. 5.3 The system *m*-toluidine-glycerol.

identical and this temperature together with the composition of the system will comprise a point on the phase diagram. By selecting a series of over-all compositions, the whole of the liquid-liquid phase diagram can be obtained.

In the system phenol-water the critical solution temperature is the *upper* limit of the temperature at which conjugate solutions can exist. In a few systems, *e.g.*, 1-ethylpiperidine-water (Figure 5.2), the critical solution temperature is a *lower* limit. Below 7.45°

C the liquid components are miscible in all proportions; only above this temperature are conjugate liquid solutions formed. The critical solution composition is 30% 1-ethylpiperidine. A number of systems, *e.g.*, *m*-toluidine-glycerol (Figure 5.3), show both a maximum and a minimum critical solution temperature; the consolute points for this particular system are 6.7°C, 54% *m*-toluidine and 120.5°C, 53% *m*-toluidine.

### 5.3 Solid Solution-Solid Solution

Nature affords so many commonplace examples of miscibility in both the gaseous and liquid states that the phenomenon is accepted without question. The completely random structure assigned to gases suggests their complete miscibility; the limited regularity assigned to the structure of liquids suggests their miscibility (at least partial), especially if both are either polar or nonpolar. On the other hand, solid pure substances are assigned a regular lattice structure; their miscibility demands the admission of the one component into the regular lattice structure of the other. Similarities of lattice structure, of size of unit cell, and of valency type might be expected to enhance such admission. The isomorphous alums which have identical crystal form and are of the same valency type, are found to be completely soluble in one another in the solid state. Other examples of complete miscibility in the solid state are found in such pairs as Pt-Au, Cu-Mn, MgO-NiO,  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ , and thiophene-benzene. Many examples of limited miscibility and immiscibility in the solid state are known.

A solution may be defined as a phase having properties which vary *continuously* as the proportions of the solution constituents are varied. This definition must, of course, apply for a solid solution. The extremely slow rate of diffusion in solids makes it most difficult to form solid solutions by direct contact of the solution constituents. In general they are formed more readily by crystallization from a binary melt (*cf.* the system Pt-Au, Figure 5.7) or by crystallization from a ternary solution consisting of the two solution constituents and a common solvent (*e.g.*, the crystallization of mixed alums from aqueous solution). The solids produced by any one of these three methods usually show variations of composition throughout the solid, at least initially. This is readily appreciated in the formation of brass. If brass were formed by placing copper and zinc in direct contact at a temperature below their melting

points, it is apparent that the slow interdiffusion of the constituents would give rise to a variation of composition ranging from pure copper at one extreme to pure zinc at the other. Homogeneity can be more rapidly achieved by "working" the alloy (analogous to stirring an inhomogeneous liquid solution) or by annealing it at a temperature slightly below its melting point (to give a high rate of diffusion). If a solution of the constituents *A* and *B* is formed by precipitation, either from the binary melt or from a ternary liquid solution, the ratio of *A* to *B* in the solid will generally differ from the ratio obtaining in the liquid. As a result the ratio of *A* to *B* in the liquid will change as the crystallization proceeds, thus pro-

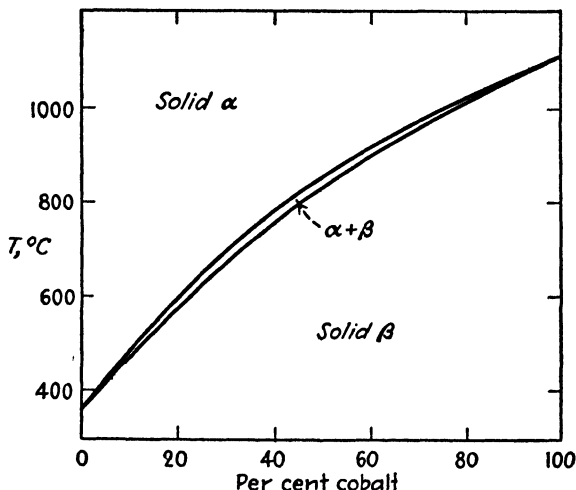


FIG. 5.4 The system nickel-cobalt.

ducing a concomitant change in the composition of the solid phase during crystallization, with a resultant lack of homogeneity. This can be overcome as described above.

Many systems having conjugate solid solutions are known. The system Ni-Co (Figure 5.4) shows this behavior. Nickel undergoes a transition from a magnetic to a nonmagnetic condition at 363°C; cobalt undergoes a similar change at 1103°C. These two components form both magnetic,  $\beta$ , and nonmagnetic,  $\alpha$ , solid solutions, which can exist in equilibrium over the range of compositions and temperatures shown in the diagram. The field of conjugate solid solutions is indicated by  $\alpha + \beta$ .

The system Mg-Cd (Figure 5.5) has two fields of conjugate solid solutions, conjoined at  $248^{\circ}\text{C}$  and 17% magnesium. This composition is that of a pure substance, the intermetallic compound MgCd. As might be predicted from considerations similar

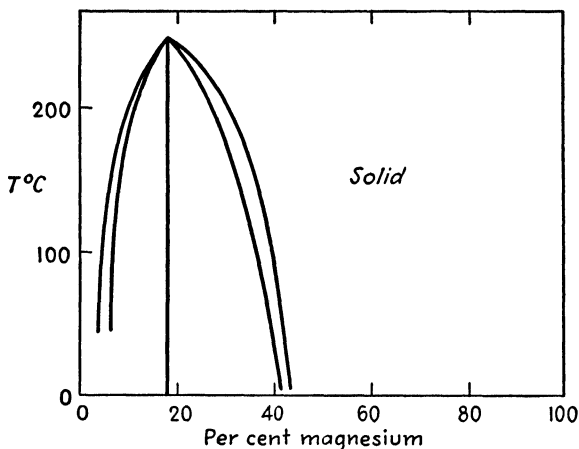


FIG. 5.5 The system magnesium-cadmium.

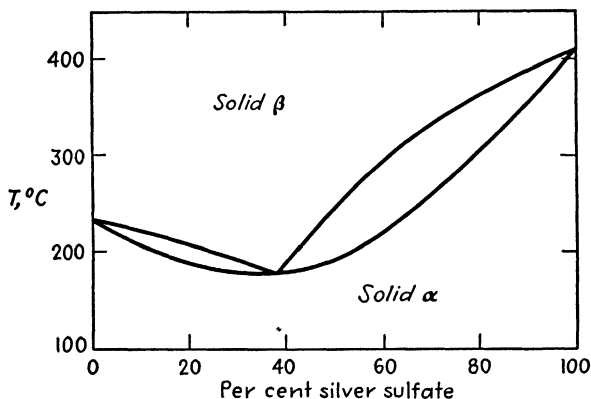


FIG. 5.6 The system silver sulfate-sodium sulfate.

to those set forth in Section 4.3, the diagram can be divided at the composition of this compound. It is apparent that the two portions of the diagram are completely independent and that each is similar in form to Figure 5.4.

Sodium sulfate undergoes a transition of crystalline form at 234°C and silver sulfate at 412°C. It is apparent from Figure 5.6 that  $\alpha$ -Na<sub>2</sub>SO<sub>4</sub> and  $\alpha$ -Ag<sub>2</sub>SO<sub>4</sub> are completely miscible at temperatures below 177°C. The corresponding  $\beta$  forms are completely miscible at temperatures above 412°C. Between these two extremes of temperature there exist two fields of conjugate solid solutions. The solid solution containing 38% silver sulfate undergoes the  $\alpha \rightleftharpoons \beta$  transition *congruently* at 177°C. The composition corresponding to the congruent transition is not that of a binary compound and hence might be expected to vary if the system were subjected to very high pressures.

#### 5.4 Liquid Solution-Solid Solution

There are many examples of equilibrium between liquid solutions and solid solutions. The simplest type of phase diagram for this kind of equilibrium is illustrated in Figures 5.7, 5.8, and 5.9. The similarity between these diagrams and that for the system Ni-Co is evident; the only essential difference is that here one of the conjugate solutions is a liquid. The locus of the point representing the liquid solution is known as the *liquidus* curve; the locus for the conjugate solid solution is the *solidus* curve.

If either of the components of a binary system can exist as a solid in equilibrium with binary liquid solutions, then that component can be obtained as a solid pure substance by simple crystallization. If, however, the solid in equilibrium with a liquid solution is itself a solution, successive *fractional* crystallization must be used. The process of fractional crystallization can be illustrated with reference to the system Pt-Au (Figure 5.7). A solid solution containing, say, 20% platinum, 80% gold is heated somewhat above its liquidus temperature (1320°C). On cooling the liquid under equilibrium conditions crystallization will begin at this temperature. As shown by the diagram, the first solid formed will be a solution of composition 62% platinum, 38% gold. Since this solid solution is enriched in platinum, the conjugate liquid solution must be impoverished in that component. As crystallization proceeds the point representing the liquid solution will follow the path of the liquidus curve in the direction of decreasing proportion of platinum; simultaneously the corresponding solidus point will follow the path of the solidus curve, also in the direction of decreasing proportion of platinum. At any temperature the

proportions of liquid and solid present can be computed with the aid of the proportioning rule applied to the appropriate tie line. It must be emphasized that the proportions calculated in this way will agree with experiment only if equilibrium conditions obtain, *i.e.*, provided that both the liquid and the solid solutions are homogeneous and in equilibrium at their interface. If the process of crystallization occurs rapidly and diffusion but slowly, it is clear that the solid will not be homogeneous, but will consist of successive layers of varying composition.

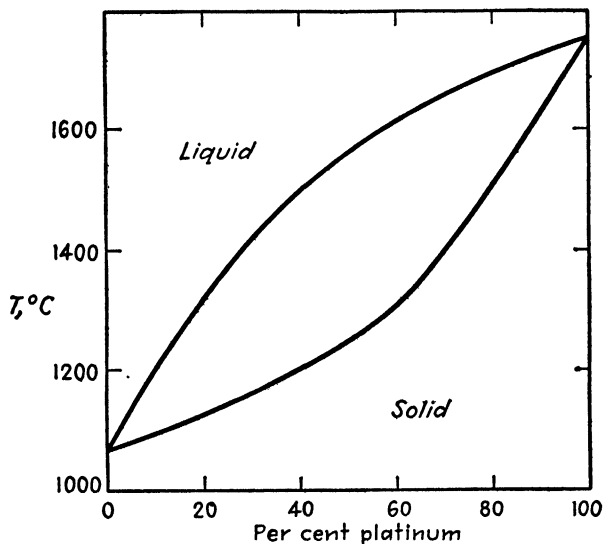


FIG. 5.7 The system platinum-gold.

If crystallization is interrupted after a *small* proportion of solid has formed, its composition will be approximately 62% platinum. This solid can then be removed, melted, and again partially crystallized. The liquid containing 62% platinum has a freezing point of 1630°C and the composition of its conjugate solid is 90% platinum. Repetition of this procedure would yield decreasing quantities of solid containing an increasing proportion of platinum, until ultimately a small quantity of practically pure platinum could be obtained.

The same initial solid, 20% platinum, 80% gold, could be made to yield practically pure gold. The melting point of the solid solu-

tion is 1130°C. If only a small proportion of the solid were melted the composition of the liquid formed would be approximately 95% gold, 5% platinum. Complete solidification of this liquid would occur at 1080°C. Successive partial liquefaction could ultimately yield a small quantity of practically pure gold.

Of considerable interest to the mineralogist is the system albite-anorthite,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ - $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , Figure 5.8. These two compounds form a complete range of solid solutions below 1100°C and are completely miscible in the liquid state above 1550°C.

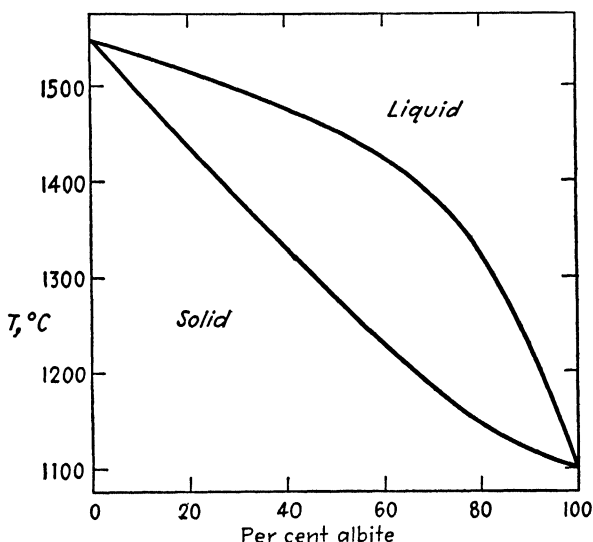


FIG. 5.8 The system albite-anorthite.

Between these temperatures there exists a series of conjugate liquid and solid solutions. The liquid solutions are richer in albite than the corresponding solid solutions.

Behavior similar to that cited above is shown by the organic system *p*-dibromobenzene-*p*-chlorobromobenzene, Figure 5.9. The former melts at 87.30°C, the latter at 64.58°C. It should be noted that the spread of composition between the liquidus and solidus curves is rather small in this system. Separation of the components by fractional crystallization would therefore require many successive steps. The effect of concentration spread on

the ease of separation will be discussed more extensively in connection with liquid-vapor equilibrium.

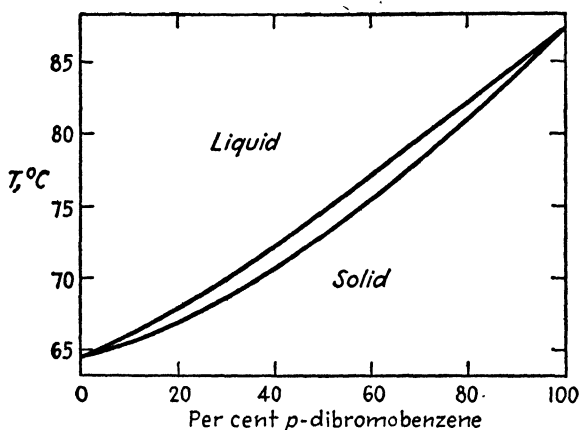


FIG. 5.9 The system *p*-dibromobenzene-*p*-chlorobromobenzene.

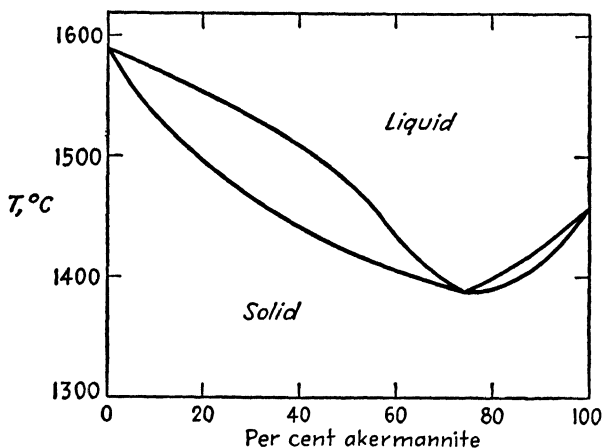


FIG. 5.10 The system åkermannite-velardeñite,  $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ - $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ .

In the diagrams of Figures 5.7 to 5.9 the liquidus and solidus curves lie completely between the melting points of the two components. There are many examples of systems in which conjugate liquid and solid solutions occur at temperatures lower than the melting point of either component, *e.g.*, Figure 5.10, for the system

åkermannite-velardeñite,  $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ - $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ . Systems rarely have conjugate liquid and solid solutions at temperatures above the melting point of either component; one of the few known examples is given in Figure 5.11 for the system lead-thallium. In both diagrams there is one unique composition for which the solid solution melts congruently. If a liquid solution of the unique composition were cooled slowly to solidification, the form of the corresponding temperature-time curve would be identical with that obtained in the cooling of a liquid pure substance (Figure 2.1). The constancy of temperature during solidification would show that the two-phase system, liquid-solid, is invariant

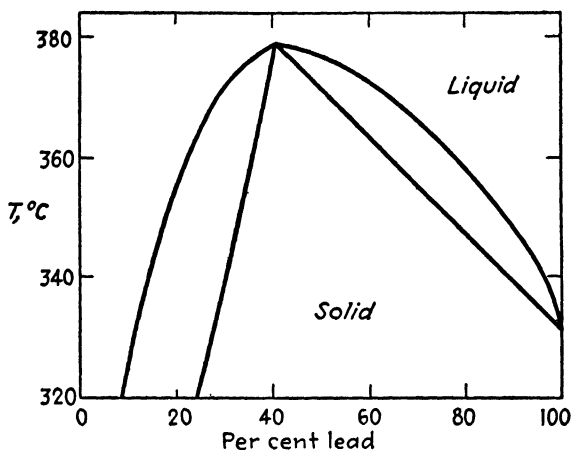


FIG. 5.11 The system lead-thallium.

at constant pressure. A system which melts congruently can, indeed, be considered as a one-component system, inasmuch as a single composition variable is sufficient to describe the composition of both the liquid and solid phases. While the thermal behavior corresponds to that of a pure substance, the system can only be accepted as a pure substance if it meets the further criteria, (1) that the composition satisfy the law of reacting weights and (2) that the congruent character of the melting point be unaffected by change of pressure. The latter criterion is difficult to apply; the former is usually considered sufficient. Neither the minimum of Figure 5.10 at 74% nor the maximum of Figure 5.11 at 41% cor-

responds to a pure substance. The maximum of Figure 5.5, on the other hand, corresponds precisely to the composition MgCd.

Fractional crystallizations in systems such as those of Figures 5.10 and 5.11 show limitations not encountered in systems such as Pt-Au (Figure 5.7). For example, a melt consisting of 80% lead, 20% thallium can be made to yield pure lead by fractional crystallization, but not pure thallium. Starting with a melt of this composition it would be impossible to obtain a phase containing more than 59% thallium, the composition corresponding to the congruently melting solution. In general, systems having a solution which undergoes transition to another phase congruently have a limitation of this kind.

### 5.5 Liquid Solution-Gaseous Solution. Constant Pressure

The existence of conjugate liquid and gaseous solutions is well known and is the basis of fractional distillation. It will be seen that the forms taken by the phase diagrams for  $L$ - $V$  equilibria are similar to those already encountered for  $S$ - $S$  and  $L$ - $S$  equilibria. For example, the phase diagram for the system chloroform-benzene (Figure 5.12) is similar to those for the systems Pt-Au (Figure 5.7) and Ni-Co (Figure 5.4), the only essential difference being in the physical states of the solutions.

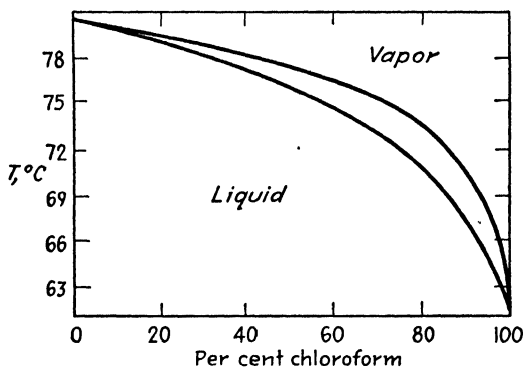


FIG. 5.12 The system chloroform-benzene at 750 mm.

In order to determine the phase diagram of Figure 5.12 experimentally it is necessary to obtain the boiling points of the two components and of solutions of various intermediate compositions. In addition it is necessary to know the composition of the vapor

which can exist in equilibrium with each liquid solution. All of these determinations would have to be made at a common pressure or be suitably corrected.

The usual experimental procedure for determining the lower, or boiling-point, curve is to boil the liquid gently under total reflux with the thermometer immersed in the *liquid*.<sup>1</sup> If sufficient liquid is used, its composition will not be appreciably modified by the small amount of vapor and returning condensate. The composition of the vapor in equilibrium with any liquid can be determined by analysis of a small sample of condensate. The analysis is frequently accomplished by measuring some property which shows appreciable dependence on composition, *e.g.*, refractive index or density. The composition and boiling temperature of the liquid and the composition of the conjugate vapor give the points required for plotting the phase diagram.

A solution containing, say, 30% chloroform, 70% benzene can be fractionated by a method analogous to that described in the discussion of the system Pt-Au. At 750 mm pressure this solution will boil at 78.3°C, yielding a vapor containing 39.5% chloroform. The liquid obtained on condensing this vapor will boil at 77.2°C, yielding a vapor containing 52.2% chloroform. Successive fractionations of this nature would yield the data shown in Table 5.1.

TABLE 5.1 FRACTIONATION OF A BENZENE-CHLOROFORM SOLUTION

| BOILING POINT, °C | LIQUID, %<br>CHLOROFORM | VAPOR, %<br>CHLOROFORM | TOTAL NUMBER OF<br>FRACTIONATIONS |
|-------------------|-------------------------|------------------------|-----------------------------------|
| 78.3              | 30.0                    | 39.5                   | 1                                 |
| 77.2              | 39.5                    | 52.2                   | 2                                 |
| 75.9              | 52.2                    | 68.3                   | 3                                 |
| 73.6              | 68.3                    | 82.4                   | 4                                 |
| 70.8              | 82.4                    | 92.0                   | 5                                 |
| 67.2              | 92.0                    | 97.1                   | 6                                 |
| 64.0              | 97.1                    | 99.0                   | 7                                 |

For the calculations leading to the data of Table 5.1 it was assumed that the amount of material removed as vapor during each fractionation was negligibly small compared with the amount of liquid remaining. If an appreciable amount of vapor were re-

<sup>1</sup> Various types of apparatus have been devised to avoid the effect of superheating the liquid in this operation.

moved in the first fractionation, the percentage of chloroform in this vapor, while initially 39.5%, would decrease as vaporization impoverished the liquid in chloroform. It is clear that with a finite take-off at each fractionation, seven successive fractionations would yield a vapor containing less than 99% chloroform. Furthermore, if even as much as 10% of the liquid were vaporized in each successive fractionation, the ultimate yield of this final vapor would amount to only one ten-millionth of the initial weight of starting material. Clearly, this is not a practical method of separation. The difficulty is overcome by the use of *fractionating columns*, of which there are many types.

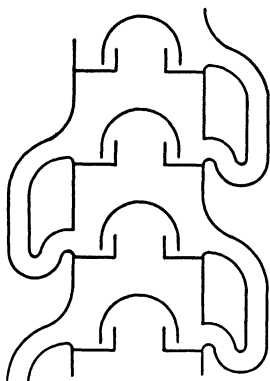


FIG. 5.13 Cross section of a bubble-cap column.

A "bubble-cap" fractionating column is illustrated in Figure 5.13. Such a distilling column is affixed to the top of the boiling flask. On boiling a solution of chloroform and benzene, say 30% chloroform, at a barometric pressure of 750 mm the vapor leaving the flask will contain approximately 39.5% chloroform, as shown in Table 5.1. The lower temperature of the column will cause some condensation of the vapor. The latent heat of condensation will raise the temperature of the column, but never as high as that of the liquid in the boiler. The condensation will only be partial and hence the remaining vapor will be enriched in chloroform.

Thus at each bubble-cap unit incoming vapor will be forced to bubble through liquid; partial condensation will occur and vapor enriched in chloroform will rise to the next higher unit. Excess condensate will pass through overflow tubes to the next *lower* unit. In a multiple-unit column there will be, then, an upward flow of vapor becoming enriched in the more volatile component at each successive unit and in the opposite direction a simultaneous counterflow of liquid becoming enriched in the less volatile component. A condenser may be placed at the top of the column so as to condense all of the enriched vapor leaving the last bubble-cap unit and return this condensate to the column. The column would then be operated at *total reflux*; under these conditions a steady state would be achieved with respect to temperature gradient up

the column and with respect to composition gradient of both vapor and liquid. The composition of the condensate at the top of the column would, of course, be identical with that of the vapor leaving the uppermost unit of the column. If this composition were found to be 99.0% chloroform, the column would be said to have *six theoretical plates*. It is apparent from Table 5.1 that a vapor of this composition would be obtained from the initial solution by *seven* successive fractionations under equilibrium conditions. In the operation with the column, the first fractionation occurs at the surface of the boiling liquid; the vapor entering the column would contain approximately 39.5% chloroform. The further separation achieved by the use of the column would thus be equivalent to *six* additional successive fractionations under equilibrium conditions; for this reason the column is said to have *six* theoretical plates.

It is found in practice that the continuous removal of a small proportion of enriched vapor by condensation into a receiver does not seriously alter the number of theoretical plates of a column. The proportion of take-off may be expressed in terms of the *reflux ratio*, *i.e.*, the ratio of the amount of liquid returned to the column to the amount diverted to the receiver. The effective number of theoretical plates for any given column is found in practice to depend on many factors, such as the reflux ratio, throughput, heat losses and, of course, the construction of the column. The number of theoretical plates of a bubble-cap column is always less than the number of bubble-cap units. Many different types of columns are used for fractional distillation; their design, construction, and operation comprise an important part of chemical engineering; their efficiency is always determined with reference to a known liquid-vapor phase diagram. Since the efficiency of any column invariably increases with its height, it is customary to compare different columns in terms of the height equal to a theoretical plate (H.E.T.P.); the smaller the value of the H.E.T.P. the more effective is the column construction.

While at first glance it might be thought that the number of theoretical plates required to achieve a particular separation would depend primarily on the difference in the boiling points of the components, it is apparent from the discussion above that the important factor is the spread between the compositions of the conjugate liquid and vapor solutions concerned. This is sometimes

shown by plotting the composition of the vapor against that of the conjugate liquid, as shown in Figure 5.14. If the compositions of the conjugate solutions were identical, the plot would follow the dashed line of unit slope. The deviation of the experimental curve from the straight line is a measure of the ease with which the components can be separated by fractional distillation. The number of theoretical plates required for a particular separation can be determined by means of this diagram. The curve shows that the vapor in equilibrium with a liquid containing 30% chloroform has the composition 39.5% chloroform, as indicated by the ordinate of  $x$ . A line drawn horizontally from  $x$  cuts the

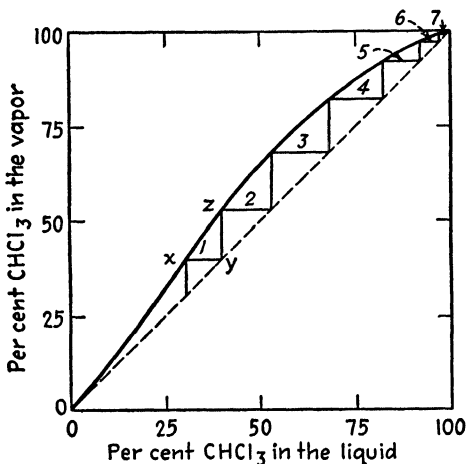


FIG. 5.14 The system chloroform-benzene at 750 mm.

dashed line at  $y$ ; since the dashed line has unit slope, the abscissa of  $y$  is 39.5% chloroform. Thus the compositions of both liquid and conjugate vapor can be read from the bottom scale. A vertical line drawn through  $y$  establishes the point  $z$  which represents, on the bottom scale, the composition of the liquid of the next theoretical plate. The horizontal lines 1 to 7 thus represent the separations achieved at successive theoretical plates. It should be noted that although Figure 5.14 may be correctly called a liquid-vapor equilibrium diagram, it does not indicate the temperatures at which the equilibria obtain, as does Figure 5.12.

In contrast to the system chloroform-benzene discussed above,

he system benzene-ethanol (Figure 5.15) shows a *minimum* in the boiling-point curve, while the system chloroform-acetone (Figure 5.16) shows a *maximum*. The similarity of these latter diagrams

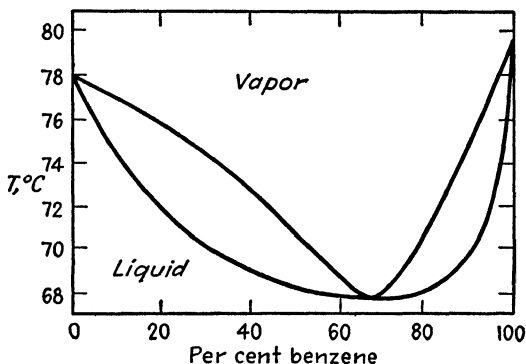


FIG. 5.15 The system benzene-ethanol at 750 mm.

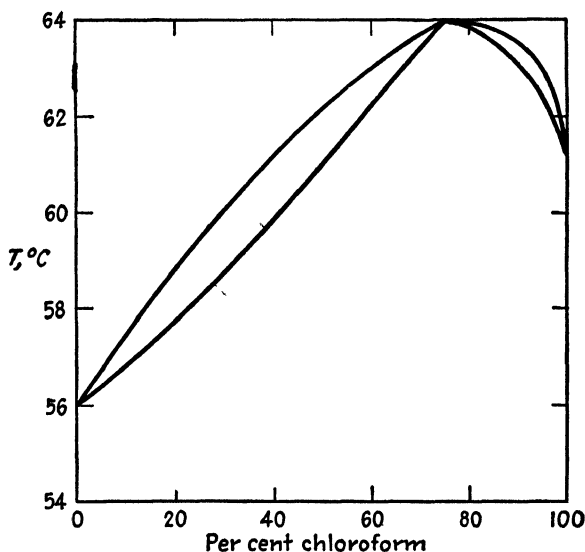


FIG. 5.16 The system chloroform-acetone at 750 mm.

to those of Figures 5.10 and 5.11 is apparent. A solution having a maximum or minimum boiling point is said to be *azeotropic*.<sup>1</sup>

<sup>1</sup> From *a*, negative, *zeo*, to distill, and *tropos*, condition.

Although such a solution vaporizes congruently, it is readily differentiated from a compound by the fact that the *composition* of the azeotropic solution is dependent on the pressure. The effect of pressure on the composition of the minimum-boiling azeotropic solution in the system ethanol-water is shown in Table 5.2.

TABLE 5.2 COMPOSITION OF THE AZEOTROPIC SOLUTION IN THE SYSTEM ETHANOL-WATER

| Pressure, mm . . . . | 100  | 200  | 400  | 760  | 1450 |
|----------------------|------|------|------|------|------|
| % ethanol . . . . .  | 99.8 | 97.5 | 96.0 | 95.8 | 95.4 |

It can be seen from Figure 5.15 that the ultimate distillate obtained by fractionation of a benzene-ethanol solution at 750 mm would have the composition 67% benzene; if the initial solution contained less than this proportion of benzene, the ultimate residue would be pure ethanol; if it contained more than this proportion the ultimate residue would be pure benzene. In the fractionation of chloroform-acetone solutions it is the *residue* which would approach the azeotropic composition, the ultimate distillate being one of the pure components.

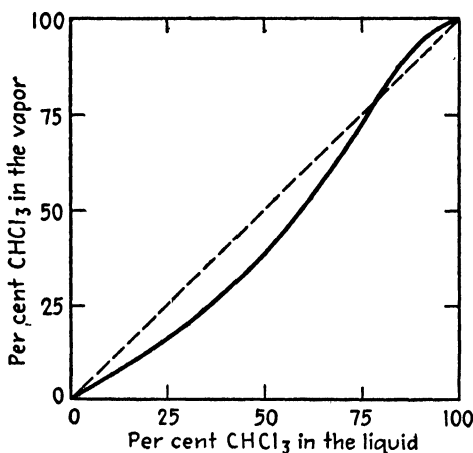


FIG. 5.17 The system chloroform-acetone at 750 mm.

In Figure 5.17 are given as abscissas and ordinates the compositions of the conjugate liquid and gaseous solutions in the system chloroform-acetone at 750 mm. In contrast to Figure 5.14, the

equilibrium curve *crosses* the line of unit slope; the intersection occurs, of course, at a composition common to both liquid and vapor, namely the azeotropic composition. If the exact composition of the azeotropic solution were not known, it could be readily determined by interpolation on this diagram. The precision would be better than that obtained by interpolation in a diagram of the form of Figure 5.16.

### 5.6 Liquid Solution-Gaseous Solution. Constant Temperature

In the previous section liquid-vapor equilibria were discussed for three typical systems at constant pressure. It is clear that such

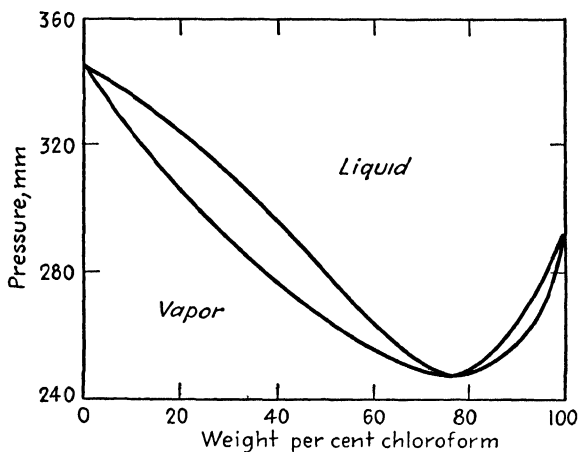


Fig. 5.18 The system chloroform-acetone at 35.2°C.

systems can be studied at a fixed temperature. The underlying factors will be illustrated with reference to the system chloroform-acetone. The method of determining the vapor pressure of a pure substance was discussed in Chapter 2; reference was made in Chapter 3 to the vapor pressure of a two-component system in which one of the components was nonvolatile. If, as in the system chloroform-acetone, both components are volatile, it is necessary not only to measure the vapor pressure, but also to determine the composition of the vapor phase.

Consideration of Figure 5.16 shows that at 56°C acetone has a vapor pressure of 750 mm. At the same temperature chloroform would be expected to have a vapor pressure less than 750 mm,

since at this pressure its boiling point is 61.2°C. The azeotropic solution, with a boiling point of 64°C, would be expected to be even less volatile. The vapor pressures of solutions of chloroform and acetone at 35.2°C are shown by the *upper* curve of Figure 5.18. As would be predicted, the azeotropic solution has the lowest vapor pressure. (It should be noted that at *this* pressure, 247 mm, the composition of the azeotropic solution differs slightly from that shown in Figure 5.16.)

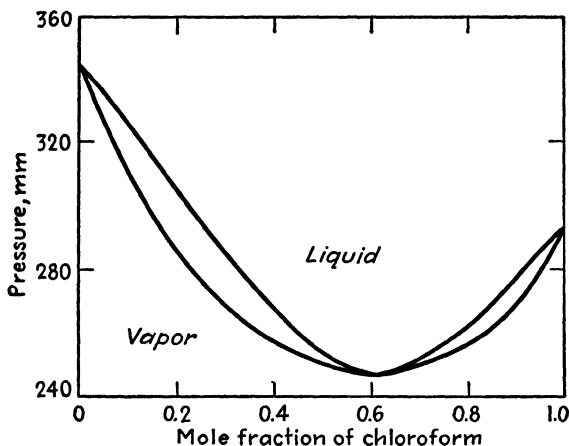


FIG. 5.19 The system chloroform-acetone at 35.2°C.

Composition, especially in the case of liquid-vapor systems, is frequently expressed in terms of the mole fraction, rather than the weight percentage, of one of the components. The mole fraction  $N_a$  of the component  $A$  is defined as the number of moles  $n_a$  of component  $A$  divided by the total number of moles of all the components. Thus for a solution of two components,  $A$  and  $B$ , of molecular weights  $M_a$  and  $M_b$ ,

$$N_a = \frac{n_a}{n_a + n_b} = \frac{w_a/M_a}{(w_a/M_a) + (w_b/M_b)}$$

in which  $w_a$  and  $w_b$  refer to the number of grams of the components  $A$  and  $B$ , respectively. The data of Figure 5.18 were converted in this way to give Figure 5.19.

The utility of the mole fraction will be apparent to those familiar

with Raoult's expression and its application to the thermodynamic treatment of liquid-vapor equilibria. Another important quantity used in this connection is the *partial vapor pressure* of a component, defined as the *partial pressure* of that component in the

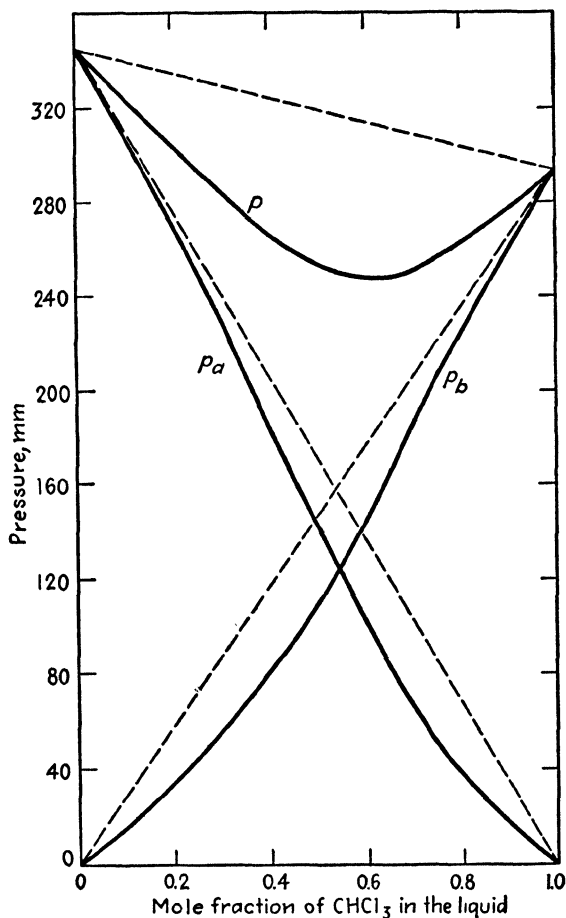


FIG. 5.20 Vapor-pressure data for the system chloroform-acetone at 35.2°C.

gaseous solution which can exist in equilibrium with a liquid solution. The partial pressure of component A is defined by the expression

$$p_a = N_a p$$

in which  $p$  is the total pressure exerted by the vapor and  $N_a$  is the mole fraction of  $A$  in the *vapor*. When  $p$  is the vapor pressure of a solution,  $p_a$  is the partial vapor pressure of component  $A$ . In Figure 5.20 the partial vapor pressure of acetone,  $p_a$ , and that of chloroform,  $p_b$ , are shown, together with the total vapor pressure,  $p$ , for the temperature 35.2°C. It is apparent from the definitions that  $p_a + p_b = p$ . Raoult's expression defines a system forming "ideal" solutions as one for which  $p$ ,  $p_a$ , and  $p_b$  are linear functions of the mole-fraction composition of the *liquid*, *i.e.*,

$$\begin{aligned} p_a &= N'_a p_a^0 & p_b &= N'_b p_b^0 \\ p &= p_a + p_b = N'_a p_a^0 + N'_b p_b^0 = (1 - N'_b) p_a^0 + N'_b p_b^0 \\ &= p_a^0 - (p_a^0 - p_b^0) N'_b \end{aligned}$$

in which  $p_a^0$  and  $p_b^0$  refer to the vapor pressures of the pure components;  $N'_a$  and  $N'_b$  are the mole fractions of the components in the *liquid*. The Raoult lines obeying the above equations are shown as dashed lines in Figure 5.20; this system shows considerable deviation from "ideality."

## 5.7 Combined $L$ - $V$ and $L$ - $L$ Equilibria

The equilibria considered so far in this chapter have involved only two phases, both of which were solutions. It is possible to have three-phase equilibria in a two-component system. If all three phases were solutions, the following equilibria would be possible:  $L$ - $L$ - $V$ ,  $L$ - $S$ - $S$ ,  $L$ - $L$ - $S$ ,  $L$ - $S$ - $V$ , and  $S$ - $S$ - $V$ . Many examples of the first two types are known, but the latter three are uncommon. That the  $L$ - $L$ - $V$  type should exist can be shown with the aid of Figure 5.21.  $A$  and  $B$  are assumed to form a series of conjugate liquid solutions, as indicated by the lower part of the diagram, and also a series of conjugate liquid and vapor solutions with a minimum boiling azeotrope, as indicated by the upper part of the diagram. At the chosen pressure  $p_1$  the boiling point of the azeotrope is higher than the critical solution temperature. The curve showing the compositions of the conjugate liquid solutions will not be appreciably affected if the pressure is lowered. The decrease in pressure will, however, lower the boiling points of  $A$  and  $B$  and their solutions and will, in general, change the shapes of the liquid-vapor curves and the composition of the azeotrope.

It is obvious that a liquid of composition and temperature shown by point  $x$  will have a definite vapor pressure, say  $p_2$ . If the pressure on the system is reduced to  $p_2$ , then solution  $x$  can exist in equilibrium with its conjugate vapor. The solution  $y$ , which is conjugate with  $x$ , must be able to exist in equilibrium with this same vapor at this same pressure,  $p_2$ . This can be made evident by considering an experiment in which some solution  $x$  and its conjugate vapor are contained in one bulb and some solution  $y$  with its conjugate vapor in another bulb. Unless the vapors are identical in composition and pressure, a distillation with resultant

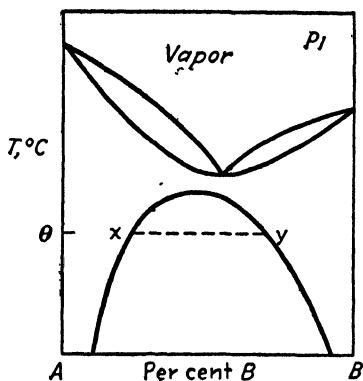


FIG. 5.21

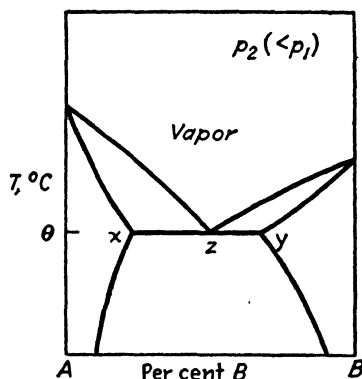


FIG. 5.22

FIGS. 5.21 and 5.22 The effect of pressure on  $L$ - $V$  and  $L$ - $L$  equilibria.

changes in the liquid compositions would occur if the two bulbs were connected by way of the vapor. Such a process would not be in harmony with the original assumption that  $x$  and  $y$  are conjugate liquids. At the pressure  $p_2$  the system  $A$ - $B$  would consequently have a phase diagram of the type shown in Figure 5.22, in which  $z$  represents the composition of the vapor which can exist in equilibrium with the conjugate solutions  $x$  and  $y$  at the temperature  $\theta$  and the pressure  $p_2$ . An example of this type of equilibrium is found in the system isobutyl alcohol-water, Figure 5.23.

The phase relationships in the system isobutyl alcohol-water can be illustrated by the following example. A system consisting

of, say, 20% isobutyl alcohol, 80% water at 80°C under equilibrium conditions will be composed of two liquid solutions, one containing 7.5% of alcohol, the other 75.5%; there will be

$$\frac{75.5 - 20}{75.5 - 7.5} \times 100 = 81.6\% \text{ of the former}$$

and

$$\frac{20 - 7.5}{75.5 - 7.5} \times 100 = 18.4\% \text{ of the latter}$$

If the temperature of the system is raised, both the compositions and the relative proportions of the conjugate solutions will be

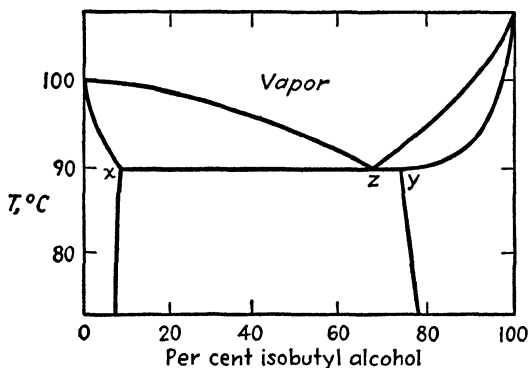


FIG. 5.23 The system isobutyl alcohol-water at 760 mm.

changed. At 89.5°C the system will consist of 82.1% of a solution, *x*, containing 8.4% alcohol and 17.9% of a solution, *y*, containing 73.4% alcohol. At this temperature the common vapor pressure of the two conjugate solutions is 760 mm. The composition of the conjugate vapor, *z*, is 68% alcohol. It should be noted that at this temperature there are three tie lines, *xy*, *xz*, and *zy*.

There is a certain similarity between Figures 4.5 and 5.23. Both systems show a minimum boiling point (triple point) at which a single vapor can exist in equilibrium with two liquid phases. In the system isobutyl alcohol-water the two liquids coexist in equilibrium. This is not true of the system decane-water; if these two liquids had been partially miscible in each other, their phase diagram would have been similar to that for the system isobutyl

alcohol-water. For the latter system the composition of the vapor in equilibrium with the immiscible liquids cannot, like that for the system decane-water, be calculated from knowledge of the vapor pressures of the pure components.

### 5.8 Combined $L$ - $S$ and $S$ - $S$ Equilibria

The system copper-silver, Figure 5.24, shows phase relationships analogous to those in the system isobutyl alcohol-water, the only essential difference being the substitution of liquid solutions for vapor solutions and of solid solutions for liquid solutions. Pure copper melts at  $1084^{\circ}\text{C}$ , pure silver at  $962^{\circ}\text{C}$ . The system has a eutectic point at 28% copper and  $778^{\circ}\text{C}$ ; the two solid phases which can exist in equilibrium with the eutectic solution are, how-

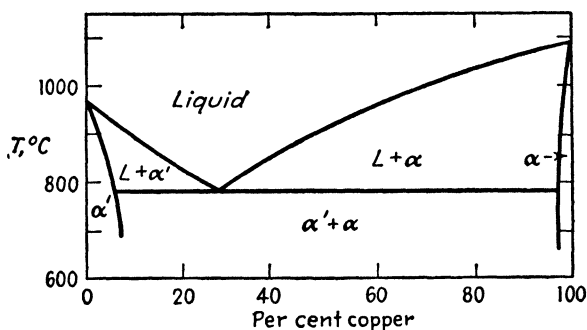


FIG. 5.24 The system copper-silver.

ever, not pure substances (*cf.* Figures 4.1 to 4.4), but conjugate solid solutions containing 6 and 98% copper, respectively. Below the eutectic temperature the partially miscible components form a series of conjugate solid solutions quite analogous to the conjugate liquid solutions of the system isobutyl alcohol-water. The two fields of unsaturated solid solutions have been designated as  $\alpha$  and  $\alpha'$ , the two fields of conjugate liquid and solid solution as  $L + \alpha$  and  $L + \alpha'$ .

The system thallium nitrate-potassium nitrate, Figure 5.25, shows many examples of equilibria involving solutions. Both pure substances undergo allotropic transitions. At room temperature the stable form of potassium nitrate is rhombic; above  $129^{\circ}\text{C}$  the stable form of the solid is trigonal; the melting point of the latter

is 334°C. Thallium nitrate exists in three different crystalline forms, rhombic with a transition point at 75°C, trigonal with a transition point at 145°C, and cubic with a melting point of 206°C. Comparison of Figures 5.24 and 5.25 shows that above 145°C this system is wholly analogous to the system copper-silver. The existence of polymorphic modifications gives rise to many complications below this temperature. For convenience the fields of unsaturated solid solutions are designated according to the particular polymorph of the pure component which forms one boundary of the field. In this diagram there are six fields of unsaturated solutions: the unsaturated liquid solutions lying above the liquidus

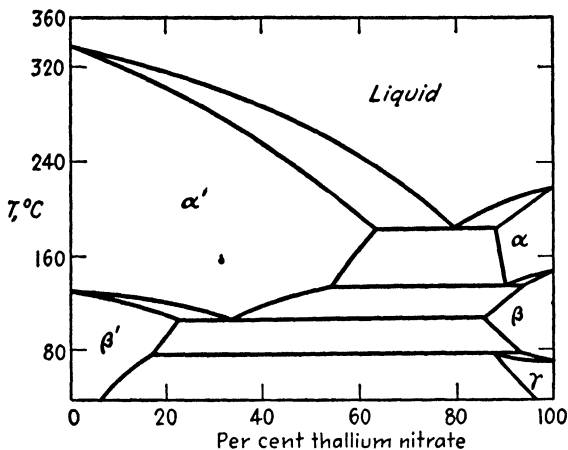


FIG. 5.25 The system thallium nitrate-potassium nitrate.

curve and the five unsaturated solid solutions  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\alpha'$ , and  $\beta'$ . The two fields of conjugate liquid and solid solutions may be designated as  $L + \alpha$  and  $L + \alpha'$ . The seven fields of conjugate solid solutions may be designated as  $\alpha + \alpha'$ ,  $\alpha + \beta$ ,  $\beta + \alpha'$ ,  $\alpha' + \beta'$ ,  $\beta + \beta'$ ,  $\beta + \gamma$ , and  $\gamma + \beta'$ . The following three-phase equilibria occur:  $L-\alpha-\alpha'$  at 182°C,  $\alpha-\beta-\alpha'$  at 134°C,  $\beta-\alpha'-\beta'$  at 106°C, and  $\beta-\gamma-\beta'$  at 78°C.

It has been emphasized in this chapter that  $L-V$ ,  $S-S$ , and  $L-S$  equilibria give rise to wholly similar phase diagrams. It is not surprising, then, that a solid-solid transition point of a pure substance can be the origin of a field of conjugate solid solutions, just as the melting point of a pure substance (liquid-solid phase transi-

tion) can be the origin of a field of conjugate liquid and solid solutions, and a boiling point of a pure substance (liquid-vapor phase transition) can be the origin of a field of conjugate liquid and gaseous solutions. In the  $L$ - $L$  equilibrium diagrams discussed so far (see Figures 5.1, 5.2, 5.3) the critical solution composition was never that of a pure substance. If a pure substance could exist in two polymorphic liquid forms,  $L$  and  $L'$ , the  $L$ - $L'$  transition point could be the origin of a field of conjugate liquid solutions. This latter behavior might be realized if one of the components were capable of forming "liquid crystals." (Cholesteryl benzoate is an example of a substance which forms liquid crystals. It melts at  $145.5^{\circ}\text{C}$  to form a turbid anisotropic liquid; this liquid undergoes a transition to a clear isotropic liquid at  $178.5^{\circ}\text{C}$ .)

### 5.9 The System Silver-Tin

The phase diagram for this system, Figure 5.26, combines several of the types of equilibrium previously discussed. The binary compound  $\text{Ag}_3\text{Sn}$  (73.1% silver) melts incongruently at  $460^{\circ}\text{C}$  to yield a liquid solution containing 50% silver and a solid solution containing 76% silver. It should be noted that both the products of the decomposition of the binary compound are solutions; it will be recalled that Glauber's salt melts incongruently to form a liquid solution and a solid *pure substance* (see Figure 3.3). It should also be noted that there are *three* tie lines at  $460^{\circ}\text{C}$ ; at the transition temperature of Glauber's salt there are only two tie lines. The conjugate liquid and solid solutions at  $460^{\circ}\text{C}$  are one pair of a series extending from this temperature to the melting point of silver,  $962^{\circ}\text{C}$ . The upper portion of this diagram is similar to the upper part of Figure 5.7. The eutectic point at 4% silver,  $221^{\circ}\text{C}$ , involving the component tin and the binary compound  $\text{Ag}_3\text{Sn}$ , is quite analogous to the eutectic point in the system sodium sulfate-water (Figure 3.3).

As mentioned above, at  $460^{\circ}\text{C}$  the binary compound can exist in equilibrium with a solid solution containing 76% silver. This solution is saturated with the binary compound. At this temperature systems containing more than 76% silver are solid solutions unsaturated with respect to the binary compound. At  $460^{\circ}\text{C}$  the solubility of the binary compound in silver (*i.e.*, the composition of the saturated solution) is 76% silver. At lower temperatures

the solubility is shown by the curved line descending from 76%, 460°C. Under equilibrium conditions below 460°C a system consisting of, say, 90% silver will be an unsaturated solid solution; a system consisting of 75% silver will be a mechanical mixture of the binary compound and its saturated solid solution. The equilibrium relationships in this system will be illustrated by discussing the courses of crystallization of a few melts.

If a melt containing 60% silver is cooled under equilibrium conditions, it will become saturated with respect to a solid solution at 615°C. The first solid formed will be a solution containing 84% silver. As the system is cooled further both the liquid solution

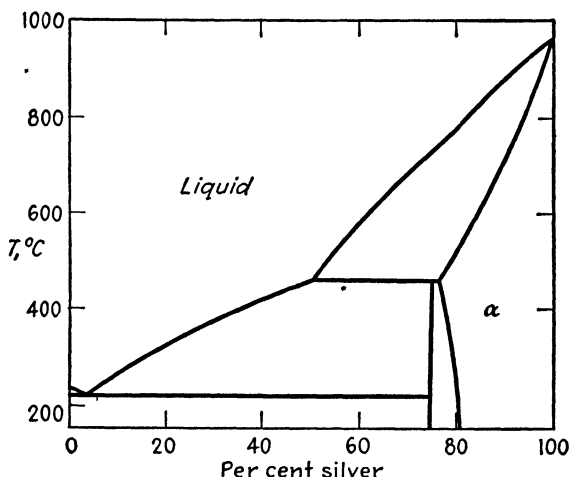


FIG. 5.26 The system silver-tin.

and its conjugate solid solution will become enriched in tin; as the temperature reaches 460°C the system will consist of 61.5% of liquid solution (50% silver) and 38.5% of solid solution (76% silver). Further removal of heat under equilibrium conditions will not change the temperature but will result in the formation of a third phase, the binary compound. During this isothermal process the solid solution will be completely resorbed; the liquid solution will be only partially used up, until the system consists of 56.7% of liquid solution and 43.3% of the binary compound. As the temperature is lowered further the proportion of liquid solution and its percentage of silver will decrease until, at the eutectic

temperature, there will be 19.0% of liquid solution of the eutectic composition and 81.0% of the binary compound. The temperature will remain constant while the solution is used up in the formation of tin and additional binary compound. Below the eutectic temperature the system will consist of 17.9% tin and 82.1% binary compound.

A melt containing 90% silver is saturated with solid solution at 870°C; the composition of the conjugate solid is 97% silver. If the system is cooled below this temperature, under equilibrium conditions, solid solution will separate from the melt. While initially 97% silver, the composition of the equilibrium solid will change as crystallization proceeds, until at 730°C it will be 90% silver. The composition of the liquid will change from 90% silver at 870°C to 74% at 730°C. At this latter temperature the liquid solution will vanish; below 730°C no further phase changes will occur.

If a melt containing 75% silver is cooled under equilibrium conditions, it will become saturated with solid solution at 750°C; the composition of its conjugate solid solution is 91% silver. Further cooling will give rise to a series of conjugate liquid and solid solutions. As the temperature reaches 460°C the system will consist of approximately 4% of a liquid solution containing 50% silver, and 96% of the conjugate solid solution containing 76% silver. Both of these solutions can exist in equilibrium with the binary compound  $\text{Ag}_3\text{Sn}$ . Further removal of heat will result in the isothermal formation of the binary compound at the expense of both conjugate solutions. Since the over-all composition of the system lies between that of the binary compound and that of the solid solution, the liquid solution will vanish completely, leaving a mechanical mixture consisting of 35% of the binary compound and 65% of the solid solution. With further removal of heat the temperature will decrease; the composition of the solid solution and its proportion relative to that of the binary compound will change in accordance with the solubility curve of the binary compound. The phase relationships obtaining below 460°C are quite analogous to those obtaining for a solid pure substance in equilibrium with its saturated *liquid* solution.

During the cooling of a melt containing 80% silver, the system will be completely liquid until the temperature reaches 790°C. Between this temperature and 550°C it will consist of a mechanical

mixture of liquid and solid solutions. Between 550 and 250°C it will be an unsaturated solid solution. Below 250°C it will consist of a mechanical mixture of the binary compound and its saturated solid solution.

### EXERCISES

1. With examples discuss qualitatively the factors which can be expected to affect the solubility of one crystalline substance in another.
2. Assuming equilibrium, describe completely the system consisting of 20% lead, 80% thallium at 340°C.
3. Trace the paths of the representative points of the liquid and the whole solids during the equilibrium cooling of a melt consisting of 40% åkermannite, 60% velardeñite from 1600 down to 1300°C.
4. Estimate the number of theoretical plates required in a distilling column for separating 95% acetone, 5% chloroform from a solution consisting of 60% chloroform, 40% acetone at 750 mm pressure.
5. Assuming equilibrium, describe completely the system consisting of 40% thallium nitrate, 60% potassium nitrate (a) slightly above 106°C and (b) slightly below 106°C.
6. From Figure 5.15 draw a diagram illustrating qualitatively the form of the isothermal liquid-vapor diagram for the system benzene-ethanol at 78°C. Indicate the fields of liquid and vapor.

## CHAPTER 6

### THREE-COMPONENT SYSTEMS

A three-component system is one for which three constituents are necessary and sufficient to describe the compositions of all the phases involved. If the three components have been specified, it is sufficient to state the proportions of any two; the proportion of the third can be obtained by subtraction. For example, if a system having the components  $A$ ,  $B$ , and  $C$  is stated to consist of 70%  $A$  and 20%  $B$ , the proportion of  $C$  is clearly 10%. To define the state of any phase in a three-component system no more than four variables need be specified, *viz.*, the temperature, the pressure, and the proportions of any two of the components. If both the temperature and the pressure are held constant, the phase relationships can be shown on a planar diagram.

#### 6.1 Methods of Representing Ternary Composition

If  $A$ ,  $B$ , and  $C$  are the three components, the proportions of any two of these, say  $B$  and  $C$ , can be represented by using two rectangular axes, as shown in Figure 6.1. The composition of pure  $A$ , since it contains 0%  $B$  and 0%  $C$ , must be represented by the origin; the compositions of pure  $B$  and pure  $C$  are represented by the terminations of the two axes. It is easily seen that a system represented by any point  $x$  on the line  $BC$  must contain 0%  $A$ . The absence of  $A$  in the system  $x$  follows directly from the proportioning rule, since its composition is completely expressed as  $Cx/CB$  of  $B$  and  $Bx/BC$  of  $C$ . Furthermore, from the geometry of the right-angled triangle it is clear that the sum of the ordinate and the abscissa of any point  $x$  on the hypotenuse is equal to the length of one side, *i.e.*, for the system  $x$ , %  $B$  + %  $C$  = 100. Any point on the line  $AC$  represents the composition of a system containing no  $B$ , and any point on the line  $AB$  represents a system containing no  $C$ . Any point *within* the triangle represents the composition of a system containing positive quantities of all three

components. A right-angled isosceles triangle of this type is commonly used to represent phase relationships in systems for which the components are two solutes and a solvent. For example, in the phase diagram for the system  $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  (Figure 6.5) the solvent, water, is conveniently represented by the origin.

When no distinction is made between solute and solvent it is customary to represent ternary composition on an equilateral triangle (Figure 6.2). As before, the compositions of the pure components are shown as the points *A*, *B*, and *C*; any point on the line *BC* represents the composition of a system containing no *A*; any point on the line *AC*, one containing no *B*; any point on the line

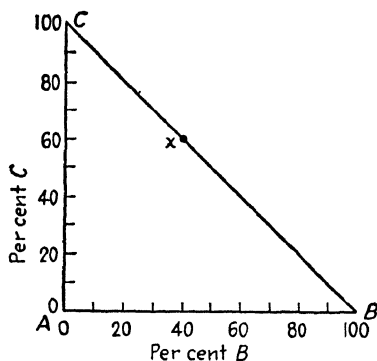


FIG. 6.1 Representation of composition on an isosceles right-angled triangle.

*AB*, one containing no *C*. The proportions of *A*, *B*, and *C* in a system represented by any point *z* can be determined in terms of scales marked off on the three sides of the triangle. A line *xy* is drawn through *z* parallel to *AB*. Then *z* can be said to consist of *x* and *y* in the ratio given by the proportioning rule, *zy* of *x* to *xz* of *y*. Further, it can be seen from the *AC* scale that *x* contains 33% *C* (67% *A*) and from the *BC* scale that *y* contains 33% *C* (67% *B*). Any system which can be made from *x* and *y* must contain 33% *C*; thus *z*, or any other point on the line *xy*, must represent 33% *C*. This composition may be read from either the *AC* or *BC* scales, or by interpolation between the convenient grid-lines parallel to the side of the triangle remote from *C*, *i.e.*, parallel to *AB*. Similarly, the percentage of *B* (54%) in the system repre-

sented by  $z$  can be interpolated between the grid lines parallel to  $AC$ . The percentage of  $A$  (13%) can be determined by interpolation between the grid lines parallel to  $BC$  or by subtracting the sum of the percentages of  $B$  and  $C$  from 100.

While the composition of any phase in a ternary system can be represented either on a right-angled isosceles or on an equilateral triangle, it is frequently necessary to consider triangles of other shapes. For example, if the point  $z$  in Figure 6.2 were to represent the composition of a ternary compound of  $A$ ,  $B$ , and  $C$ , it might be necessary to describe the composition of a system in terms of  $A$ ,  $B$ , and  $z$ , which define the vertices of an irregular triangle.

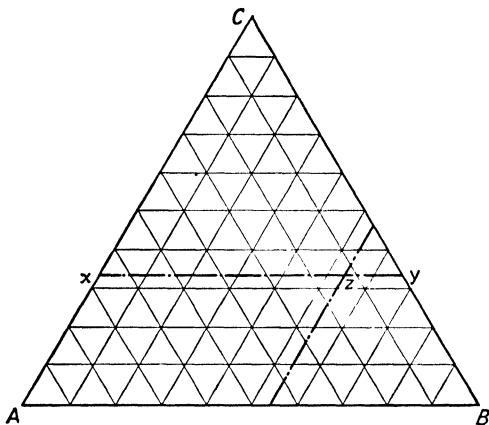


FIG. 6.2 Representation of composition on an equilateral triangle.

In Figure 6.3 the composition  $z$  can be described in terms of  $A$ ,  $B$ , and  $C$  by a procedure identical with that used for Figure 6.2. As before, the line  $xy$  is drawn through  $z$  parallel to one of the sides, say  $AB$ . If  $AC$  and  $BC$  are divided into scales having the same number of units, the proportion of  $C$  in  $z$  can be read from either the  $AC$  or the  $BC$  scale, even though the length of a division differs on the two scales. Similarly, the proportions of  $A$  and  $B$  can be obtained by drawing lines through  $z$  parallel to  $BC$  and  $AC$ , respectively.

The composition represented by  $z$  can also be read from a single scale. As before, the fraction of  $C$  in  $z$  is obtained, with the aid of the line  $xy$ , as  $By/BC$ ; if the line  $pq$  is drawn through  $z$  parallel to the side  $AC$ , it follows that the fraction of  $B$  in  $z$  is given by  $qC/BC$ .

Clearly the fraction of  $A$  is given by the difference, that is,  $yq/BC$ . In general, if any side of a triangle is divided into three parts by two lines drawn through the point representing the composition in question and parallel to the other two sides, the middle segment is a measure of the proportion of the constituent represented by

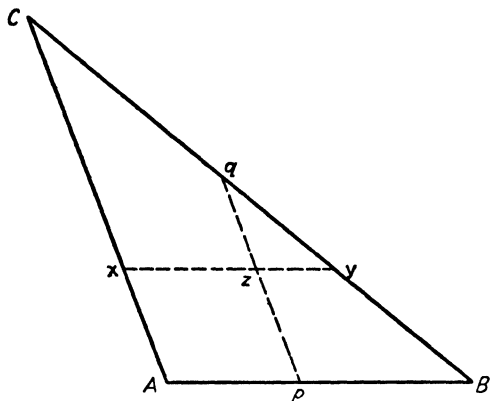


FIG. 6.3 Representation of composition on an irregular triangle.

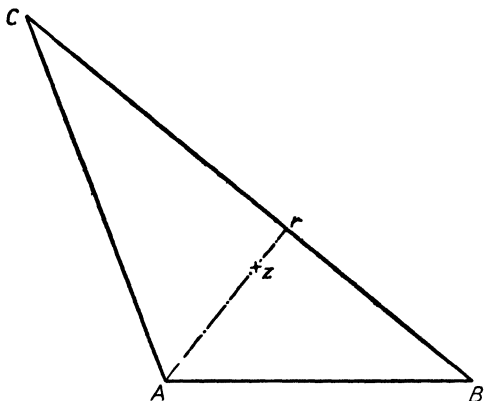


FIG. 6.4 Representation of composition on an irregular triangle.

the apex opposite the scale line; the end segments are measures of the proportions of the constituents represented at the *opposite* ends of the scale line.

A third method sometimes used can be shown by means of Figure 6.4. If a straight line is drawn from  $A$  through  $z$  to meet

the side  $BC$  at  $r$ , it is evident from the proportioning rule that  $z$  can be described in terms of  $A$  and  $r$  and, in turn,  $r$  can be described in terms of  $B$  and  $C$ . Thus the fraction of  $A$  is  $zr/Ar$ ; the fraction of  $B$  is  $(Cr/CB)(Az/Ar)$ ; the fraction of  $C$  is  $(rB/BC)(Az/Ar)$ . It should be noted that all systems having a composition lying on the line  $Ar$  contain  $B$  and  $C$  in the same ratio. If  $A$  is added to a system of composition  $r$ , the composition of the resulting system will lie on the line  $Ar$ .

It has been shown that if the compositions of three components are represented by the apices of any triangle, a point within the triangle represents a composition which can be described in terms of positive quantities of the three components. As a corollary it can be shown that if any composition  $z$  can be described in terms of positive values of three *independent* composition variables, their compositions must constitute the apices of a triangle containing  $z$ . These three independent composition variables need not be the components used to designate the system; they might, for example, be the phase constituents of the system represented by the composition  $z$ . If the system of over-all composition  $z$  consists of two salts and a solution saturated with respect to both of these, then  $z$  must lie within the triangle defined by the compositions of these three phase constituents; the relative proportions of the three phases present could be calculated by any of the methods shown above.

## 6.2 Degrees of Freedom in Three-component Systems

The maximum number of phases which can coexist in equilibrium in a three-component system is five; the temperature and pressure, as well as the compositions of the five phases, would then have unique values and not one could be chosen arbitrarily. In the present chapter equilibria will be considered in systems under conditions of fixed temperature and pressure; the maximum number of phases involved in these equilibria will then be three, except at unique values of the temperature and/or the pressure.

## 6.3 The System $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$

The system sodium sulfate-water was discussed at some length in order to illustrate the principles and terminology used in the treatment of two-component systems. In a similar way the sys-

tem sodium sulfate-magnesium sulfate-water will be used to exemplify many of the features of three-component systems.

The equilibrium diagram for this system at 18.5°C and 1 atm pressure is shown in Figure 6.5. The components (sodium sulfate, magnesium sulfate, and water) are represented by the apices (*S*, *M*, and *W*) of the isosceles right-angled triangle, conventionally used for a system consisting of two solutes and a solvent. Under the conditions of temperature and pressure imposed in the rubric, the stable hydrates of the solute components are Glauber's salt,

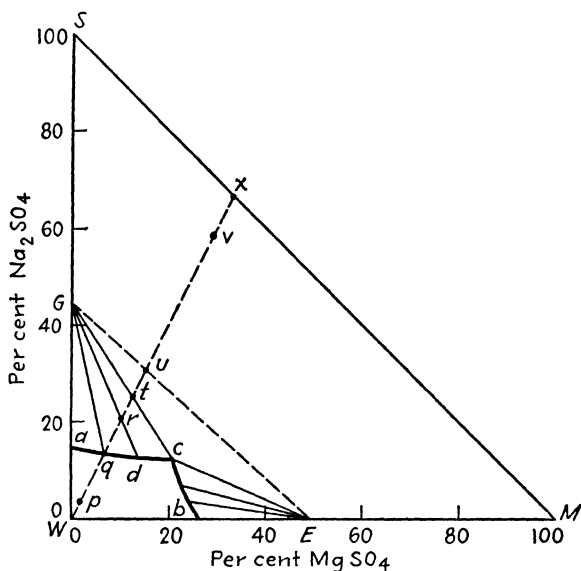


FIG. 6.5 The system  $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  at 18.5°C and 1 atm.

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and Epsom salt,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , represented by points *G* and *E*. The line *WS* is an isothermal section of Figure 3.3, from which it is seen that the solubility of Glauber's salt in water is 14.4% sodium sulfate, 85.6% water. The composition of this saturated solution is represented by the point *a*. Points lying in the segment *Wa* therefore represent solutions of sodium sulfate and water which are unsaturated with respect to Glauber's salt; points in the segment *aG* represent mechanical mixtures of Glauber's salt and the saturated solution *a*; mechanical mixtures of the solid phases Glauber's salt and sodium sulfate are repre-

sented by points in the segment  $GS$ . The solubility of Epsom salt in water at  $18.5^\circ\text{C}$  and 1 atm pressure is 25.4% magnesium sulfate, 74.6% water and is represented by the point  $b$ . As might be expected, the solubility of Glauber's salt in solutions of magnesium sulfate differs from its solubility in water. The effect on the solubility of Glauber's salt of an increase in the proportion of magnesium sulfate is shown by the line  $ac$ ; any point lying on this line represents the composition of a solution which can exist in equilibrium with Glauber's salt. The point  $G$  is then the origin of a system of radial tie lines terminating on the line  $ac$ ; a few of these are shown on the diagram. Analogously,  $bc$  is the solubility curve of Epsom salt. The point  $c$ , at the intersection of the two solubility curves, represents the composition of a solution (11.8% sodium sulfate, 20.6% magnesium sulfate) which can exist simultaneously in equilibrium with both Glauber's salt and Epsom salt. At fixed temperature and pressure the composition  $c$  is unique;  $c$  is therefore an *invariant point* under these conditions. Further, since the point  $c$  occurs in a three-component system, it is referred to as a *ternary invariant point*.

The area  $Wacb$  is the field of unsaturated solutions in the three-component system. The area  $Gca$  is the field of Glauber's salt; under equilibrium conditions any system lying within this field will consist of a mixture of Glauber's salt and a solution saturated with respect to Glauber's salt. Similarly, the area  $Ecb$  is the field of Epsom salt. A system in which the phase constituents are Glauber's salt, Epsom salt, and the solution  $c$  saturated with respect to both salts must, in view of the discussion at the beginning of this chapter, lie within the triangle  $GEc$ . The composition of the solution  $c$  is clearly unaffected by the proportions of the two salts present, since  $c$  is an invariant point. It is apparent, then, that any system lying within the triangle  $GEc$  will, under equilibrium conditions, consist of a mixture of Glauber's salt, Epsom salt, and the solution  $c$  saturated with respect to both salts. Under the conditions imposed the only systems capable of manifesting stable equilibria are those for which the over-all composition lies within one of the three areas  $Gca$ ,  $Ecb$ , or  $GEc$ . It has already been noted that a system lying within the area  $Wacb$  consists of an unsaturated solution. The remaining area of the diagram,  $GEMS$ , can be arbitrarily divided into triangles:  $GME$  and  $GMS$  or  $ESM$  and  $ESG$ . Any point lying within the quadrilateral  $GEMS$  is

common to two of these triangles, *e.g.*, the point *v* (60%  $\text{Na}_2\text{SO}_4$ , 30%  $\text{MgSO}_4$ , 10%  $\text{H}_2\text{O}$ ) lies within the triangles *GMS* and *ESM*. It is impossible to predict from the diagram whether a system of composition *v* will consist of a mixture of *G*, *M*, and *S* or of *E*, *S*, and *M*, or, for that matter, of *S*, *M*, and *W* (vapor): It is clear that with the data at hand it is impossible to state the most stable phase constituents of the system *v*.

Diagrams such as 6.5 are of considerable value in predicting the course of crystallization resulting from isothermal evaporation from a solution initially unsaturated.<sup>1</sup> Such a solution might be represented by the point *p* (5%  $\text{Na}_2\text{SO}_4$ , 2.5%  $\text{MgSO}_4$ ). During the removal of water by evaporation the ratio of  $\text{Na}_2\text{SO}_4$  to  $\text{MgSO}_4$  must, of course, remain constant and hence the path of the point representing the over-all composition of the system will follow the straight line *Wp* in the direction *away from W*. The solution will remain unsaturated until its composition reaches *q*, at which point it will be saturated with respect to Glauber's salt. Further evaporation will advance the over-all composition of the system to a point within the field of Glauber's salt, say the point *r*. Although *r* might well represent a single solution phase supersaturated with respect to Glauber's salt, under equilibrium conditions the system will consist of two phases, Glauber's salt, *G*, and the solution *d* saturated with respect to it; the proportions of the two phases will be  $dr/dG$  of *G* and  $Gr/Gd$  of *d*. When the system has attained the composition *t* the solution composition will have followed the solubility curve *ac* from *q* to *c*; at *c* the solution will be saturated with respect to Epsom salt as well as Glauber's salt. Further evaporation will advance the over-all composition of the system into the triangle *GEc* and, as noted in the previous paragraph

<sup>1</sup> The isothermal evaporation might be conducted in a number of ways. A simple method would be to pass dry air over the system; the pressure could thus be maintained constant at 1 atm. A more usual procedure would be to reduce the pressure below the vapor pressure of the system by continuous pumping. While this clearly violates the condition of 1 atm pressure indicated in the diagram, it should be recalled that such a reduction in pressure would not appreciably alter the data of the diagram. At any stage of the evaporation the pressure could, of course, be restored to 1 atm. The evaporation might even be effected by boiling off water at atmospheric pressure (and hence at a higher temperature) and subsequently cooling the system to 18.5°C. The compositions and the relative amounts of the various phases obtaining at 18.5°C for progressively decreasing water content could still be computed with the aid of this diagram.

the system will, under equilibrium conditions,<sup>1</sup> consist of a mixture of Glauber's salt, Epsom salt, and the solution *c* saturated with respect to both. So long as the composition of the system lies within the triangle *GEc* the composition of the liquid phase is invariant; the relative amounts of the three phases can be obtained by any of the general methods described earlier in this chapter. As the evaporation is continued the amount of the liquid phase will decrease and finally become zero when the over-all composition of the system reaches the point *u*. The system will then consist of a mixture of *Eu/EG* of Glauber's salt and *Gu/GE* of Epsom salt. Dehydration of this salt mixture will ultimately result in the formation of the anhydrous salts in the proportions *Mx/MS* of sodium sulfate and *Sz/SM* of magnesium sulfate. The course of this dehydration, from *u* to *x*, cannot be predicted from the data of this diagram alone.

As would be expected, at lower temperatures the solubilities of Glauber's salt and Epsom salt decrease and the field of unsaturated solutions becomes smaller. Below 0°C the diagram would show a field of ice, with the solubility curve of ice subtending the right angle at *W*.

The system  $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  exhibits a double salt, astracanite, having the formula  $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ ; this is a ternary compound of the three components chosen. Below 22°C this compound can exist as an individual solid, but it decomposes when in contact with any solution of the three components; therefore it does not possess a solubility curve below 22°C. The equilibrium diagram for 23°C is shown in Figure 6.6. The solubility curves of Glauber's salt, astracanite, and Epsom salt are designated by *ae*, *ef*, and *bf*; the fields of these compounds by *Gea*, *Aef*, and *Ebf*, respectively. The solution having the composition of the ternary invariant point *e* can exist in equilibrium with Glauber's salt and astracanite simultaneously; if the three phases are present the over-all composition of the mixture will lie within the triangle *GAe*. For the ternary invariant point *f* the solid phases are astracanite and Epsom salt.

<sup>1</sup> It is conceivable that removal of water from the system *t* might yield a mixture of only two phases, Glauber's salt and a solution which would be saturated with respect to Glauber's salt but supersaturated with respect to Epsom salt. The composition of such a solution would lie on the extension of the curve *ac* beyond *c*.



this the equation representing the decomposition of astracanite in the presence of water at  $23^\circ\text{C}$  may be written

$$\begin{aligned} \frac{gW}{AW} \text{ of astracanite} + \frac{Ag}{AW} \text{ of water} \\ = \frac{ge}{Ge} \text{ of Glauber's salt} + \frac{Gg}{Ge} \text{ of solution } e \end{aligned}$$

As its composition is changed from  $g$  to  $d$  by the continued addition of water, the system will consist of Glauber's salt and its saturated

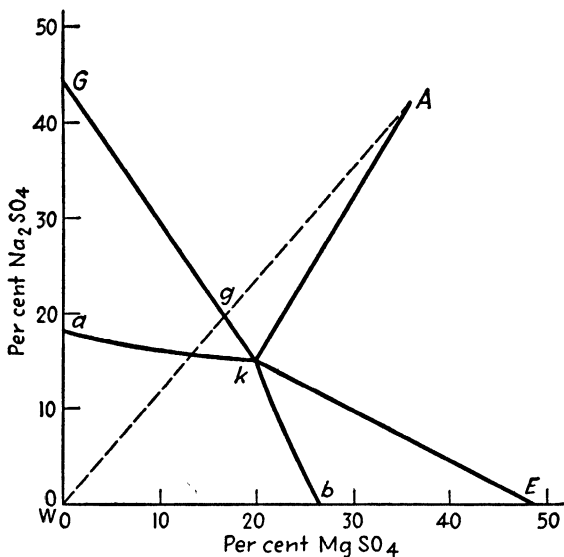


FIG. 6.7 The system  $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  at  $22.0^\circ\text{C}$  and 1 atm.

solution; the composition of this solution will follow the path  $ed$ ; the proportion of Glauber's salt will decrease, and will vanish when the composition of the system reaches  $d$ . During further addition of water the composition of the system will cross the field of unsaturated solutions by the path  $dW$ .

Below  $23^\circ\text{C}$  the field of astracanite becomes narrower; at  $22^\circ\text{C}$  its solubility curve is reduced to a single invariant point  $k$  (14.9%  $\text{Na}_2\text{SO}_4$ , 20.0%  $\text{MgSO}_4$ , Figure 6.7) which is the origin of three tie lines, one to each of the points  $G$ ,  $A$ , and  $E$ . At the chosen pressure of 1 atm it is therefore possible to have a solution of this

unique composition existing in equilibrium with the three salts at  $22^{\circ}\text{C}$ , four phases in all;  $k$  is therefore a *quadruple point*. In accordance with the phase rule such a system of four phases in equilibrium will have but one degree of freedom. Thus at 1 atm pressure  $22^{\circ}\text{C}$  is an invariant temperature and is referred to as the transition temperature of astracanite. Although astracanite can exist both below and above this temperature, it does not possess a solubility curve below this temperature. It is apparent from Figure 6.7 that the point  $k$  does not lie on the line  $WA$  and hence as water is added to astracanite the double salt is decomposed in a manner similar to that described for  $23^{\circ}\text{C}$  (Figure 6.6). The equation for the decomposition may be obtained by substituting  $k$  for  $e$  in the expression above. Astracanite will invariably decompose on contact with water below  $25.6^{\circ}\text{C}$ , at which temperature its solubility curve intersects the line  $WA$ ; as the temperature is increased above  $22^{\circ}\text{C}$  the curve corresponding to  $ef$  of Figure 6.6 expands, until at  $25.6^{\circ}\text{C}$  the point  $e$  lies on the line  $WA$ . The temperature range from 22 to  $25.6^{\circ}\text{C}$  is referred to as the *transition interval* for astracanite. Above the transition interval the extremities of the solubility curve of astracanite lie on opposite sides of the line  $WA$  and hence the double salt does not undergo decomposition on the addition of water.

It will be recalled that in the system  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  the stable solid above  $32.4^{\circ}\text{C}$  is anhydrous sodium sulfate. In the system  $\text{MgSO}_4\text{-H}_2\text{O}$  the hydrate Epsom salt is stable up to  $46^{\circ}\text{C}$ . The phase diagram for the three-component system at  $40^{\circ}\text{C}$  is shown in Figure 6.8. It should be noted that here  $ae'$  is the solubility curve of sodium sulfate and  $e'$  is the ternary invariant point for the solution saturated with respect to both astracanite and sodium sulfate.

Applying the phase rule to the equilibrium between Glauber's salt, sodium sulfate, and the saturated solution in the two-component system shows that, of the three variables *pressure*, *transition temperature*, and *composition of the saturated solution*, only one is independent. For example, if the composition of the saturated solution is arbitrarily chosen, both the transition temperature and the pressure will be uniquely defined. However, in the three-component system one additional degree of freedom is available and the transition temperature is not uniquely defined unless both the pressure and the composition of the saturated solution are specified. Similarly, specification of the pressure and the transi-

tion temperature will define the composition of the unique ternary solution which can exist in equilibrium with both Glauber's salt and sodium sulfate. An example of such a solution is given by the point  $x$  in Figure 6.9. At  $30^\circ\text{C}$  and 1 atm the three-component system shows four solubility curves and three ternary invariant points,  $x$ ,  $e'$ , and  $f$ .

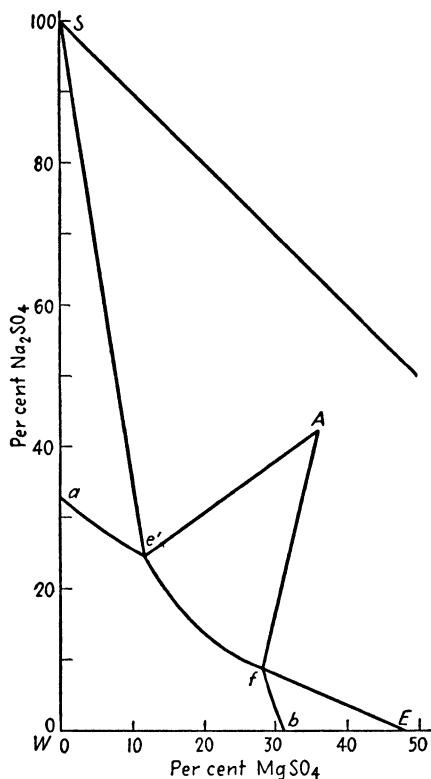


FIG. 6.8 The system  $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  at  $40^\circ\text{C}$  and 1 atm.

For a fixed pressure of 1 atm, the composition  $x$  varies from 33.2% sodium sulfate, 0% magnesium sulfate at  $32.4^\circ\text{C}$  to 23.3% sodium sulfate, 12.5% magnesium sulfate at  $27^\circ\text{C}$ . At this lower temperature the field of sodium sulfate is reduced to a single tie line and its solubility curve to a single ternary invariant point<sup>1</sup>

<sup>1</sup> The quadruple point  $h$  in Figure 6.10.

which is the origin of three tie lines, one to each of the points  $G$ ,  $S$ , and  $A$ . At 1 atm pressure the four phases  $G$ ,  $S$ ,  $A$ , and solution can exist together in equilibrium only at a unique temperature,  $27^{\circ}\text{C}$ , as predicted by the phase rule. It is possible, of course, to have a five-phase equilibrium by including the additional phase water vapor; in this case, however, the pressure, the transition

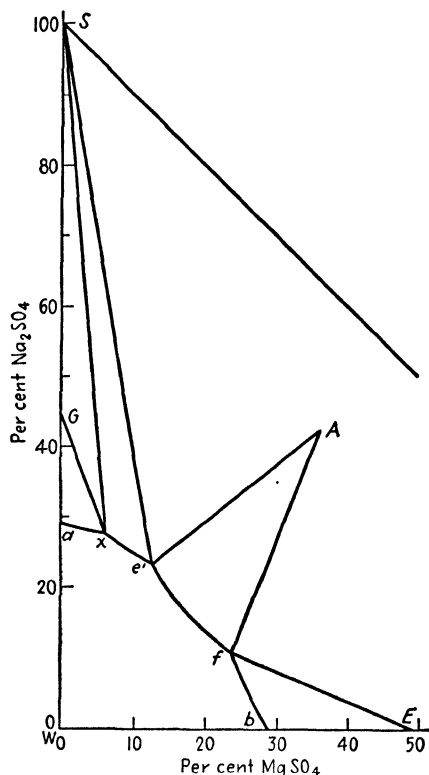


FIG. 6.9 The system  $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  at  $30^{\circ}\text{C}$  and 1 atm.

temperature, and the composition of the saturated solution would all be fixed by nature, since there would be no degree of freedom.

Much of the information regarding the invariant points of the system  $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  can be given on a single isobaric diagram. Temperature is chosen as one of the coordinates; the other coordinate cannot, of course, give complete information

about composition. In Figure 6.10 the ratio of the weights of the solute components has been chosen as the second coordinate; while the proportion of water is not indicated, the pertinent data can still be shown. The horizontal line at the ratio 0.847 refers to the composition of astracranite. The solid curves are the loci of the various ternary invariant points; they are lettered to correspond with Figures 6.5 to 6.9. The known extensions of these curves into regions of metastability are indicated by dashed lines.

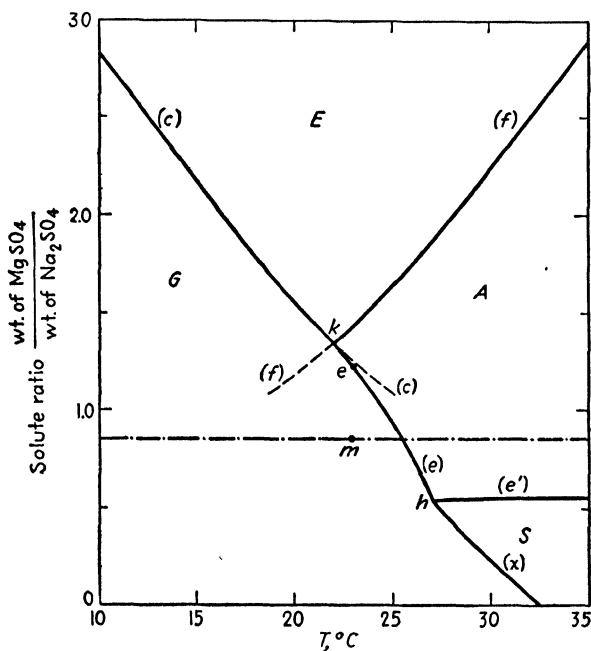


FIG. 6.10 Solute ratios of saturated solutions in the system  $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ .

The effect of temperature on the composition of a solution simultaneously saturated with respect to Glauber's salt and Epsom salt (see point *c*, Figure 6.5) is shown by the line *c*. As indicated by the dashed continuation of this line, such a solution is metastable above 22°C; it would be supersaturated with respect to astracranite. The curve *f* indicates the effect of temperature on the composition of a solution simultaneously saturated with respect to Epsom salt and astracranite. It is clear that any solution satu-

rated with respect to Epsom salt alone must have a solute ratio lying between the curves  $c$  and  $f$ . Since this diagram does not indicate the proportion of water in a solution, it does *not* follow that a solution having a solute ratio in the field marked " $E$ " will be saturated with respect to Epsom salt; it could be a very dilute solution.

The solute ratio for solutions simultaneously saturated with respect to astracanite and Glauber's salt is shown by the curve  $e$ . The curves  $e$ ,  $f$ , and  $c$  intersect at the quadruple point  $k$  (see Figure 6.7). The divergence of the curves  $e$  and  $f$  above  $22^{\circ}\text{C}$  corresponds to the broadening of the field of astracanite with rising temperature. The curves  $f$  and  $e$  form two of the boundary lines of the field  $A$  for solutions saturated with respect to astracanite. The curve  $e'$  is also a boundary line of the field  $A$ , since it represents the solute ratio of solutions simultaneously saturated with respect to astracanite and sodium sulfate (see point  $e'$ , Figure 6.8). This solute ratio is not markedly dependent on temperature and hence  $e'$  appears as an almost horizontal line.

The curve  $x$  represents the solute ratio for solutions simultaneously saturated with respect to sodium sulfate and Glauber's salt (see point  $x$ , Figure 6.9). In the binary system sodium sulfate-water the ratio of magnesium sulfate to sodium sulfate is zero and hence the curve  $x$  has a solute ratio of zero at  $32.4^{\circ}\text{C}$ , the transition point of Glauber's salt in the binary system. The quadruple point  $h$  gives the temperature, ( $27^{\circ}\text{C}$ ) and solute ratio for the solution which can exist in equilibrium simultaneously with Glauber's salt, sodium sulfate, and astracanite. The curves  $e'$  and  $x$  form two of the boundary curves of the field  $S$ ; solute ratios of solutions saturated with respect to sodium sulfate will lie within this field. Stable solutions saturated with respect to Glauber's salt can only obtain for solute ratios lying in the field  $G$ , bounded by the curves  $c$ ,  $e$ , and  $x$ .

The transition interval of astracanite,  $22$  to  $25.6^{\circ}\text{C}$ , is shown clearly in Figure 6.10. The point  $k$  represents the low-temperature limit of the field for astracanite and hence astracanite cannot exist in stable equilibrium with any saturated solution below  $22^{\circ}\text{C}$ . The line representing the solute ratio (0.847) of astracanite intersects the curve  $e$  at  $25.6^{\circ}\text{C}$ . It can be shown that this is the upper limit of the transition interval; between the temperatures  $22$  and

25.6°C the addition of astracanite to water cannot form a solution saturated with respect to astracanite without the precipitation of Glauber's salt. If, for example, astracanite is added to water at 23°C, the solute ratio of the resulting system will be given by the point *m*. For small additions the solution will be unsaturated, corresponding to points between *W* and *d* on the line *WA* of Figure 6.6. If sufficient astracanite is added, Glauber's salt will be formed and the system will consist of two phases, Glauber's salt and a saturated solution having a composition lying between *d* and *e* on the curve *ae* of Figure 6.6. Since the solute ratio for Glauber's salt is zero, that of the saturated solution must be greater than 0.847, *i.e.*, the solution will have a solute ratio lying between *m* and *e* of Figure 6.10. When sufficient astracanite has been added to saturate the solution with respect to this substance, the solute ratio for the solution will be given by the point *e* of Figure 6.10 (corresponding to the point *e* of Figure 6.6). Further addition of astracanite will not affect the composition of the solution or, of course, its solute ratio. It is clear that the addition of astracanite to water at *any* temperature between 22 and 25.6°C cannot yield a solution saturated with respect to astracanite without giving rise to Glauber's salt as a phase constituent. Above 25.6°C the solute ratio 0.847 lies in the field *A* and hence it is possible, by adding astracanite to water, to form a solution saturated with respect to astracanite without producing a third phase.

It is immediately apparent from diagrams such as Figure 6.10 what fields will be encountered in an isothermal diagram. For example, it is seen from Figure 6.10 that the isotherm at 30°C passes through the fields *G*, *S*, *A*, and *E* and intersects the curves *x*, *e'*, and *f*, which shows that the isothermal diagram for 30°C will have fields of Glauber's salt, sodium sulfate, astracanite, and Epsom salt and will show three ternary invariant points (*cf.* Figure 6.9).

### EXERCISES

1. Using the numerical data of Section 6.3, replot on an equilateral triangle having the apices *W*, *G*, and *E* the portion of Figure 6.5 contained in the triangle *WGE*.
2. Assuming equilibrium, describe completely the system consisting of 5% sodium sulfate, 30% magnesium sulfate, 65% water at 23.0°C.

3. Assuming equilibrium, list the phase constituents at 30°C of the systems consisting of

|     | % SODIUM<br>SULFATE | % MAGNE-<br>SIUM SULFATE | % WATER |
|-----|---------------------|--------------------------|---------|
| (a) | 20                  | 10                       | 70      |
| (b) | 30                  | 2                        | 68      |
| (c) | 50                  | 2                        | 48      |
| (d) | 30                  | 10                       | 60      |
| (e) | 20                  | 40                       | 40      |

4. How many grams of pure astracanite could be obtained as a precipitate by dehydrating 1 kg of a solution of composition *e*, Figure 6.6, at 23.0°C?

5. It is required to prepare 500 g of a solution having the composition 10% sodium sulfate, 20% magnesium sulfate, 70% water. Calculate the required weights of each constituent in the following sets of available ingredients:

- Glauber's salt, magnesium sulfate, and water
- Glauber's salt, Epsom salt, and water
- Astracanite, Epsom salt, and water

6. Assuming equilibrium conditions, state the changes in the proportions and compositions of the phases during the isothermal evaporation to complete solidification at 23°C of a solution consisting of 10% sodium sulfate, 5% magnesium sulfate, 85% water. Trace the paths of the representative points of the liquid and the whole solids during this evaporation.

## CHAPTER 7

### THREE-COMPONENT SYSTEMS AT FIXED TEMPERATURE AND PRESSURE

The systems discussed in this chapter will, for convenience, be classified in the same way as in the treatment of two-component systems, according to the number of phases of variable composition (solutions) which can coexist in equilibrium.

#### 7.1 One Phase of Variable Composition. The System $\text{Na}_2\text{SO}_4\text{-NaCl-Na}_2\text{SO}_4\cdot\text{NaF}$

This system, which is a part of the system sodium sulfate-sodium chloride-sodium fluoride, has been chosen to illustrate a simple type of three-component diagram; here there appear no binary or ternary compounds of the components, no transition points, and no solid solutions. This diagram is characterized by a single ternary eutectic point. The three components melt congruently, sodium sulfate at  $884^\circ\text{C}$ , sodium chloride at  $801^\circ\text{C}$ , and the double salt at  $786^\circ\text{C}$ . The phase relationships obtaining in the binary systems are shown in Figure 7.1; isothermal sections have been ruled at  $760$ ,  $743$ ,  $706$ , and  $615^\circ\text{C}$ . The phase relationships obtaining at these same temperatures in the ternary system are shown in Figures 7.2 to 7.5.

The relationship of the perimeter of Figure 7.2 to the isothermal section at  $760^\circ\text{C}$  of Figure 7.1 is made obvious by the correspondence of the letters  $m$ ,  $n$ ,  $p$ ,  $q$ ,  $r$ , and  $s$ . In both diagrams  $m$  is the composition of a solution saturated with respect to sodium sulfate and containing only sodium sulfate and sodium chloride;  $s$  is the composition of a solution saturated with respect to sodium sulfate and containing only sodium sulfate and the double salt. In Figure 7.2 the compositions of ternary solutions saturated with respect to sodium sulfate lie on the line  $ms$ . The sodium sulfate apex,  $A$ , is therefore the origin of a system of radial tie lines terminating

on the line  $ms$ ; the area  $Ams$  is the field of sodium sulfate. Under equilibrium conditions at  $760^{\circ}\text{C}$ , any system having an over-all composition lying within this area will consist of a mixture of solid sodium sulfate and a liquid solution saturated with respect to

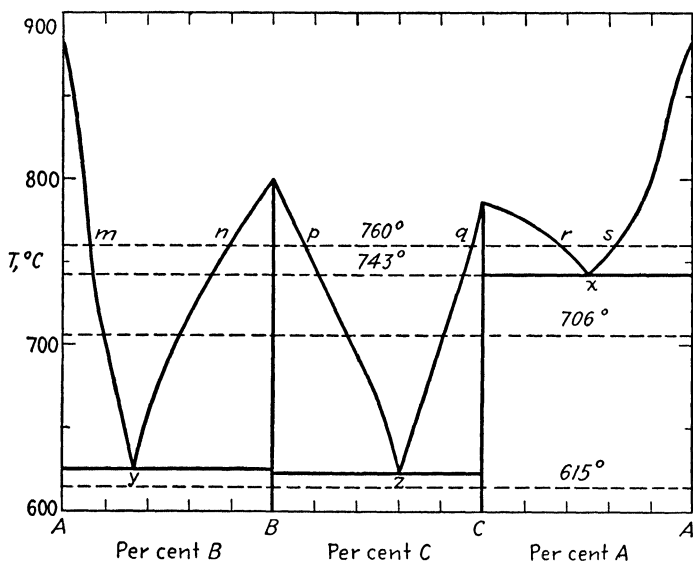


FIG. 7.1 Phase diagrams for the systems  $\text{Na}_2\text{SO}_4\text{-NaCl}$  (A-B);  $\text{NaCl-Na}_2\text{SO}_4\cdot\text{NaF}$  (B-C);  $\text{Na}_2\text{SO}_4\cdot\text{NaF-Na}_2\text{SO}_4$  (C-A).

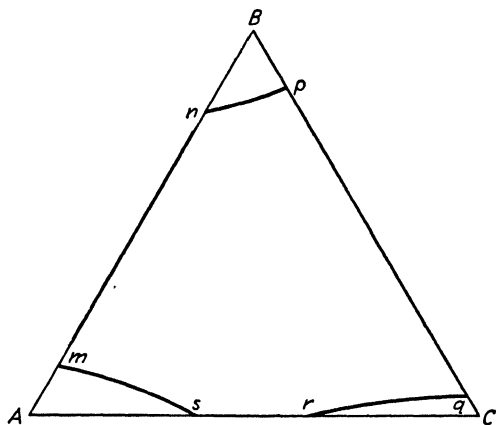


FIG. 7.2 The system  $\text{Na}_2\text{SO}_4(\text{A})\text{-NaCl}(\text{B})\text{-Na}_2\text{SO}_4\cdot\text{NaF}(\text{C})$  at  $760^{\circ}\text{C}$  and 1 atm.

sodium sulfate. The proportions of the two phases can be obtained by applying the proportioning rule to a tie line drawn through the over-all composition. The fields of sodium chloride and the double salt are defined as the areas  $Bnp$  and  $Cqr$ , respectively. The area  $mnpqrs$  defines the field of unsaturated liquid solutions at  $760^{\circ}\text{C}$ .

The perimeter in Figure 7.3 is derived from the isothermal section of Figure 7.1 at  $743^{\circ}\text{C}$ . This temperature was chosen to be the same as the eutectic temperature of the binary system  $\text{Na}_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4 \cdot \text{NaF}$ ; the eutectic point is designated as  $x$ . A solution of composition  $x$  is saturated simultaneously with respect to sodium

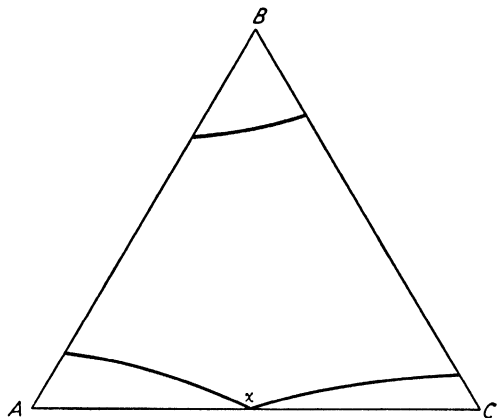


FIG. 7.3 The system  $\text{Na}_2\text{SO}_4(A)$ - $\text{NaCl}(B)$ - $\text{Na}_2\text{SO}_4 \cdot \text{NaF}(C)$  at  $743^{\circ}\text{C}$  and 1 atm.

sulfate and the double salt and therefore  $x$  must be common to the two fields in the ternary as well as in the binary diagram. The isothermal section at  $706^{\circ}\text{C}$  lies below the eutectic temperature  $x$  and therefore points on the line  $AC$  of Figure 7.4 represent mixtures of the two solid components. According to the phase rule a system consisting of a *binary* (two-component) solution simultaneously saturated with respect to the two solid components is univariant (invariant at fixed pressure); a system consisting of a *ternary* (three-component) solution simultaneously saturated with respect to two of the three components is bivariant (univariant at fixed pressure). For Figure 7.4 both the temperature and the pressure have been fixed; under these conditions, therefore, the

system is invariant and the composition of the solution  $x'$  is unique. It should be emphasized that  $x'$  is a *binary eutectic point*<sup>1</sup> in a *ternary* diagram and that it possesses one degree of freedom at fixed pressure; its compositional variation with temperature is shown by  $x$ ,  $x'$ , and  $x''$  of Figures 7.3, 7.4, and 7.5. Systems of over-all composition lying within the triangle  $ACx'$  (Figure 7.4) will, under equilibrium conditions, consist of mixtures of solid  $A$ , solid  $C$ , and the liquid solution  $x'$ .

At 615°C, below all three eutectic temperatures in the binary systems, the field of unsaturated solutions is reduced to the triangular area  $x''y''z''$  (Figure 7.5); the three binary eutectic points

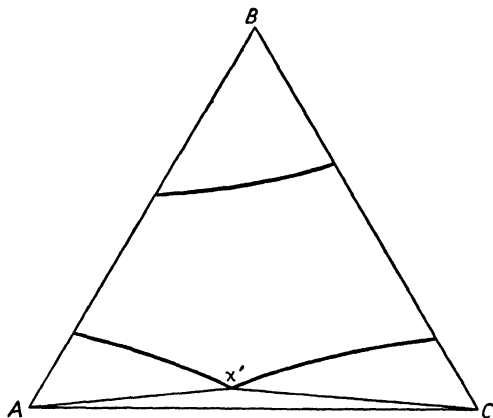


FIG. 7.4 The system  $\text{Na}_2\text{SO}_4(A)\text{-NaCl}(B)\text{-Na}_2\text{SO}_4\cdot\text{NaF}(C)$  at 706°C and 1 atm.

comprise the apices. Of the other six areas,  $Ax''y''$ ,  $By''z''$ , and  $Cz''x''$  are the fields of  $A$ , of  $B$ , and of  $C$ , respectively; the remaining areas represent mixtures of three phases, as described in the previous paragraph. With lowering of temperature the field of unsaturated solutions becomes smaller and at the *ternary eutectic* temperature is reduced to a single point. A ternary eutectic solution is one which can exist in equilibrium with three solid phases (in this case the components) and which can form these three solids on the removal of heat; in accordance with the phase rule,

<sup>1</sup> Here the term "binary" does not refer to the number of components required to describe the solution; it refers to the number of solids with respect to which the solution is saturated.

such a system of four phases is invariant at fixed pressure and thus the ternary eutectic temperature and solution composition are both unique. The ternary eutectic composition is 32% sodium sulfate, 46% sodium chloride, 22% double salt; the ternary eutectic temperature has not been reported, but is probably in the vicinity of 600°C. This temperature is the lowest at which a stable liquid solution of the three components can exist; hence diagrams for lower temperatures are of no interest, since they would represent only mixtures of the three solid components.

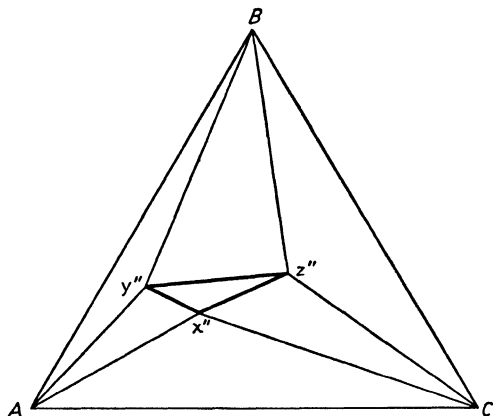


FIG. 7.5 The system  $\text{Na}_2\text{SO}_4(A)\text{-NaCl}(B)\text{-Na}_2\text{SO}_4\cdot\text{NaF}(C)$  at 615°C and 1 atm.

## 7.2 Two Phases of Variable Composition. The System Diethyl Ether-Ethyl Alcohol-Water

In the three-component systems previously discussed the equilibria concerned only one phase of variable composition; the other phase or phases participating in the equilibria were pure substances and hence of invariant composition. The tie lines joining the compositions of the conjugate phases therefore always radiated from single points representing the compositions of the pure substances. However, when two solutions exist together in equilibrium, the corresponding tie lines are defined by *two* variable points.

At 25°C water and alcohol are miscible in all proportions, as are ether and alcohol. On the other hand, ether and water show a limited miscibility; they form a pair of conjugate liquid solutions having the compositions 6.0% ether (94.0% water) and 98.7%

ether (1.3% water). The line  $qq'$  joining these compositions in Figure 7.6 is therefore a tie line. The compositions of the conjugate layers vary with the proportion of alcohol in the system; for example, any system with over-all composition lying on the tie line  $aa'$  will, under equilibrium conditions, consist of two liquid phases of composition  $a$  and  $a'$ . Similarly  $bb'$  is a tie line joining the compositions of the conjugate ternary solutions  $b$  and  $b'$ , which will be the equilibrium phase constituents for any system having an over-all composition lying on the line  $bb'$ . With increasing

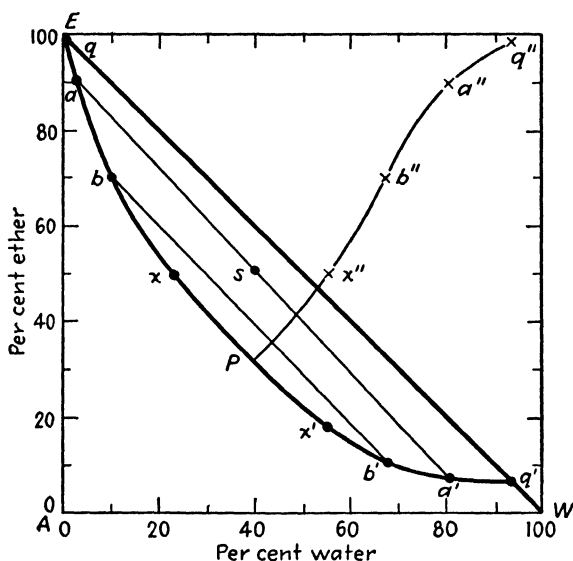


FIG. 7.6 The system diethyl ether-ethyl alcohol-water (E-A-W) at 25°C and 1 atm.

proportion of alcohol the compositions of the conjugate solutions approach one another, with a consequent shortening of the tie line, until in the limit the tie line is reduced to a single point,  $P$ , called the *plait point* (31.6% ether, 40% water, 28.4% alcohol). The loci of the points  $a, b, \dots$  and the points  $a', b', \dots$  define the two branches of the *binodal curve*, continuous through the plait point. The tie line becomes tangential to the binodal curve at the plait point. It should be observed that the tie lines are not parallel to the base line,  $qq'$ , of the binodal curve, except fortuitously

To give complete information about the compositions of con-

jugate solutions in systems of this type, the chemist records the compositions of pairs of conjugate solutions. From these data the binodal curve is drawn; this curve alone does not, however, indicate which compositions are conjugate. This difficulty can be partly overcome by showing a few tie lines in the diagram. The compositions of conjugate pairs other than those for which tie lines have been shown can be found by interpolation; this procedure may not always give the accuracy required. A more elegant method involves the use of a "reference curve." The reference curve  $q''P$  of Figure 7.6 is obtained by plotting the percentage of ether in the ether-rich solution against the percentage of water in the water-rich solution. The coordinates of the point  $q$  are 98.7% ether, 1.3% water; the coordinates of the point  $q'$  are 94.0% water, 6.0% ether. The coordinates of the point  $q''$  on the reference curve are 98.7% on the ether scale, 94.0% on the water scale. The coordinates of the point  $a''$ , derived from those of the points  $a$  and  $a'$ , are 90.0% on the ether scale, 80.5% on the water scale. For every pair of experimental points on the binodal curve there will be a corresponding point on the reference curve. The reference curve is constructed by drawing a smooth curve through  $q''$ ,  $a''$ ,  $b''$ , etc. Clearly, it will intersect the binodal curve at the plait point  $P$ ; in fact, this is usually the most accurate way of determining the coordinates of the plait point. To find the composition of the solution conjugate to any particular ether-rich solution, say  $x$ , it is merely necessary to draw a horizontal line from  $x$  to cut the reference line, in this case at  $x''$ ; a vertical line through  $x''$  is then drawn to cut the binodal curve at  $x'$ , which is the composition of the solution conjugate with  $x$ .

Any system having a composition lying outside the area bounded by the binodal curve and the line  $qq'$  will consist of a single solution. If the over-all composition lies within the area enclosed by the binodal curve and its base line, the system at equilibrium will consist of a mixture of two conjugate ternary solutions. The relative amounts of the two phases can be obtained through the proportioning rule. For example, the system having the over-all composition  $s$ , lying on the tie line  $aa'$ , would consist of  $as/aa'$  of  $a'$  and  $sa'/aa'$  of  $a$ . If the tie line through the particular over-all composition has not been placed on the diagram, it will be necessary to interpolate between known tie lines or to make successive approximations, using the reference line  $Pq''$ .

### 7.3 Two Phases of Variable Composition. The System $(\text{NH}_4)_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$

At 25°C solid ammonium sulfate and solid potassium sulfate are completely miscible, forming a complete series of solid solutions ranging from pure ammonium sulfate to pure potassium sulfate. If a small quantity of water be added to one of these binary solid solutions the system will consist, at equilibrium, of a liquid ternary solution and a solid binary solution; the solute ratios of the two solutions will, in general, be different from one another and from that of the initial solid solution. The compositions of a few of the pairs of conjugate phases at 25°C are indicated by the tie lines in the upper half of Figure 7.7. In this diagram there are two ternary fields, that of the unsaturated liquid solutions and that of the conjugate liquid and solid solutions.

It is apparent from Figure 7.7 that neither of the solute components can be obtained in pure form by a simple crystallization from a ternary solution; such crystallization would yield only solid solutions. For example, if water is evaporated from an unsaturated solution containing equal weights of the two solutes, the first solid formed will be a solution containing approximately 95% potassium sulfate, 5% ammonium sulfate. If the rate of interdiffusion of the dissolved constituents of the solid solution were sufficiently rapid, the solid solution would remain homogeneous during the crystal growth; the ratio of the solute components in the solid would vary continuously until, when the last of the liquid solution disappears, it would become unity; the composition of the last drop of liquid would be 4% potassium sulfate, 36% ammonium sulfate, 60% water. During such a crystallization the composition of the liquid solution would follow the liquidus curve from the point 9% potassium sulfate, 9% ammonium sulfate, 82% water to the point 4% potassium sulfate, 36% ammonium sulfate, 60% water. The representative point of the solid solution would follow a path from the point 95% potassium sulfate, 5% ammonium sulfate to the point 50% potassium sulfate, 50% ammonium sulfate.

The reference curve for Figure 7.7 (analogous to the curve  $q''P$  of Figure 7.6) is the curve which relates the composition of any liquid solution to the composition of its conjugate solid solution. For example, to establish a point  $a''$  on the reference curve, a

straight line is drawn through the point  $a$  parallel to  $AD$ ; a second straight line is drawn through the point  $a'$  parallel to  $CD$ ; the point  $a''$ , relating the compositions of the two conjugate solutions, is the intersection of these two straight lines. By similar construction the experimentally determined compositions of pairs of con-

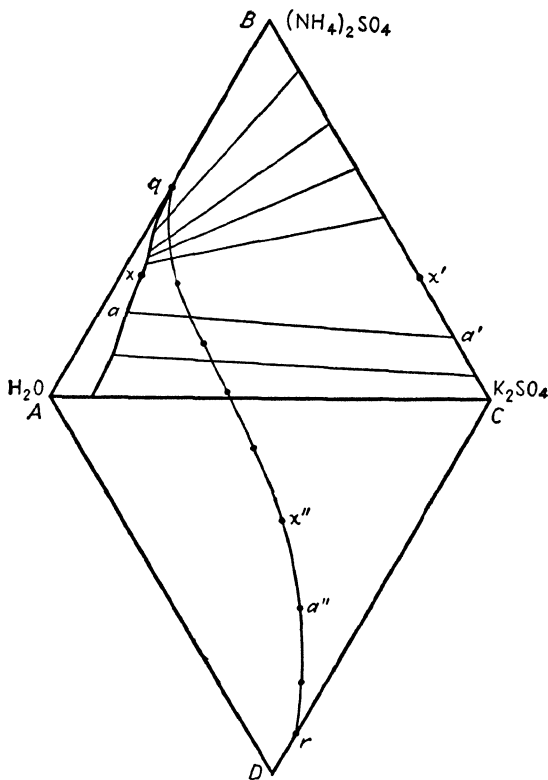


FIG. 7.7 The system  $(\text{NH}_4)_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ - $\text{H}_2\text{O}$  at  $25^\circ\text{C}$  and 1 atm.

jugate solutions can be used to derive the complete reference curve  $rq$ . The reference curve can then be used to determine the composition of a solution conjugate with any given solution. For example, to determine the composition of the solid solution which can exist in equilibrium with a liquid solution of composition  $x$ , a straight line is drawn through  $x$  parallel to  $AD$  to cut the reference curve at  $x''$ ; from  $x''$  a straight line drawn parallel to  $CD$  will cut  $BC$  at  $x'$ , the composition of the conjugate solid solution.

It should be apparent that the line  $rq$  is not the only choice of reference curve. The point  $a$ , for example, can be defined by the intersection of the liquidus curve with any one of three straight lines, parallel to  $AB$ ,  $BC$ , or  $CA$ ; the point  $a'$  can be defined by the intersection of the solidus curve  $BC'$  with either of two straight lines, parallel to  $AB$  or  $CA$ . The point  $a''$  of a reference curve can be the intersection of one of the first three lines with one of the second group; it will be seen that there are four possible positions for  $a''$ , and hence four possible reference curves can be drawn.

#### 7.4 Two Phases of Variable Composition. The System Phenol-Water-Aniline

As shown in Chapter 5 the two-component system phenol-water exhibits conjugate liquid solutions below  $66^{\circ}\text{C}$ . The two-component system aniline-water also shows conjugate liquid solutions with a consolute temperature in the vicinity of  $170^{\circ}\text{C}$ . Above

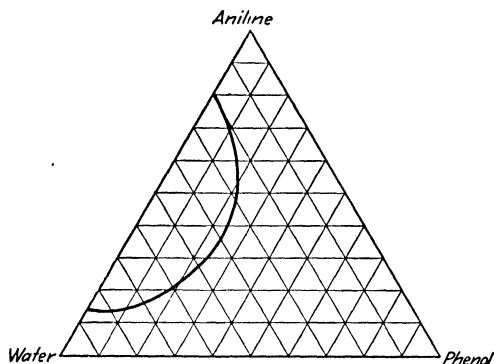


FIG. 7.8 The system phenol-water-aniline at  $140^{\circ}\text{C}$ ; pressure greater than 1 atm.

$40.5^{\circ}\text{C}$ , the melting point of phenol, aniline and phenol are completely miscible liquids in the two-component system aniline-phenol. Above the consolute temperature for water and aniline the three components, phenol, water, and aniline, are miscible in all proportions. The phase relationships at lower temperatures are shown in Figures 7.8, 7.9, and 7.10.

At  $140^{\circ}\text{C}$  (Figure 7.8) the system shows a single continuous binodal curve similar to that shown by the system diethyl ether-

ethyl alcohol-water at 25°C (Figure 7.6). The area within the binodal curve, *i.e.*, the field of conjugate liquid solutions, increases as the temperature is lowered. At the consolute temperature of

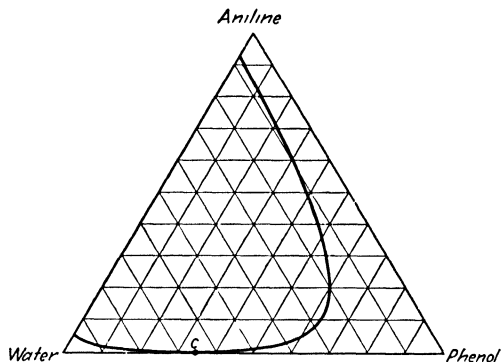


FIG. 7.9 The system phenol-water-aniline at the consolute temperature, 66°C, of the system phenol-water.

the system phenol-water, 66°C (Figure 7.9), the binodal curve just touches the phenol-water axis at the consolute composition of the system phenol-water, 34% phenol, 66% water. At 50°C the bi-

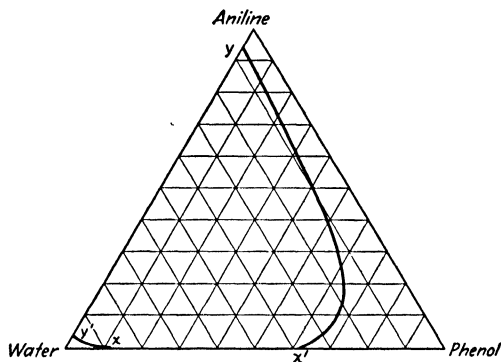


FIG. 7.10 The system phenol-water-aniline at 50°C.

nodal curve intersects the phenol-water axis at two points which are, of course, the compositions of the conjugate phenol-water solutions, 11.8 and 62.6% phenol (see Section 5.2), as shown by the points  $x$  and  $x'$  of Figure 7.10. The line  $xx'$  is a tie line joining conjugate compositions on the binodal curve at 0% aniline; the line

$yy'$  is a tie line on the binodal curve at 0% phenol. Between 0% phenol and 0% aniline the slope of the tie lines therefore changes continuously from that of  $yy'$  to that of  $xx'$ . From this it can be seen that at 66°C the point of contact between the phenol-water axis and the binodal curve is the *plait point* of the latter, since the *plait point* must be the limit of a series of tie lines which become parallel to the phenol-water axis at 0% aniline.

### 7.5 Two Phases of Variable Composition. Systems Showing More than One Binodal Curve

It has been shown that below 66°C the system phenol-water-aniline exhibits an area of immiscibility which forms a band across

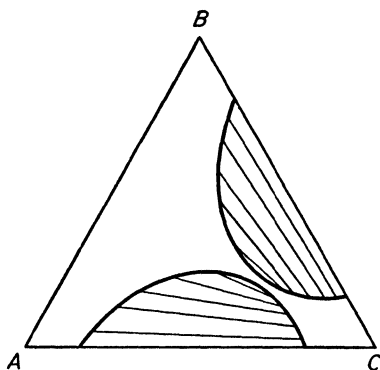


FIG. 7.11 Phase diagram for a system  $A$ - $B$ - $C$ , showing two binodal curves at  $T^\circ\text{C}$ .

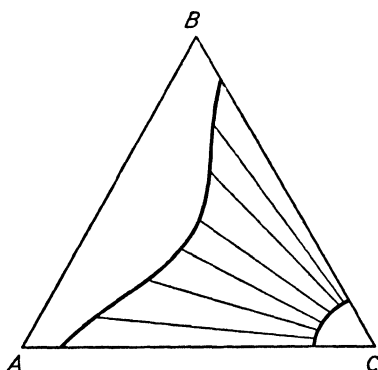


FIG. 7.12 Phase diagram for system  $A$ - $B$ - $C$  at  $T'^\circ\text{C}$  ( $T' < T$ ).

the diagram. Such a band can also exist in the diagram for a system which at higher temperatures shows two binodal curves. For example, at  $T^\circ\text{C}$  the system  $A$ - $B$ - $C$  of Figure 7.11 shows two areas of immiscibility. If the areas of immiscibility increase as the temperature is lowered, the two plait points can approach one another and can become coincident at a unique temperature. At lower temperatures the areas of immiscibility can merge into a band such as that shown in Figure 7.12.

If a system shows three areas of immiscibility (Figure 7.13), it is conceivable that at lower temperatures the diagram could take the form shown in Figure 7.14. At a still lower temperature the

plait point  $P$  of the lower binodal curve could touch the other field of immiscibility, as shown in Figure 7.15. Here the solution having the composition of the plait point can exist in equilibrium with a conjugate solution having the composition  $S$ . At temperatures below this the diagram could take the form shown in Figure 7.16, in which the tie lines indicate that the solutions  $a$ ,  $b$ , and  $c$  can coexist in equilibrium simultaneously. Figure 7.16 shows four areas of immiscibility; three of these concern pairs of conjugate

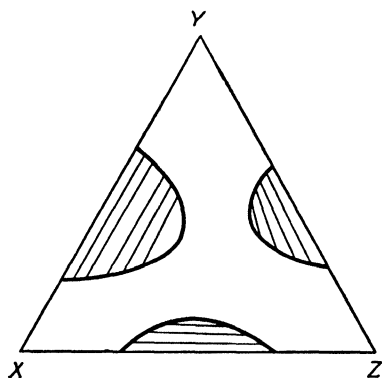


FIG. 7.13 Phase diagram for a system  $X$ - $Y$ - $Z$ , showing three binodal curves at  $T_1^\circ\text{C}$  ( $T_1 > T_2 > T_3 > T_4$ ).

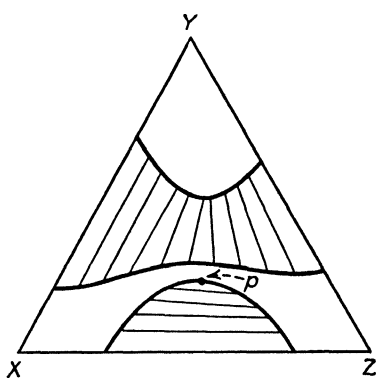


FIG. 7.14 Phase diagram for the system  $X$ - $Y$ - $Z$  at  $T_2^\circ\text{C}$  ( $T_1 > T_2 > T_3 > T_4$ ).

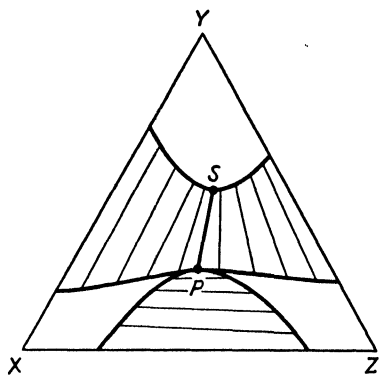


FIG. 7.15 Phase diagram for the system  $X$ - $Y$ - $Z$  at  $T_3^\circ\text{C}$  ( $T_1 > T_2 > T_3 > T_4$ ).

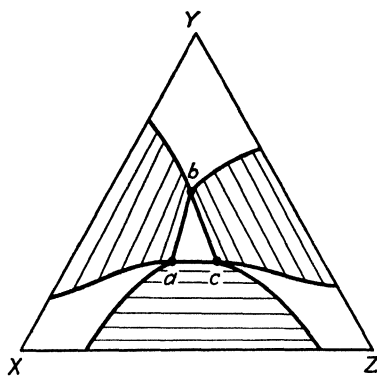


FIG. 7.16 Phase diagram for the system  $X$ - $Y$ - $Z$  at  $T_4^\circ\text{C}$  ( $T_1 > T_2 > T_3 > T_4$ ).

liquids and any system having a composition within one of these three areas will be univariant at fixed temperature and pressure. Any system having a composition lying within the fourth area, the triangle *abc*, will consist of three liquid phases (*a*, *b*, and *c*) and will thus be invariant at fixed temperature and pressure; the proportions of the three liquid phases could, of course, be determined with the aid of the proportioning rule.

### EXERCISES

1. Assuming equilibrium, state the weights and compositions of the phase constituents of the system represented by point *s*, Figure 7.6, and having a total weight of 200 g.

2. A system consists of 60 g of ether and 40 g of water at 25°C. Assuming equilibrium, describe this system completely. Calculate the weight of 80% aqueous alcohol (20% water) which, when added to the above system, would be sufficient to render it homogeneous.

3. At 25°C water is gradually added to a solution consisting of 60% ether, 40% alcohol. State the changes in the compositions and proportions of the phases which would occur under equilibrium conditions.

4. A solid solution consisting of 25% potassium sulfate, 75% ammonium sulfate is completely dissolved in water and the resulting solution is then evaporated at 25°C. What would be the composition of the first solid formed on evaporation?

## CHAPTER 8

### THREE-COMPONENT SYSTEMS. SOLID DIAGRAMS AND THEIR PLANE PROJECTIONS

#### 8.1 The System $\text{Na}_2\text{SO}_4\text{-NaCl-Na}_2\text{SO}_4\text{-NaF}$

The diagrams for the three-component systems discussed so far have been both isothermal and isobaric. This limitation allowed representation on a plane diagram. The effect of temperature or pressure can be shown by the use of a third coordinate to give a "solid diagram." For condensed systems the isobaric diagram is the obvious choice. In Figure 8.1 is shown an isometric drawing of the isobaric diagram for the system  $\text{Na}_2\text{SO}_4\text{-NaCl-Na}_2\text{SO}_4\text{-NaF}$ , which was discussed in Chapter 7. Composition is represented in the horizontal plane and temperature by the vertical coordinate. The base of the prism is the familiar equilateral triangle and the sides, each representing the isobaric diagram for the corresponding two-component system, are identical with Figure 7.1.

Any point on the upper (liquidus) surface of Figure 8.1 represents the temperature and composition of a liquid which can exist in equilibrium with one or more solid phases. The liquidus surface for this system is comprised of three well-defined portions (solubility surfaces) corresponding to the three solid components with respect to which saturation can occur. The three portions of the surface meet along the "valley" lines,  $xe$ ,  $ye$ , and  $ze$ . A point on a valley line is common to two solubility surfaces and therefore represents the temperature and composition of a liquid solution saturated with respect to two solid components; such a liquid solution would be univariant at fixed pressure. The intersection  $e$  of the three valley lines is a point common to all three solubility surfaces and represents the temperature and composition of a liquid solution saturated with respect to all three of the

solid components, and is therefore invariant at fixed pressure. The point  $x$  is the binary eutectic point in the binary system  $A$ - $C$ ;  $xe$  is the  $A$ - $C$  binary eutectic line, *i.e.*, the locus of the  $A$ - $C$  binary eutectic point in the ternary system  $A$ - $B$ - $C$ ;  $e$  is the ternary eutectic point in the ternary system (*cf.* Section 7.1).

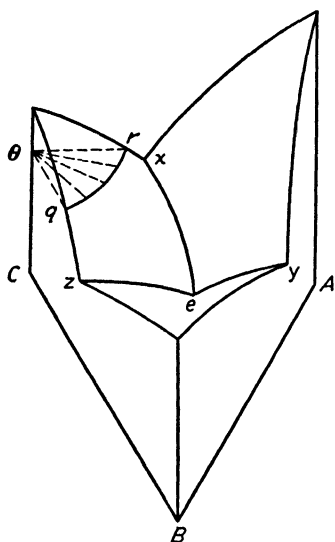


FIG. 8.1 The isometric projection of the solid phase diagram for the system  $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$ - $\text{Na}_2\text{SO}_4 \cdot \text{NaF}$  ( $A$ - $B$ - $C$ ).

The condition of fixed temperature (as well as fixed pressure) defines a plane parallel to the basal plane  $ABC$  of Figure 8.1. The intersection of the isothermal plane at the temperature  $\theta = 760^\circ\text{C}$  with the solubility surface of  $C$  is shown by the contour line  $qr$ . Points on this contour line represent the compositions of solutions saturated with respect to  $C$  at  $760^\circ\text{C}$  and 1 atm. The point  $\theta$  is the origin of a system of tie lines terminating on the contour line  $qr$ ; a few of these are shown. Clearly, the isothermal contour line  $qr$  of Figure 8.1 is identical with the solubility curve  $qr$  of Figure 7.2. Moreover, it can be seen that the solubility surface of  $A$ ,  $B$ , or  $C$  can be considered as being generated by a series of solubility curves (contour lines) extending from the melting point of the compound down to the ternary eutectic temperature.

In addition to being cumbersome, the solid diagram suffers from the disadvantage that the temperature and composition coordinates of a point on the liquidus surface are difficult to evaluate. It is convenient to make use of the plane projection of the solid diagram, as shown in Figure 8.2. With sufficient contour lines such a diagram gives as much information as the solid diagram, and in a more accessible way. Thus Figure 8.2 shows the solubility curves of Figures 7.2 to 7.5, and in addition, the ternary eutectic point  $e$  and the loci  $xe$ ,  $ye$ , and  $ze$  of the binary eutectic points. The area  $Czex$  of Figure 8.2 is the projection of the solu-

In addition to being cumbersome, the solid diagram suffers from the disadvantage that the temperature and composition coordinates of a point on the liquidus surface are difficult to evaluate. It is convenient to make use of the plane projection of the solid diagram, as shown in Figure 8.2. With sufficient contour lines such a diagram gives as much information as the solid diagram, and in a more accessible way. Thus Figure 8.2 shows the solubility curves of Figures 7.2 to 7.5, and in addition, the ternary eutectic point  $e$  and the loci  $xe$ ,  $ye$ , and  $ze$  of the binary eutectic points. The area  $Czex$  of Figure 8.2 is the projection of the solu-

bility surface of  $C$  in Figure 8.1, and hence is called the *field* of the compound  $\text{Na}_2\text{SO}_4 \cdot \text{NaF}$  ( $C$ ). Similarly  $Axey$  is the field of  $A$  and  $Byez$  is the field of  $B$ . The arrows on the binary eutectic curves of Figure 8.2 indicate the direction of *rising* temperature; they are not always included in the plane projection since, as will be shown later, their directions can be determined even in the absence of contour lines.

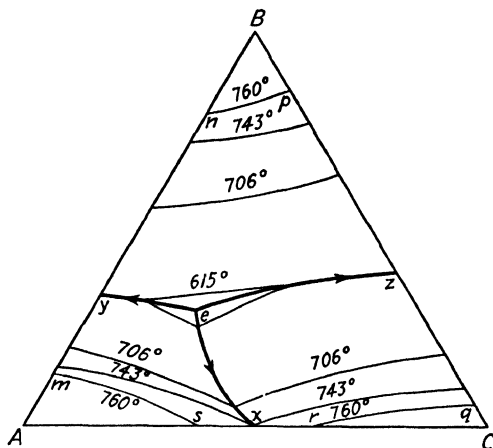


FIG. 8.2 The plane projection of the diagram of Figure 8.1.

## 8.2 Courses of Crystallization in a System Having a Single Ternary Invariant Point

The course of a typical crystallization in the system  $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$ - $\text{Na}_2\text{SO}_4 \cdot \text{NaF}$  is illustrated in Figure 8.3. A melt consisting of 60%  $A$ , 10%  $B$ , and 30%  $C$  is represented by the point  $S$ ; at elevated temperatures it is an unsaturated solution. As the temperature is lowered, the melt will become saturated with respect to  $A$  at the liquidus temperature for that particular composition ( $S$  would then lie on the liquidus surface of Figure 8.1). Crystallization of  $A$  from the melt must decrease the proportion of  $A$  in the melt without affecting the relative proportions of  $B$  and  $C$ . The composition of the remaining melt must therefore lie on the prolongation of the line  $AS$  remote from  $A$ . The proportioning rule makes this evident, in that the addition of a substance  $h$  to the substance  $A$  in the proportions  $AS/Ah$  of  $h$  to  $Sh/Ah$  of  $A$  will yield a system having the over-all composition  $S$ . On further

cooling, the crystallization of  $A$  will continue and the composition of the melt will follow the same straight line until it reaches the binary eutectic curve  $xe$  at the point  $j$ . The melt will then be saturated with respect to both  $A$  and  $C$ . Further removal of heat will cause simultaneous separation of  $A$  and  $C$  from the melt. The composition of the melt will then change, but in such a way that it will remain saturated with respect to both  $A$  and  $C$ , that is, the composition of the melt must remain on the binary eutectic curve  $xe$ . Since the removal of both  $A$  and  $C$  causes an increase in the proportion of  $B$  in the melt, its composition will follow the

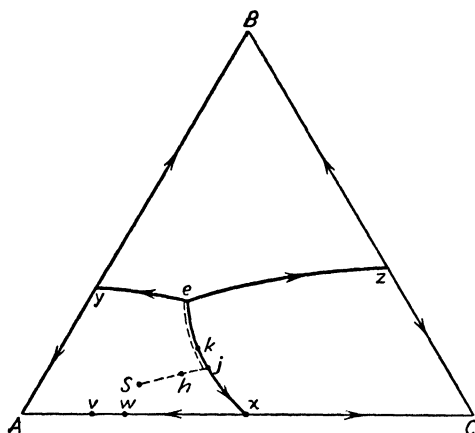


FIG. 8.3 A course of crystallization in the system  $\text{Na}_2\text{SO}_4(A)\text{-NaCl}(B)\text{-Na}_2\text{SO}_4\cdot\text{NaF}(C)$ .

binary eutectic curve in the direction  $je$  rather than  $jx$ . Although three phases are present, the temperature is still lowered by the removal of heat; the system is univariant at fixed pressure.

Before the crystallization of  $C$ , the composition of the solid was represented by the point  $A$ . However, as the composition of the melt changes from  $j$  toward  $e$  the solids will consist of a mixture of  $A$  and  $C$ . Furthermore, since the over-all composition of the melt plus the whole solids is identical with  $S$ , then, by the proportioning rule,  $S$  must lie on the straight line between the point representing the composition of the melt and that representing the composition of the whole solids. For example, when the melt has the composition  $k$  the composition of the whole solids is defined by the intersection of the line  $AC$  with the prolongation

of the line  $kS$ , that is, the point  $v$ . By this construction  $k$ ,  $S$ , and  $v$  are collinear, as required. As the composition of the melt follows the path  $je$  the composition of the whole solids follows the path  $Aw$ . It is convenient to visualize these simultaneous changes of composition by imagining a rod pivoted at the point  $S$ . As the rod is rotated in an anticlockwise direction it will continuously intersect the lines  $AC$  and  $xe$  at the simultaneous compositions of the whole solids and the melt, respectively.

When its composition has reached the point  $e$  the melt will be saturated not only with respect to  $A$  and  $C$ , but also with respect to  $B$ . Under equilibrium conditions further removal of heat will cause simultaneous crystallization of all three of the components. The phase constituents will then be four in number and at constant pressure the system will be invariant. Under this condition of invariance further removal of heat can neither alter the temperature nor change the composition of the melt. The only endothermic process possible, therefore, is the simultaneous crystallization of  $A$ ,  $B$ , and  $C$  in such proportions that the composition of the melt remains fixed, *i.e.*, in the proportions present in the melt  $e$ .

Just as the melt reaches the composition  $e$ , the composition of the whole solids will be given by the point  $w$ . The *new* solids, obtained by the further removal of heat, will have the composition  $e$ , and are therefore referred to as the "eutectic mixture." The whole solids could be considered as being composed of the mixture  $w$  and the eutectic mixture of composition  $e$ ; the composition of the whole solids must therefore lie on the line  $we$ . As the melt solidifies, the proportion of the eutectic mixture in the whole solids increases; the composition of the latter must change from  $w$  toward  $e$  until, when the last of the melt has solidified, the whole solids have the composition  $S$ . During the course of the crystallization the composition of the melt follows the path  $Sje$ , while that of the whole solids simultaneously follows the path  $AwS$ .

### 8.3 Systems Having a Single Binary Compound Which Melts Congruently. The System $\text{Na}_2\text{SO}_4\text{-NaCl-NaF}$

In the system discussed immediately above, the compound  $\text{Na}_2\text{SO}_4\cdot\text{NaF}$  was one of the components, and properly so, since the composition of any phase encountered in that system could be expressed in terms of sodium sulfate, sodium chloride, and the

double salt. In the system to be described in this section the components are sodium sulfate, sodium chloride, and sodium fluoride; the double salt  $\text{Na}_2\text{SO}_4 \cdot \text{NaF}$  is thus a *binary compound* in this system, since its composition can be described in terms of *two* of the components, sodium sulfate and sodium fluoride. The phase diagram for this system is given in Figure 8.4. The portion of the diagram enclosed by the triangle  $ABC$  is identical with that of Figure 8.3, with the exception that the triangle  $ABC$  is no longer equilateral.

It will be recalled that in the case of a two-component system exhibiting a binary compound, if the compound melts *congruently*

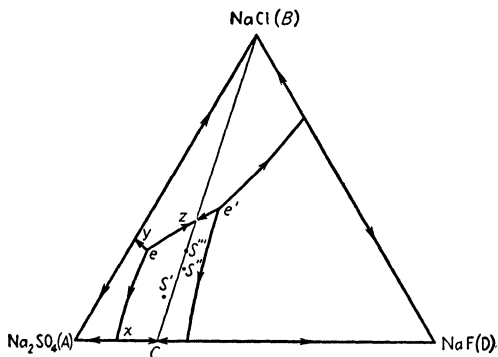


FIG. 8.4 The system  $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$ - $\text{NaF}$ ;  $C = \text{Na}_2\text{SO}_4 \cdot \text{NaF}$ .

the phase diagram can be divided into two completely independent diagrams, the phase relationships in the one having no bearing on those in the other. Similarly, a division into two independent parts is possible in the diagram for a three-component system exhibiting a binary compound which melts *congruently*. Such a division is made by the line  $BC$  in Figure 8.4. The phase relationships for the triangle  $ABC$  are independent of those for the triangle  $BCD$ , as can be shown by the following considerations.

A typical course of crystallization for a system lying in the field of sodium sulfate has already been given in Section 8.2. The course of crystallization for a system  $S'$  lying within the field of the binary compound  $C$  and a little to the *left* of the line  $BC$  will follow a similar pattern. The path of the representative point of the liquid will be a straight line from  $S'$  directly away from  $C$  until it reaches the binary eutectic line  $ze$ . With the subsequent

precipitation of  $B$ , the path of the whole solids must move along the straight line from  $C$  toward  $B$ ; the path of the representative point of the liquid will simultaneously follow the line  $ze$  until it reaches  $e$ , at which point it terminates. No matter how close the composition  $S'$  is to the line  $BC$  (provided it does not lie *on*  $BC$ ), a similar course of crystallization will obtain. It can be seen that the temperature represented by the point  $z$  must be the *maximum* temperature for the line  $ze$ . Consideration of the course of crystallization for any system  $S''$  lying within the field of  $C$ , but a little to the *right* of the line  $BC$ , will show that the path of the liquid will terminate at the eutectic point  $e'$  and that the point  $z$  represents the *maximum* temperature along the line  $ze'$ , and therefore along the line  $ee'$ . The maximum temperature at  $z$  is indicated by the arrows meeting head to head at that point. This is invariably the case when the straight line between the representative points of two compounds which melt congruently (for example,  $B$  and  $C$ ) intersects *their* binary eutectic curve.

It has been pointed out that  $z$  is the binary eutectic point for the binary system  $B$ - $C$ . This can be illustrated from another point of view by considering the course of crystallization of a melt  $S'''$  lying *on* the line  $BC$  of Figure 8.4. As  $C$  precipitates, the composition of the liquid will follow a straight line from  $S'''$  directly away from  $C$ ; it will remain on the line  $BC$  from  $S'''$  to  $z$ . With the precipitation of  $B$ , as well as  $C$ , the composition of the whole solids will move from  $C$  toward  $B$ . The compositions of all three phases present can be expressed in terms of  $B$  and  $C$  only; the system is therefore two-component, regardless of the fact that the composition of the liquid may be expressed in terms of three constituents,  $A$ ,  $B$ , and  $D$ . At fixed pressure,  $z$  is an invariant point; the temperature of the system and the composition of the liquid will remain fixed until crystallization is complete and the composition of the whole solids has reached  $S'''$ . The temperature represented by  $z$  is thus a *minimum* along the line  $BC$  and a *maximum* along the line  $ee'$ ;  $z$  is therefore the mid-point of a "saddle-back" on the three-dimensional solid diagram for the system  $A$ - $B$ - $D$ .

To summarize, the phase diagram for a ternary system having a single binary compound which melts *congruently* can be divided into two completely independent diagrams, each of which is of the simple type shown in Figure 8.3.

### 8.4 Systems Having a Single Binary Compound Which Melts Incongruently

The two-component diagrams for a system of this kind are typified in Figure 8.5;  $F$  is a binary compound (of  $A$  and  $C$ ) which melts incongruently. The ternary diagram for the system  $A$ - $B$ - $C$  is shown in Figure 8.6. In this diagram the line  $AC$  is the projection of the liquidus curve of the two-component system  $A$ - $C$ , with the invariant points  $x$  and  $y$  included. The line  $xy$  in Figure 8.6 represents the range of composition of the binary liquids which can exist in equilibrium with  $F$ . The solubility surface of  $F$  must therefore include the line  $xy$  as part of its boundary. Since  $F$  lies outside the line  $xy$ , as is always the case with compounds

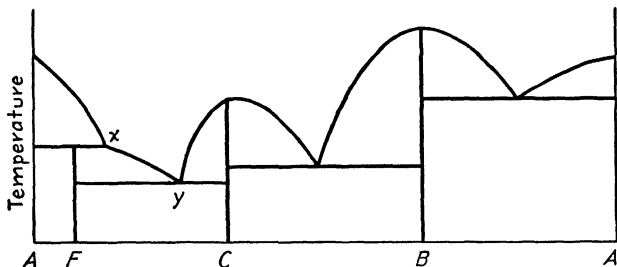


FIG. 8.5 Phase diagrams for the binary systems  $A$ - $C$ ,  $C$ - $B$ ,  $B$ - $A$ .

melting incongruently, it must also lie outside its solubility surface in the three-component system. This is in contrast to the case for compounds which melt congruently, for example,  $A$ ,  $B$ , and  $C$ . The area  $xtey$  represents the field of  $F$ .

While the directions of rising temperature along the "binary lines" of Figure 8.6 are shown by arrows, it would be well to prove that they must lie as shown. If a melt having an over-all composition  $M$  lying within the field of  $B$  is cooled, the first solid formed will be  $B$ . The subsequent path of the representative point of the liquid will be directly away from  $B$  until it meets the binary line  $ev$ ; with the subsequent precipitation of  $C$ , as well as  $B$ , the composition of the whole solids will follow a path from  $B$  directly toward  $C$ . The liquid composition, constrained to remain on the binary line  $ev$ , will proceed in the direction of  $e$  since, in accordance with the proportioning rule, a straight line drawn from the representative point of the whole solids to that of the



arrow on the line  $ye$  can be justified by a consideration of the course of crystallization of any melt having a composition within the area bounded by the curve  $ye$  and the two straight lines  $yC$  and  $Ce$ , that is, any melt from which  $C$  will crystallize as the first solid and  $F$  as the second.

In order to prove that there is a temperature rise along the line  $tx$  from  $t$  toward  $x$ , it is necessary to consider the course of crystallization of any melt lying within the triangle  $ABF$  below a line joining  $A$  and  $t$ . (The necessity for this restriction will become apparent in the consideration of the courses of crystallization to be discussed with the aid of Figures 8.7 to 8.12.) The first solid to be formed in the crystallization of a melt chosen in this way will be  $A$ . When the path of the liquid composition reaches the binary curve  $tx$  the liquid will be saturated with respect to  $F$  as well as  $A$ . With further cooling  $F$  will precipitate as well and the composition of the whole solids will move from  $A$  toward  $F$ . The liquid composition will therefore follow the binary curve  $xt$  in the direction toward  $t$ , that is,  $x$  is the maximum temperature on the binary curve  $tx$ .

The course of crystallization of any melt having a composition lying either in the field of  $C$  or in that portion of the field of  $B$  to the right of a line  $Bt$  will be analogous to the one illustrated in Figure 8.3. The composition of the liquid will follow a path across the field of the initial solid (directly away from the composition of that solid) until it intersects a binary curve ( $ye$ ,  $ve$ , or  $te$ ); it will follow the binary curve until the liquid attains the eutectic, and final, composition  $e$ . If  $B$  is the initial solid the second solid to be formed will be either  $C$  or  $F$ , depending on whether the path of the liquid intersects  $ve$  or  $te$ ; the subsequent path of the whole solids will follow along either  $BC$  or  $BF$  until the liquid composition reaches  $e$ ; the composition of the whole solids will then proceed directly toward  $e$  until it reaches the composition of the original melt. If  $C$  is the initial solid the second solid will be either  $B$  or  $F$ , depending on whether the path of the liquid intersects  $ve$  or  $ye$ ; the subsequent path of the whole solids will follow along either  $CB$  or  $CF$  until the liquid composition reaches  $e$ ; the composition of the whole solids will then proceed directly toward  $e$  until it reaches the composition of the original melt.

A somewhat different course of crystallization will result on cooling a melt having the composition  $P$  within the field of  $F$

(Figure 8.7). The first solid formed will be  $F$ ; the composition of the liquid will follow the dashed line until it reaches  $e$ . The composition of the solids will follow the double line until it reaches  $P$ . The course of crystallization for any system having a composition lying in the field of  $F$  and *below* a line  $Fe$  will be similar. If, on the other hand, the over-all composition of the system lies in the field of  $F$  but *above* the line  $Fe$ , the paths of the liquid and the whole solids will be similar to those shown for the system  $Q$  of Figure 8.8.

The course of crystallization of the melt  $R$  (Figure 8.9) is rather interesting. While  $B$  alone is crystallizing the composition of the liquid follows the path  $Rs$ ; at  $s$  the liquid will be saturated with respect to  $A$  as well as  $B$ . As  $A$  and  $B$  crystallize simultaneously the composition of the liquid will follow the path  $st$ . The composition of the whole solids will follow the path  $BA$  until, when the liquid has the composition  $t$ , the solids will be represented by  $a$ . ( $a$ ,  $R$ , and  $t$  are, of course, collinear.) A liquid having the composition  $t$  is saturated with respect to the three solids  $B$ ,  $A$ , and  $F$ . Further removal of heat will cause the crystallization of  $F$ . The presence of four phases demands that the system be invariant at fixed pressure; the composition of the liquid and the temperature will remain fixed until one of the four phases is used up. If  $t$  were within the triangle  $BAF$  it is clear that a reaction could occur in which the liquid would be used up and positive quantities of  $B$ ,  $A$ , and  $F$  would be formed. With  $t$  *outside* the triangle  $BAF$  such a process cannot occur. However, a reaction is possible whereby some liquid  $t$  and solid  $A$  can produce a mixture of the solids  $B$  and  $F$ . This can be seen from the fact that a line drawn between  $A$  and  $t$  will intersect the line  $BF$  at the point  $m$ . Solid  $A$  and liquid  $t$  in the proportions  $mt$  of  $A$  to  $Am$  of  $t$  can form  $B$  and  $F$  in the proportions  $mF$  of  $B$  to  $Bm$  of  $F$ . Thus, without change in the composition of the liquid, some of the liquid will react with  $A$  to form additional  $B$  and  $F$ . The solid  $A$  is said to be "resorbed."

That the resorption of  $A$  will occur can also be shown by consideration of the composition of  $t$  in terms of  $A$ ,  $B$ , and  $F$ . The percentage of  $A$  in a system represented by the point  $A$  will obviously be 100, that in a system represented by a point lying on the line  $BF$  will clearly be zero. Points on the  $A$  side of the line  $BF$  will represent *positive* percentages of  $A$ ; points on the side

of the line  $BF$  remote from  $A$  will therefore represent *negative* percentages of  $A$ . Similarly,  $AF$  is the reference line for percentages of  $B$ , and  $AB$  is the reference line for percentages of  $F$ . Thus the composition of solution  $t$ , in terms of  $A$ ,  $B$ , and  $F$ , will

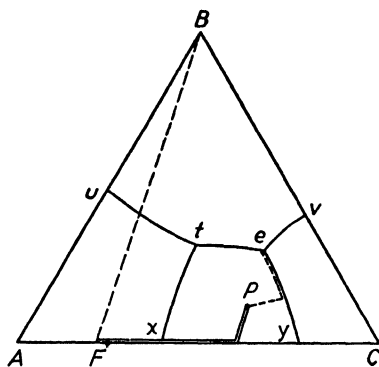


FIG. 8.7

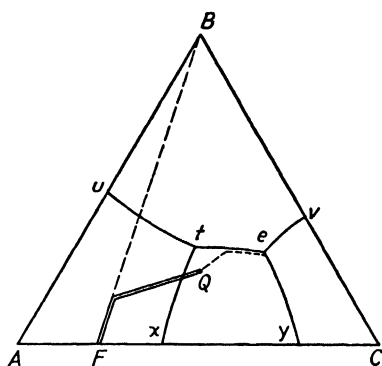


FIG. 8.8

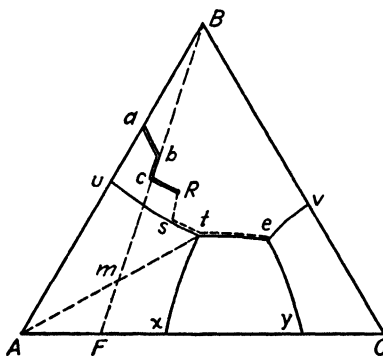


FIG. 8.9

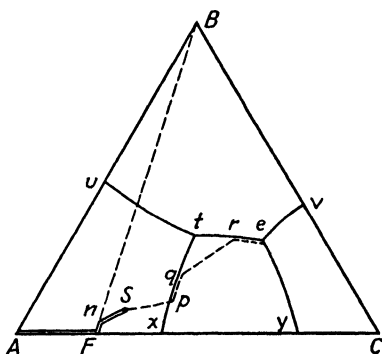


FIG. 8.10

FIGS. 8.7 to 8.10 Courses of crystallization in a ternary system having a binary compound which melts incongruently.

be a negative percentage of  $A$  and positive percentages of  $B$  and  $F$ . This is in agreement with the statement in the previous paragraph,

$$m = A + t = B + F \quad \text{whence } t = B + F - A$$

Quantitatively, the composition  $t$  can be expressed by means of the proportioning rule as  $At/Am$  of  $m$  and  $tm/Am$  of  $A$ . It

should be noted that  $At/Am$  is positive (since  $At$  and  $Am$  are measured in the same direction) but that  $tm/Am$  is negative (since  $tm$  and  $Am$  are measured in opposite directions). The composition  $m$  is positive in both  $B$  and  $F$ .

The invariance of the composition of the solution  $t$  during the isothermal resorption of  $A$  demands that the new solids formed as the solution is used up during this process must have the composition  $t$ , that is, positive proportions of  $B$  and  $F$  and a negative proportion of  $A$ . At the beginning of the isothermal process the composition of the solids is represented by  $a$  of Figure 8.9. As the new solids of composition  $t$  are formed the representative point of the whole solids will move along a straight line between  $a$  and  $t$  in the direction toward  $t$ . When the composition of the whole solids reaches  $b$ , on the line  $BF$ , the resorption of  $A$  will be complete. The system will consist of the three phases, solid  $B$ , solid  $F$ , and liquid  $t$ . The system will then be univariant at fixed pressure and the only constraint on the liquid will be that its composition remain on the common boundary of the fields of  $B$  and  $F$ . As  $B$  and  $F$  crystallize, and the composition of the liquid proceeds along the curve  $te$  to  $e$ , the composition of the whole solids will move along the line  $BF$  from  $b$  to  $c$ . The liquid of composition  $e$  will be saturated with respect to  $C$ , as well as  $B$  and  $F$ ; further removal of heat will cause isothermal crystallization of all three solids. The composition of the new solids formed by the crystallization from the liquid will be identical with  $e$ . The composition of the whole solids will then proceed along a straight line  $ce$  until it reaches the point  $R$ ; the system will then be completely solid.

In the previous example resorption was shown to occur when the liquid composition was at an invariant point,  $t$ ; a different type of resorption can be illustrated by considering the cooling of a melt having the composition  $S$  within the field of  $A$  in Figure 8.10. The liquid composition will follow the path  $Sp$  as  $A$  crystallizes. When the liquid attains the composition  $p$  it will be saturated with respect to  $F$  as well as  $A$ . The liquid composition will then be constrained to follow the binary curve  $xt$  in the direction toward  $t$ . At all times the composition of the liquid, the composition of the whole solids, and the over-all composition of the system,  $S$ , must be collinear. It is clear, then, that when the composition of the liquid reaches  $q$  the composition of the whole

solids will be represented by  $F$ , since  $q$ ,  $S$ , and  $F$  are collinear. This can only mean that all of the solid  $A$  which was produced while the composition of the liquid changed from  $S$  to  $p$  must have been resorbed as the liquid composition changed from  $p$  to  $q$ . The simultaneous resorption of  $A$  and crystallization of  $F$  as the liquid composition changes from  $p$  to  $q$  can be shown in another way.

With the aid of Figure 8.11 it is seen that the composition of the new solids formed when the liquid composition changes from

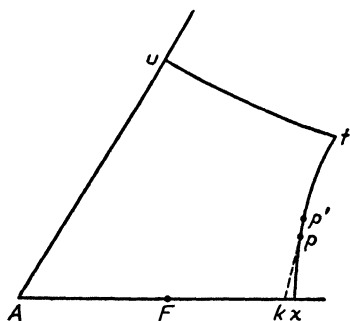


FIG. 8.11 Construction used to show the composition change of the solids when resorption occurs (binary saturation).

$p$  to  $p'$  is governed by two constraints: (1) the composition of the new solids must lie on a straight line through  $p'$  and  $p$ , remote from  $p'$ ; (2) the composition of the new solids must lie on a straight line through  $A$  and  $F$ , since the liquid is saturated with respect to these solids. The composition of the new solids must therefore be represented by  $k$ . The first constraint is required in order to satisfy the proportioning rule in respect to the formation of the new solids,  $k$ , and the new liquid,  $p'$ , from the

liquid  $p$ . It should be noted that the line  $p'p$  is a *chord* of the binary curve  $xt$ . From its position with respect to  $A$  and  $F$ ,  $k$  is seen to represent a positive quantity of  $F$  and a negative quantity of  $A$ ; in other words,  $A$  is resorbed as  $F$  crystallizes. If  $p'$  is taken sufficiently close to  $p$ ,  $k$  will be the intersection of the line through  $A$  and  $F$  with the tangent (at  $p$ ) to the curve  $xt$ . It should be noted that a consideration of the tangent to a binary curve will always give information about the instantaneous composition of new solids, whether resorption occurs or not.

When the liquid has attained the composition  $q$  (Figure 8.10) the resorption of  $A$  will be complete; further removal of heat will only result in the crystallization of  $F$ . The composition of the liquid will then follow the path  $qr$ , collinear with  $S$  and  $F$ ; during this change there will be only one solid present, namely  $F$ . When the liquid attains the composition  $r$  it will be saturated with re-



will be a mixture of  $B$ ,  $F$ , and  $C$ ; the last liquid will have the composition  $e$ , since it will be saturated with respect to  $B$ ,  $F$ , and  $C$ . For any melt having a composition within the triangle  $BAF$  the ultimate solids will be a mixture of  $B$ ,  $A$ , and  $F$ ; the last liquid will be the one saturated with respect to these solids, namely that of composition  $t$ . Both  $e$  and  $t$  are ternary invariant points. The point  $e$  is a ternary eutectic point; the point  $t$  is a ternary transition point. A ternary eutectic point is characterized as follows: (1) It is the junction of three binary curves, all showing increase in temperature as they diverge from the point. (2) The point lies *within* the triangle defined by the three solid phases with respect to which a solution of this composition would be saturated. A ternary transition point is characterized as follows: (1) It is the junction of three binary curves, but as they diverge from this point at least one shows a decrease in temperature. (2) The point lies *outside* the triangle defined by the three solid phases with respect to which a solution of this composition would be saturated.

### 8.5 Systems Having a Ternary Compound Which Melts Congruently

Phase diagrams for systems of this kind are typified by Figure 8.13, in which  $G$  represents the ternary compound which melts congruently.

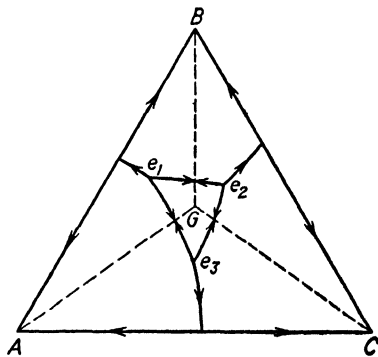


FIG. 8.13 The phase diagram for a system having a ternary compound which melts congruently.

congruently. Since  $G$  melts congruently, its composition must lie within the field of  $G$ . The diagram exhibits three ternary

eutectic points,  $e_1$ ,  $e_2$ , and  $e_3$ . It can be shown that this diagram can be divided into three completely independent parts by the lines  $AG$ ,  $BG$ , and  $CG$ . During the course of crystallization of a melt having a composition within any one of the triangles  $ABG$ ,  $BCG$ , or  $ACG$ , no phase will be produced having a composition outside the confines of that triangle. The final liquid will have the composition  $e_1$ ,  $e_2$ , or  $e_3$ , depending on whether the composition of the melt is taken within the triangle  $ABG$ ,  $BCG$ , or  $ACG$ . Consideration of courses of crystallization will also show that the arrows in Figure 8.13 have been drawn in the proper directions. It should be noted that these conclusions follow from the methods used in the discussion of Figure 8.4 (Section 8.3).

### 8.6 Systems Exhibiting a Binary Compound Which Has a Ternary Field, but Not a Binary Field

In the binary system  $A$ - $C$ , Figure 8.14, the binary compound  $H$  undergoes an incongruent transition to form the solids  $A$  and  $C$  at the temperature  $t$ . This temperature is lower than any temperature on the liquidus curve of the binary system, and hence the compound  $H$  cannot exist in equilibrium with any binary liquid solution of the components  $A$  and  $C$ . The temperature at which  $A$  and  $C$  can exist in equilibrium with a binary liquid solution is, of course, that of the binary eutectic point  $x$ . Addition of a third component, say  $B$ , will lower the temperature at which  $A$  and  $C$  can exist in equilibrium with a common (ternary) liquid. With sufficient addition of  $B$  this temperature may be lowered to the value  $t$ ; at this temperature the ternary solution can exist in equilibrium with  $H$ , as well as  $A$  and  $C$ . This is shown in Figure 8.15, in which  $xt$  is the binary eutectic curve between the fields of  $A$  and  $C$ , and  $t$  represents the temperature and composition of the ternary solution which can exist in equilibrium with  $A$ ,  $C$ , and  $H$ . From the phase rule it is apparent that at atmospheric pressure the four phases can exist in equilibrium only at a unique temperature,  $t$ . The point  $t$  is the origin of three binary curves,  $tx$  for  $A$  and  $C$ ,  $te_1$  for  $A$  and  $H$ , and  $te_2$  for  $H$  and  $C$ . The binary curve  $e_1e_2$  is the common boundary of the fields of  $B$  and  $H$ . Since  $t$  is the highest temperature at which  $H$  can exist in equilibrium with a ternary solution, it is clear that the temperatures corresponding to  $e_1$  and  $e_2$  are both lower than that of  $t$ .

The directions shown for the arrows in Figure 8.15 can be confirmed by considering the courses of crystallization of a number of suitably chosen melts. It will be found that any melt having a composition lying within the triangle  $ABH$  will yield a final liquid having the composition  $e_1$ ; that any melt having a composition within the triangle  $BHC$  will yield a final liquid having the composition  $e_2$ . The existence of the temperature maximum at  $m$  on the binary curve  $e_1e_2$  can be shown by considering the course of crystallization of the melts  $p_1$  and  $p_2$ . In both cases  $B$  will be the first solid formed, and  $H$  the second; in both cases the composition of the whole solids will follow a path along the line  $BH$  from  $B$  toward  $H$ . Since, at any time, the composition of the whole solids, the composition of the liquid, and the composition of the

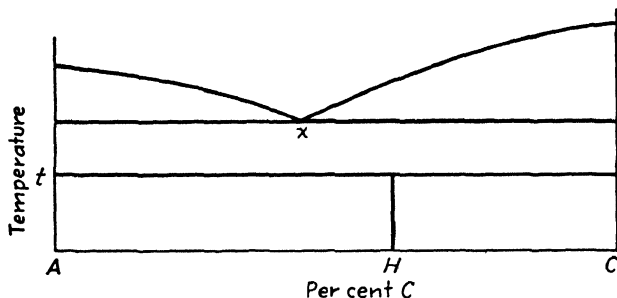


FIG. 8.14 The system  $A-C$  having a binary compound which undergoes an incongruent transition to form solid  $A$  and solid  $C$ .

original melt must be collinear, it is clear that for the melt  $p_1$  the path of the liquid composition along the binary curve will be in the direction toward  $e_1$ ; for the melt  $p_2$  it will be in the direction toward  $e_2$ . This will be true no matter how close to the line  $BH$  the points  $p_1$  and  $p_2$  are taken. It follows, therefore, that the temperature corresponding to  $m$  is a maximum on the line  $e_1e_2$ .

The maximum at  $m$  on the line  $BH$  of Figure 8.15 bears some resemblance to the maximum at  $z$  on the line  $BC$  of Figure 8.4.  $B$  and  $C$  of Figure 8.4 form a true binary system, regardless of the proportions in which they are taken.  $B$  and  $H$  of Figure 8.15, on the other hand, do not form a true binary system over the whole range of intermediate compositions. This can be shown by considering the courses of crystallization of melts which can be made up from  $B$  and  $H$  alone. For example, on cooling the

melt  $p_3$  the liquid composition will proceed from  $p_3$  to  $m$  as  $B$  crystallizes. With the subsequent precipitation of  $H$  the composition of the solids will move along the line  $BH$  toward  $H$ . Since the composition of the solids, the composition  $p_3$ , and the composition of the liquid must be collinear, it is clear that the composition of the liquid must remain on the line  $BH$ ; since the liquid is simultaneously saturated with respect to  $B$  and  $H$ , its composition must also remain on the boundary curve  $e_1e_2$ . The

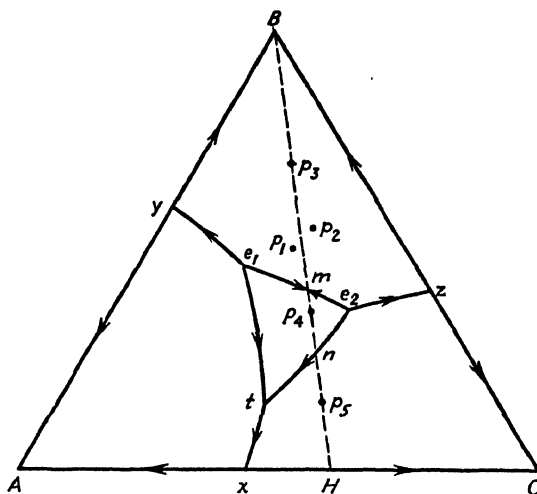


FIG. 8.15 A system having a binary compound with a ternary field but not a binary field.

liquid composition will therefore remain at  $m$  until crystallization is complete and the solids have attained the composition  $p_3$ .

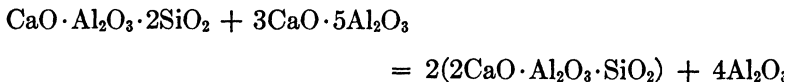
The course of crystallization of the melt  $p_4$  of Figure 8.15 will be similar to that of  $p_3$ , except that  $H$  will be the first solid formed and  $B$  the second. The path of the liquid composition will be  $p_4m$ , that of the solid composition,  $Hp_4$ . It is clear that any melt having a composition on the line  $BH$  between  $B$  and  $n$  will comprise a binary system, since the compositions of all the phases involved in crystallization can be expressed in terms of  $B$  and  $H$  alone. This is not true for any melt having a composition lying on the line  $BH$  between  $n$  and  $H$ . For example, if the melt  $p_5$  is cooled the first solid formed will be  $C$ . The liquid composition will follow a straight line from  $p_5$  directly away from  $C$  until it

reaches the binary curve  $te_2$ . With the subsequent precipitation of  $H$  and resorption of  $C$ , the liquid composition will follow the binary curve  $te_2$  until it reaches  $n$ , at which time the composition of the solids will have reached  $H$  on the path  $CH$ , and the resorption of  $C$  will be complete. The subsequent course of the crystallization will be similar to that for the melt  $p_4$ ; the liquid composition will proceed from  $n$  to  $m$  as the composition of the solids changes from  $H$  to  $p_5$ . Thus, although the final solids and their saturated solution comprise a binary system, the course of crystallization involved phases, the composition of which could not be expressed in terms of  $B$  and  $H$  alone. The compounds  $B$  and  $H$ , therefore, do not form a true binary system.

### 8.7 The Quadrilateral Diagram, Required to Represent Certain Types of Three-component Systems

This type of diagram will be exemplified by a system met with in the study of silicate chemistry, the system  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ - $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ - $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ . For simplicity these three compounds will be referred to as  $X$ ,  $Y$ , and  $Z$ , respectively.

As might be expected, the cooling of various melts made up from  $X$ ,  $Y$ , and  $Z$  can give, as a first precipitate, solid  $X$ ,  $Y$ , or  $Z$ ; in addition, it has been found that certain melts prepared from these three compounds yield solid alumina,  $\text{Al}_2\text{O}_3$ , as the first precipitate. It should be apparent from the compositions of  $X$ ,  $Y$ , and  $Z$  that alumina,  $A$ , cannot be made from *positive* quantities of  $X$ ,  $Y$ , and  $Z$ . However, it can be seen that  $Y$  and  $Z$  might react to form  $X$  and  $A$  according to the equation



that is,  $Y + Z = 2X + 4A$ . The composition of  $A$  can therefore be expressed in terms of  $X$ ,  $Y$ , and  $Z$  as  $A = (Y + Z - 2X)/4$ . Thus the three components,  $X$ ,  $Y$ , and  $Z$ , are sufficient to describe the composition of  $A$  and, as well, the composition of a system made up from any proportion of  $X$ ,  $Y$ ,  $Z$ , and  $A$ .

In Figure 8.16  $X$ ,  $Y$ , and  $Z$  are represented as the apices of a right-angled isosceles triangle. The point  $A$  clearly must lie outside this triangle on the side of the line  $YZ$  remote from  $X$ .

From the proportioning rule  $A$  consists of  $XA/XP$  of  $P$  minus  $PA/XP$  of  $X$ ;  $P$  consists of  $YP/YZ$  of  $Z$  and  $PZ/YZ$  of  $Y$ . It follows from the molecular weights of  $Y$  and  $Z$  that  $YP/YZ = 0.709$  and  $XA/XP = 2.34$ ; this information is sufficient to establish the position of  $A$  on the diagram.

This system exhibits a binary eutectic point for each of the four binary systems, a ternary eutectic point  $e$  at the junction of the fields of  $X$ ,  $Y$ , and  $A$ , and a ternary transition point  $t$  at the junction of the fields of  $X$ ,  $Z$ , and  $A$ . Courses of crystallization in this system are essentially similar to those for the system shown in Figure 8.6 and discussed at some length in Section 8.4. Any melt having a composition lying within the triangle  $XYA$  of

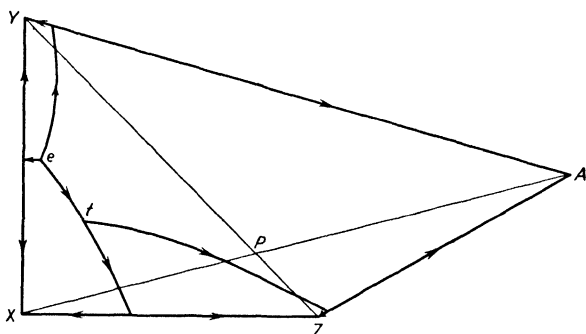


FIG. 8.16 The system  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ - $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ - $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$  ( $X$ - $Y$ - $Z$ );  $A = \text{Al}_2\text{O}_3$ .

Figure 8.16 will yield  $X$ ,  $Y$ , and  $A$  as the final solids and the final liquid will have the composition  $e$ ; any melt having a composition within the triangle  $XZA$  will yield  $X$ ,  $Z$ , and  $A$  as the final solids and the final liquid will have the composition  $t$ .

Additional types of quadrilateral diagrams will be discussed in Chapter 9.

## 8.8 The Division of a Complicated Diagram into Simpler Independent Parts

By applying the principles developed in this chapter it is possible to predict, for a great variety of systems, courses of crystallization in which the equilibria involve a single phase of variable composition. In treating the more complicated of these systems

it is convenient to divide the diagram into as many independent parts as possible. In many cases the independent portions will be similar to the simple types already discussed, *e.g.*, Figures 8.3, 8.6, 8.15, and 8.16.

The division of a complicated diagram into simpler parts can be illustrated by reference to the system lime-alumina-silica, Figure 8.17. The compounds  $C$ ,  $A$ , and  $S$  melt congruently (otherwise they would not be suitable as components). The principle that a compound which melts congruently must have a composition lying within its own field is sufficient to establish that the binary compounds  $C \cdot S$ ,  $2C \cdot S$ ,  $5C \cdot 3A$ ,  $C \cdot A$ , and  $3C \cdot 5A$ , and the ternary compounds  $C \cdot A \cdot 2S$  and  $2C \cdot A \cdot S$  melt congruently. Compounds undergoing incongruent transitions have been underlined on the diagram. The binary field lying between the compositions  $C \cdot S$  and  $3C \cdot 2S$  (and hence the ternary field extending from it) must be assigned to an incongruently melting compound. This compound must be  $3C \cdot 2S$ , since the composition of a compound which melts incongruently must lie between its field and the composition of the compound which it forms on melting. Further application of this principle is sufficient to establish that the compound  $3C \cdot A$ , with a field lying between that of  $C$  and that of  $5C \cdot 3A$ , and the compound  $3A \cdot 2S$ , with a field lying between that of  $A$  and that of  $S$ , also melt incongruently. The ternary field which is bounded by the fields of  $2C \cdot S$ ,  $C$ , and  $3C \cdot A$  must be assigned to the compound  $3C \cdot S$ , which undergoes an incongruent transition and has a ternary field but no binary field (*cf.* Section 8.6).

The number of independent parts into which the phase diagram for the system lime-alumina-silica can be divided is limited by the principle that a division cannot be made originating at the composition of a compound which melts incongruently. Without violation of this principle, division of this diagram into independent parts can be made by drawing the following lines: from  $C \cdot A \cdot 2S$  to each of  $S$ ,  $C \cdot S$ ,  $2C \cdot A \cdot S$ , and  $A$ ; from  $2C \cdot A \cdot S$  to each of  $C \cdot S$ ,  $C \cdot A$ ,  $2C \cdot S$ , and  $3C \cdot 5A$ ; from  $2C \cdot S$  to  $5C \cdot 3A$ . This gives rise to the three triangles  $S-C \cdot S-C \cdot A \cdot 2S$ ,  $C \cdot A \cdot 2S-C \cdot S-2C \cdot A \cdot S$ , and  $2C \cdot A \cdot S-C \cdot A-3C \cdot 5A$ , which are similar to the type illustrated in Figure 8.3; the two triangles  $2C \cdot A \cdot S-C \cdot S-2C \cdot S$  and  $C \cdot A \cdot 2S-A \cdot S$ , which are of the type illustrated in Figure 8.6; the triangle  $2C \cdot S-C-5C \cdot 3A$ , which may be considered as a combination of the types shown in Figures 8.6 and 8.15; and the two

quadrilaterals  $2C \cdot A \cdot S - 2C \cdot S - 5C \cdot 3A - C \cdot A$  and  $C \cdot A \cdot 2S - 2C \cdot A \cdot S - 3C \cdot 5A - A$ , of which the latter has been discussed in Section 8.7.

It should be apparent that a dividing line can only be drawn between the compositions of compounds which form true binary systems. It will be seen that wherever a dividing line cuts a boundary line between two fields, the point of intersection corresponds to a maximum temperature along the particular binary curve, *i.e.*, the arrows meet head to head at the point of intersection.

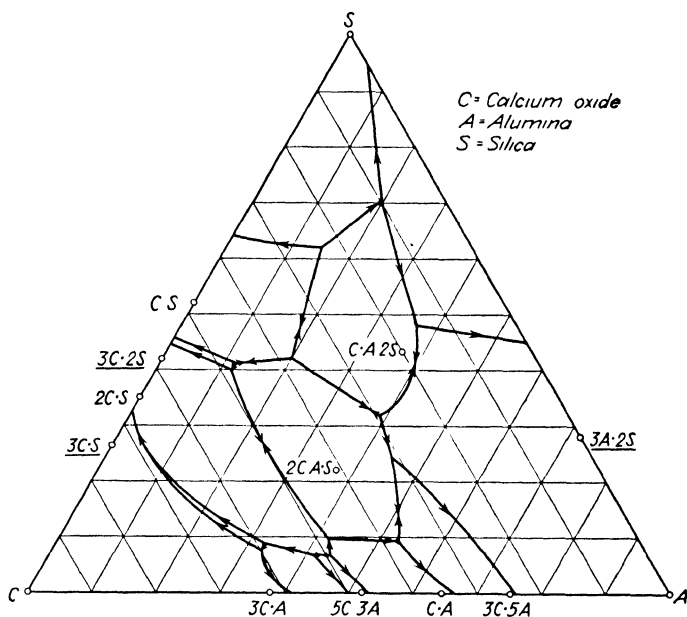


FIG. 8.17 The system lime-alumina-silica. Compounds which melt incongruently are underlined.

tion. It is clear that the two quadrilaterals referred to above cannot be further subdivided.

### EXERCISES

1. Draw temperature-composition phase diagrams typical of the binary systems  $A-D$ ,  $D-B$ ,  $B-A$ , and  $B-C$  of Figure 8.4.
2. Draw temperature-composition phase diagrams typical of all possible binary systems in the ternary system  $A-B-C$  of Figure 8.13. Include tie lines.

3. Draw a temperature-composition phase diagram typical of the vertical section through the points *B* and *H* of the solid diagram corresponding to Figure 8.15. Include tie lines where possible.

4. *a.* Define and compare the characteristics of ternary eutectic and ternary transition points.

*b.* Prove that a ternary transition point must lie outside the triangle having as apices the compositions of the three pure substances with respect to which the liquid having the temperature and composition of the ternary transition point is saturated.

5. *a.* Trace the paths of the representative points of the liquid and the whole solids during the cooling, under equilibrium conditions, of a melt having the composition *x* of Figure 8.5.

*b.* Trace the paths of the representative points of the liquid and the whole solids during the cooling, under equilibrium conditions, of a melt having the composition *t* of Figure 8.6.

6. In Figure 8.17, (*a*) label the solubility fields of the fourteen compounds shown; (*b*) draw a temperature-composition diagram typical of the system silica-calcium oxide; (*c*) show that any melt having a composition lying within the triangle  $C-3C \cdot S-3C \cdot A$  will, on being cooled under equilibrium conditions, yield a final liquid having the composition of the ternary point at 60% *C*, 7.5% *S*, 32.5% *A*; (*d*) trace the paths of the representative points of the liquid and the whole solids during the cooling, under equilibrium conditions, of the melts having the compositions: (1) 20% *C*, 50% *S*, 30% *A*; (2) 5% *C*, 40% *S*, 55% *A*. Draw typical temperature-time curves for the cooling of these melts.

## CHAPTER 9

### FOUR-COMPONENT SYSTEMS

A four-component system is one for which four constituents are necessary and sufficient to describe the compositions of all phases which can exist over the range of conditions considered. In order to specify the state of any phase completely it is also necessary to state the temperature and the pressure. Since the *proportions* of only three of the four components need be specified, the total number of independent variables is five. If both the temperature and the pressure are held constant, the phase relationships can be shown by a three-dimensional figure.

#### 9.1 Considerations Bearing on the Choice of Components

Before considering four-component systems in any detail it will be necessary to recall the difference between the number of components of a system and the number of constituents from which the system may be prepared. In the simplest instance, a system which is a single pure substance under one set of conditions can be poly-component under altered conditions. For example, if the pure substance Glauber's salt is heated, it will yield two phases at its melting point. The compositions of these phases cannot be expressed in terms of Glauber's salt alone; the system must then be considered as two-component. On the other hand, sodium chloride both melts and vaporizes *congruently* and this system remains one-component through all its phase transitions.

In Chapter 6 it was seen that over a wide range of conditions in the system  $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  there occurred no phases with compositions which could not be expressed in terms of the three components. However, as will be discussed in some detail later, a system made up from sodium sulfate, potassium chloride, and water can give rise to the solid phases potassium sulfate and sodium chloride; the composition of neither of these phases can be

expressed in terms of the three constituents used in making up the system. It is therefore obvious that, although the system can be unambiguously designated by the expression  $\text{Na}_2\text{SO}_4\text{-KCl-H}_2\text{O}$ , the three constituents used in this designation do not comprise a set of components of the system. The appearance of potassium sulfate as a phase constituent indicates that sodium sulfate and potassium chloride can undergo a metathetical reaction ("double decomposition") in aqueous solution, according to the equation  $\text{Na}_2\text{SO}_4 + 2\text{KCl} = \text{K}_2\text{SO}_4 + 2\text{NaCl}$ . Because this metathesis occurs the system cannot be three-component. The composition of any phase occurring in this system can be expressed in terms of water and any three of the four salts appearing in the equation for the metathesis, *e.g.*, the composition of potassium sulfate can be expressed in the form  $\text{K}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{KCl} - 2\text{NaCl}$ ; the composition of a solution prepared from water, sodium sulfate, and potassium chloride and from which potassium sulfate has been precipitated cannot be expressed in terms of water, sodium sulfate, and potassium chloride alone, but can be expressed in terms of water, sodium sulfate, potassium chloride, and sodium chloride. The system is evidently four-component when metathesis occurs. If metathesis does not occur within the range of conditions investigated, as for example in the study of the vapor pressure of unsaturated solutions prepared from various proportions of water, sodium sulfate, and potassium chloride, the system is three-component.

Salt pairs such as the pairs  $\text{Na}_2\text{SO}_4\text{-KCl}$  and  $\text{K}_2\text{SO}_4\text{-NaCl}$ , which are involved in a metathesis, are referred to as *reciprocal salt pairs*. In a system made up of water and  $n$  salts having a *common* anion and different cations or a *common* cation and different anions reciprocal salt pair relationships are not possible. Provided that metatheses and decompositions of the  $n + 1$  constituents do not occur, such a system would have  $n + 1$  components.

The hydrolysis of a salt which gives rise to an acid, a base, or an acidic or basic salt as a *separate phase* is a type of metathesis frequently encountered and has an important bearing on the number of components in such systems. An example of such a system is  $\text{CuSO}_4\text{-H}_2\text{O}$ . The designation of this system as three-component arises from the fact that basic copper sulfate can precipitate from aqueous solutions of copper sulfate. The composition of the basic sulfate,  $\text{Cu(OH)}_2 \cdot x\text{CuSO}_4$ , cannot be

expressed in terms of  $\text{CuSO}_4$  and  $\text{H}_2\text{O}$ , but requires a further component; it should also be noted that precipitation of basic sulfate from aqueous copper sulfate would render the solution acidic and the solution composition would no longer be expressible in terms of copper sulfate and water alone. Possible sets of components for the system  $\text{CuSO}_4\text{-H}_2\text{O}$  are  $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{CuSO}_4\text{-Cu(OH)}_2\text{-H}_2\text{O}$ . The composition of the basic salt can be expressed as  $(x + 1)\text{CuSO}_4 - \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$  or directly in terms of the second set. The composition of the acidic solution can be expressed directly in terms of the first set; or, using the second set, the sulfuric acid can be expressed as  $\text{CuSO}_4 + 2\text{H}_2\text{O} - \text{Cu(OH)}_2$ . It is clear that the system  $\text{CuSO}_4\text{-H}_2\text{O}$  can be three-component.

From the preceding discussion it is evident that, in giving consideration to the number of components for a system prepared from a particular set of constituents, it is essential to inquire into the composition of all phases, bearing in mind that decomposition and metathesis may alter the number of components.

## 9.2 Components in Systems Showing Reciprocal Salt Pair Transformations

In view of the importance of reciprocal salt pair transformations in poly-component systems, it is of interest to consider the number of components in such systems in a general way.

Among the phases which might be encountered in the system designated as  $\text{NaCl-KBr-LiF}$ , on the assumption that reciprocal salt pair transformations can occur, are the nine simple salts  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{LiCl}$ ,  $\text{NaBr}$ ,  $\text{KBr}$ ,  $\text{LiBr}$ ,  $\text{NaF}$ ,  $\text{KF}$ , and  $\text{LiF}$ . Other possible phases would be solutions and compounds having compositions which can be expressed in terms of these simple salts. In order to determine the number of components in this system, it is necessary to determine the least number of constituents in terms of which the compositions of all possible phases can be expressed. It is clear that the compositions of all possible phases can be expressed in terms of the nine simple salts. These nine salts cannot, however, all be chosen as components, since there exists a number of interrelating stoichiometric equations among them. These equations can be expressed as relations among reciprocal salt pairs, for example,  $\text{NaCl} + \text{KBr} = \text{NaBr} + \text{KCl}$ , or  $\text{KBr} = \text{NaBr} + \text{KCl} - \text{NaCl}$ . The use of  $\text{NaBr}$ ,  $\text{KCl}$ , and  $\text{NaCl}$  as components would therefore eliminate  $\text{KBr}$  as a com-

ponent; the systematic elimination of unnecessary constituents is readily carried out by arranging the nine simple salts in the form of a square array in which each row has a common anion and each column a common cation, *viz.*,



If the five simple salts comprising any one row and any one column of the array are chosen, the compositions of the remaining four simple salts can be expressed in terms of these five through reciprocal salt pair relationships. For example, by choosing the top row and the left-hand column as components, the compositions of the salts KBr, KF, LiBr, and LiF can be expressed by the relations

$$\text{KBr} = \text{NaBr} + \text{KCl} - \text{NaCl} \quad (1)$$

$$\text{KF} = \text{NaF} + \text{KBr} - \text{NaBr} \quad (2)$$

and by elimination of KBr from (1) and (2),

$$\text{KF} = \text{NaF} + \text{KCl} - \text{NaCl} \quad (2a)$$

Also,

$$\text{LiBr} = \text{KBr} + \text{LiCl} - \text{KCl} \quad (3)$$

and by elimination of KBr from (1) and (3),

$$\text{LiBr} = \text{LiCl} + \text{NaBr} - \text{NaCl} \quad (3a)$$

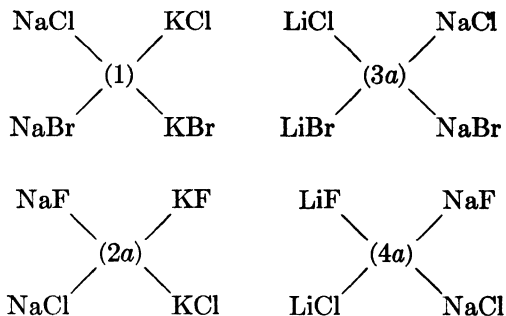
Furthermore,

$$\text{LiF} = \text{KF} + \text{LiBr} - \text{KBr} \quad (4)$$

and from (1), (2a), (3a), and (4),

$$\text{LiF} = \text{NaF} + \text{LiCl} - \text{NaCl} \quad (4a)$$

The expression of the compositions of KBr, KF, LiBr, and LiF in terms of the five chosen salts can be shown directly from the extended array. If the first row and the first column of the array are repeated, as shown below, the required reciprocal salt pair relations can be indicated as (1), (2a), (3a), and (4a).



The five chosen salts are seen to be sufficient in number to describe the compositions of all nine salts. Examination of the array or of the above equations will show that the choice of less than five salts would make it impossible to express the compositions of the rest of the salts in the array.

It can readily be seen by constructing the appropriate array that for a system comprised of  $a$  different anionic species and  $c$  different cationic species, and which can undergo all possible reciprocal salt pair transformations, the number of components,  $\mathcal{C}$ , is given by the expression  $\mathcal{C} = a + c - 1$ . The appropriate array would have  $a$  rows and  $c$  columns; the total number of different salts in any one row and any one column, taken together, would be  $a + c - 1$  and would comprise a possible set of components. In the case of a system consisting of salts having a common anion and  $n$  different cations, or a common cation and  $n$  different anions, the expression for  $\mathcal{C}$  reduces to  $\mathcal{C} = n$ .

Since a great many reciprocal salt pair transformations have been encountered in aqueous systems, the role of water in such systems is of considerable interest. If there is no formation of acids, bases, or acidic or basic salts *as separate phases*, water is simply added to the list of components to give  $\mathcal{C} = a + c - 1 + 1 = a + c$ ; if such phases are formed it will be necessary to consider the water as participating in reciprocal transformations, thus necessitating the addition of one row and one column to the array for the salts. Hydrogen would then be included in evaluating the number of cationic species and hydroxyl in evaluating the number of anionic species; the number of components would be two greater than the number derived from the salt array. It would not be necessary to make separate provision for water since water would be included as a member of the new array.

### 9.3 Graphical Representation of a Four-component System of Water and Three Salts Having a Common Ion, by a Regular Tetrahedron

It will be assumed in this section that no decompositions or reciprocal transformations occur among the components. For systems of this type the phase relationships at constant temperature and pressure can be shown graphically on two types of solid diagrams: (1) a regular tetrahedron and (2) a triangular prism.

With all four-component systems there will be associated six two-component and four three-component systems of the components. Of the three-component systems the most interesting are those in which water is one of the components. Typical isothermal isobaric diagrams for simple systems of this type are

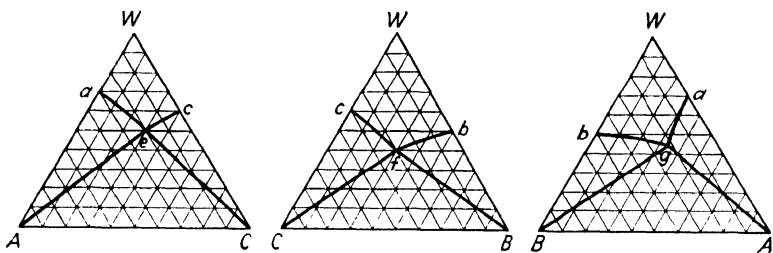


FIG. 9.1 The phase diagrams for the systems  $A$ - $C$ - $W$ ,  $C$ - $B$ - $W$ , and  $B$ - $A$ - $W$  at fixed temperature and pressure

illustrated by Figure 9.1, in which water is designated by  $W$  and the three salts having a common ion by  $A$ ,  $B$ , and  $C$ . The solubility of  $A$  in water is designated by  $a$ , that of  $B$  by  $b$ , and that of  $C$  by  $c$ . The invariant points in the three-component systems are designated by  $e$ ,  $f$ , and  $g$ . Alteration of the shapes of the triangles of Figure 9.1 makes it possible to assemble the three triangles in one plane as shown in Figure 9.2; the letters and the tie lines have the same significance as in Figure 9.1. Although each of the triangles  $AWC$ ,  $CWB$ , and  $BWA$  represents a separate three-component system, it is clear that the triangle  $ABC$  does *not* represent a single three-component system, since water,  $W$ , cannot be made from  $A$ ,  $B$ , and  $C$ .

If the three equilateral triangles of Figure 9.1 are assembled in such a way as to form three sides of a regular tetrahedron in which  $W$  forms the upper apex, then the triangle  $ABC$  will form the base.

The apex  $A$  represents a system consisting of 100%  $A$ ; a point on the face  $BCW$  of the tetrahedron represents a system containing 0%  $A$ ; all points representing some fixed intermediate proportion of  $A$  will lie in a plane parallel to the face  $BCW$ . The proportion of  $A$  represented by this plane can be read on a scale marked off along one of the lines  $AB$ ,  $AC$ , or  $AW$ , from 100% at  $A$  to 0% at  $B$ ,  $C$ , or  $W$ . Similarly, points representing a fixed proportion of  $B$  will lie on a plane parallel to the face  $ACW$ . Points representing a fixed proportion of  $A$  and a fixed proportion of  $B$  must lie on the line of intersection of the planes defining the

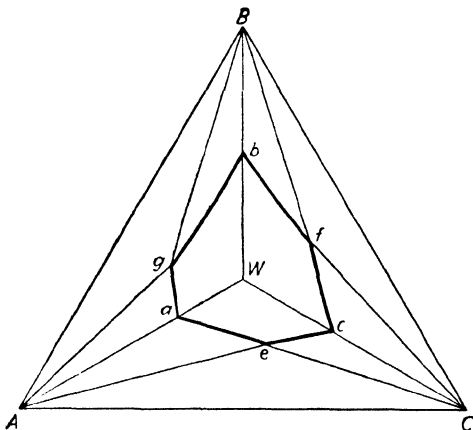


FIG. 9.2 This diagram shows that the three-component diagrams of Figure 9.1, when replotted and assembled on a plane, are identical with the vertical projection on the base  $ABC$  of the three-component diagrams of Figure 9.1 when they are assembled to form a regular tetrahedron.

proportions of  $A$  and  $B$ . The intersection of this line with a plane defining the proportion of  $C$  (i.e., parallel to the face  $ABW$ ) will define a point representing the fixed proportions of  $A$ ,  $B$ , and  $C$ . The proportion of  $W$  follows from the relation  $\% W = 100\% - \% A - \% B - \% C$ . Thus it is seen that any point within the tetrahedron defines the proportions of each of the four components represented by its apices.

A point can be defined as the intersection of three surfaces, whether these surfaces are plane or curved. For a two-phase equilibrium in a four-component system at fixed temperature and pressure, the number of degrees of freedom is two. This bivariance

is, of course, in the solution composition. Thus, in order to specify the composition of a quaternary aqueous solution saturated with respect to one of the components, it will be necessary to state the proportions of two of the components in the solution, *i.e.*, to define two planes. It is evident that compositions of solutions saturated with respect to *one* of the components must lie on a *surface* within the tetrahedron; the intersection of this solubility surface with the two planes corresponding to the two degrees of freedom gives the point which specifies the composition of the saturated solution.

The intersection of *two* solubility surfaces within the tetrahedron will give rise to a *line*. Points on this line will represent the compositions of solutions saturated with respect to two of the components simultaneously; the composition of such a solution will be univariant at fixed temperature and pressure (a single plane would be sufficient to define a point on the line). The intersection of *three* solubility surfaces within the tetrahedron will define a *point* representing the composition of a solution saturated with respect to three of the components simultaneously (an invariant composition at fixed temperature and pressure).

The solubility surface of a component must intersect two of the tetrahedral faces, *e.g.*, if *B* is the saturating phase, its solubility surface will intersect the face *BAW* of the tetrahedron along the line *bg* and will intersect the face *BCW* along the line *bf* (Figure 9.1). The lines *bg* and *bf* of Figure 9.2 are simply the vertical projections of these same intersections on the base *ABC* of the tetrahedron. Similarly, *ag* and *ae* are the vertical projections on the base *ABC* of the intersections of the solubility surface of *A* with the faces *ABW* and *ACW*; *ce* and *cf* are the vertical projections on the base *ABC* of the intersections of the solubility surface of *C* with the faces *ACW* and *BCW*.

In Figure 9.3 is shown the vertical projection on the base *ABC* of the three solubility surfaces within the tetrahedron. The vertical projections of the points representing the compositions of the univariant solutions saturated with respect to *B* and *C* are shown by the line *fq*; the corresponding projections for solutions simultaneously saturated with respect to *C* and *A* are shown by *eq*; with respect to *A* and *B*, by *gq*. The point *q* is the vertical projection of the invariant point representing the composition of the solution saturated with respect to *A*, *B*, and *C*.

The areas  $qeag$  ( $A$ ),  $qgbf$  ( $B$ ), and  $qfce$  ( $C$ ) of Figure 9.3 represent the vertical projections of the solubility surfaces of the salts  $A$ ,  $B$ , and  $C$  on the base  $ABC$  of the tetrahedron. It must be emphasized that in this figure the perimeter of the projection of the solubility surfaces represents relationships in the three-component systems  $A$ - $B$ - $W$ ,  $B$ - $C$ - $W$ , and  $C$ - $A$ - $W$ , and gives complete information about the compositions of the saturated solutions in these three-component systems, including the percentage of water. On the other hand, the areas  $A$ ,  $B$ , and  $C$  refer to saturated solutions in the four-component system  $A$ - $B$ - $C$ - $W$ , but do not give complete

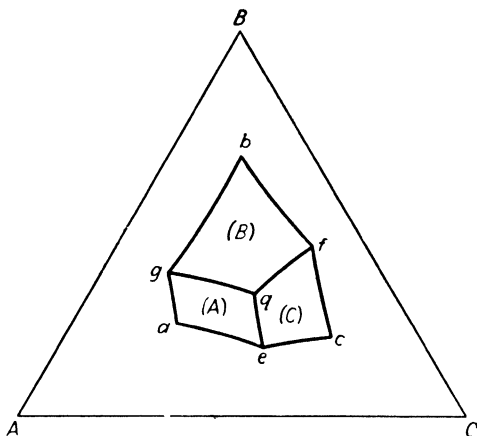


FIG. 9.3 The vertical projection of the tetrahedral diagram for the system  $A$ - $B$ - $C$ - $W$ .

information about the compositions of these solutions, since their proportion of water cannot be expressed on the projection.

The following method may be used to obtain the projection of the point representing a solution consisting of  $w\%$  water,  $x\%$   $A$ ,  $y\%$   $B$ , and  $z\%$   $C$ , that is,  $w\%$  of water and  $(100 - w)\%$  of solute. Let the point  $Q$  of Figure 9.4 represent the solute composition. The coordinates of  $Q$  in the triangle  $ABC$  will be  $100x/(x + y + z)\%$   $A$ ,  $100y/(x + y + z)\%$   $B$ ,  $100z/(x + y + z)\%$   $C$ , or  $100x/(100 - w)\%$   $A$ ,  $100y/(100 - w)\%$   $B$ ,  $100z/(100 - w)\%$   $C$ . In Figure 9.4,  $W'$  represents the vertical projection of the apex  $W$  of the tetrahedron. The solution formed by the addition of  $w$  parts of water to  $100 - w$  parts of solute of anhydrous com-

position  $Q$  will be represented by a point  $P$  lying within the tetrahedron on the straight line joining  $Q$  and  $W$ . It is evident that  $P$  will lie on the vertical plane through  $W$ ,  $W'$ , and  $Q$ ; this plane

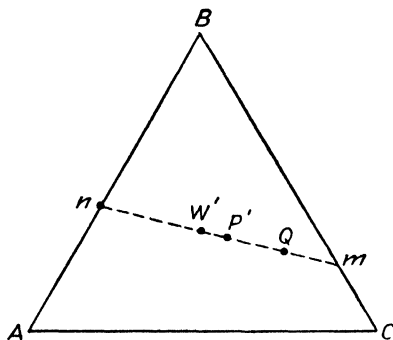


FIG. 9.4 Vertical projection of a tetrahedral diagram.  $Q$  = solute composition;  $P'$  = vertical projection of solution composition.

is shown in Figure 9.5.  $P'$ , the vertical projection of  $P$ , will lie on the line  $W'Q$ . It is seen from Figure 9.5 that  $W'P'/W'Q = WP/WQ = (100 - w)/100$ . The coordinates of  $P'$  on the base

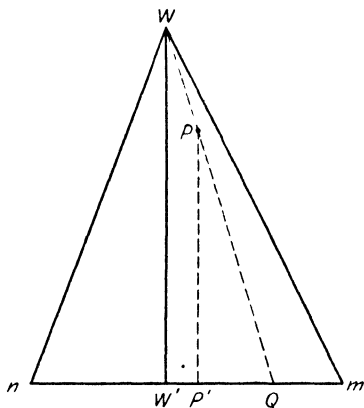


FIG. 9.5 Vertical plane through the tetrahedron  $A-B-C-W$  (see Figure 9.4).

$ABC$  can be expressed in terms of the coordinates of  $W'$  and  $Q$  by means of the proportioning rule,  $P' = W'P'/W'Q$  of  $Q + P'Q/W'Q$  of  $W' = (100 - w)/100$  of  $Q + w/100$  of  $W'$ . The coordinates of  $Q$  have already been given in terms of %  $A$ , %  $B$ ,

and %  $C$ . On the same scales  $W'$  has the coordinates  $100/3\%$   $A$ ,  $100/3\%$   $B$ ,  $100/3\%$   $C$ . Thus the  $A$  coordinate of  $P'$  is  $\frac{100-w}{100} \times \frac{100x}{100-w} + \frac{100}{3} \times \frac{w}{100}\%$   $A$ , or simply  $\left(x + \frac{w}{3}\right)\%$   $A$ . Similarly the  $B$  and  $C$  coordinates of  $P'$  are  $\left(y + \frac{w}{3}\right)\%$   $B$  and  $\left(z + \frac{w}{3}\right)\%$   $C$ .

#### 9.4 Graphical Representation of a Four-component System of Water and Three Salts Having a Common Ion, by a Triangular Prism (Jänecke's Method)

In the tetrahedral method of representing compositions in a four-component system, the solvent was represented as the apex of a tetrahedron; the three salts were represented by the three corners of the triangle forming the base. In the prismatic representation the three salts are again represented by the three corners of the triangular base, but the proportion of water is indicated by a *vertical* coordinate. The three-dimensional diagram therefore takes the form of a triangular prism with three sides perpendicular to the triangular base. The proportion of water may be represented on the vertical scale in a number of ways. It is customary to use as the vertical coordinate the number of parts of water associated with 100 parts of total solute. For example, if a solution contains  $x$  parts of  $A$ ,  $y$  of  $B$ ,  $z$  of  $C$ , and  $w$  of water, the ordinate would be  $100w/(x + y + z)$ . The "parts" may be expressed as grams, moles, or equivalents.

The transformation from a tetrahedral face, for example,  $ABW$ , to the corresponding prismatic face is shown in Figure 9.6. For every point on the tetrahedral face, Figure 9.6a, there will be a corresponding point on the prismatic face, Figure 9.6b. The point corresponding to  $g$ , the ternary invariant point, is obtained as follows. A straight line is drawn from  $W$  through  $g$  to cut the line  $AB$  at the point  $g'$ ;  $g'$  represents the ratio of  $A$  to  $B$  in the solution  $g$ , namely,  $Ag'$  of  $B$  to  $g'B$  of  $A$ , and hence represents the proportions of  $A$  and  $B$  which would obtain in the residue if all the water were removed. The point  $g'$  on the line  $AB$  of Figure 9.6b is identical with  $g'$  of Figure 9.6a. To evaluate the ordinate

on Figure 9.6b of the ternary invariant solution, it is necessary to determine the value of the quantity  $100w/(x + y + z)$ . In this example  $z = 0$ ;  $w/(x + y) = gg'/Wg$ . Thus the coordinates

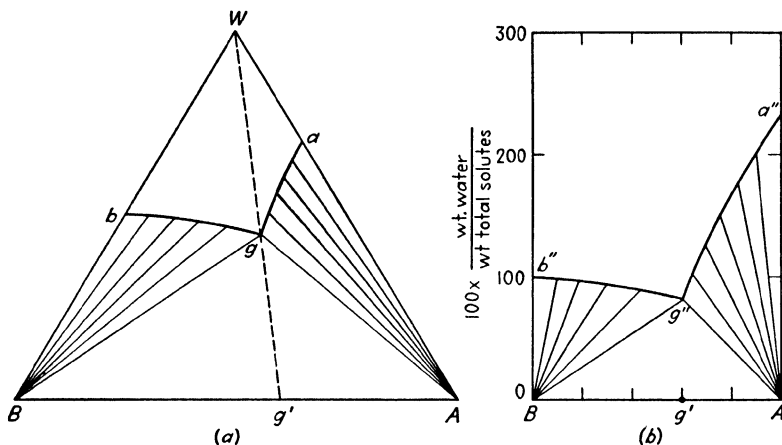


FIG. 9.6 Transformation from a tetrahedral face (a) to a prismatic face (b).

of  $g''$  are  $g'$  and  $100gg'/Wg$ . Other points of Figure 9.6a can be transformed in the same way. The three three-component diagrams in which water is one of the components are shown in Figure

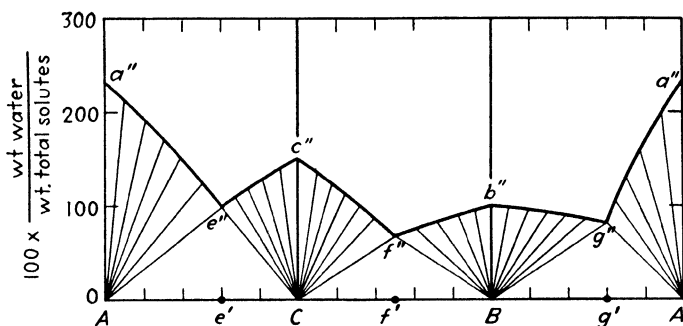


FIG. 9.7 The phase diagrams for the three-component systems  $A-C-W$ ,  $C-B-W$ , and  $B-A-W$ . These diagrams form the sides of the triangular prism for the system  $A-B-C-W$ .

9.7. By folding this diagram along the verticals through  $B$  and  $C$  in such a way that the points  $A$ ,  $B$ , and  $C$  form the corners of an equilateral triangle, the faces of the triangular prism are ob-

tained. The three solubility surfaces comprising the top of the prism will intersect the sides of the prism along the lines  $a''g''$ ,  $g''b''$ ,  $b''f''$ ,  $f''c''$ ,  $c''e''$ , and  $e''a''$ . As in the tetrahedral diagram any two solubility surfaces will intersect along a univariant line and all three surfaces will intersect at an invariant point.

The vertical projection on the base  $ABC$  of the solubility surfaces of the prism is shown in Figure 9.8. It should be noted that the position of the point  $q'$  is not identical with the position of  $q$  in Figure 9.3. The points  $g'$ ,  $f'$ , and  $e'$  of Figure 9.8, corresponding to the points  $g$ ,  $f$ , and  $e$  of Figure 9.3, are on the pe-

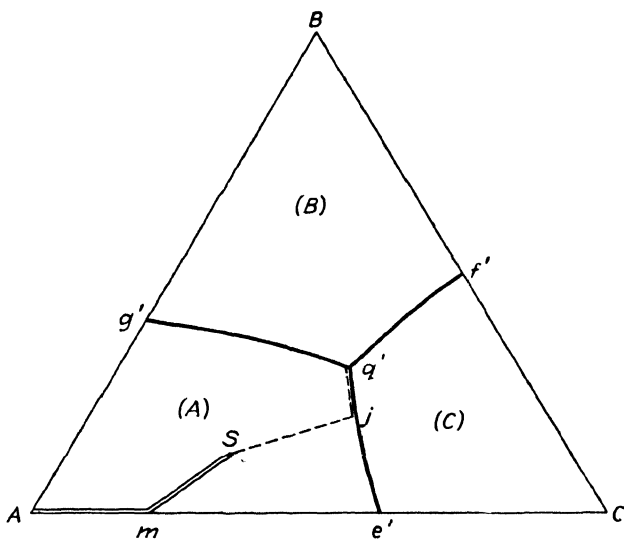


FIG. 9.8 Vertical projection of the prismatic diagram for the system  $A-B-C-W$ .

riphery of the triangle; the points corresponding to  $a$ ,  $b$ , and  $c$  are coincident with  $A$ ,  $B$ , and  $C$ . The solubility fields have been designated, as before, by  $A$ ,  $B$ , and  $C$ .

### 9.5 The Use of Jänecke's Projection to Predict Courses of Crystallization during Isothermal Evaporation of a Quaternary Solution $A-B-C-W$

It can be seen that Figure 9.8 is similar in appearance to Figure 8.3 and furthermore that the upper surface of the prism is not

unlike the upper surface of Figure 8.1. It will be shown that the course of crystallization resulting from the removal of water from a quaternary solution is quite analogous to the course of crystallization resulting from the removal of heat from a ternary solution.

Let  $S$  in Figure 9.8 represent the vertical projection of the point representing the composition of an unsaturated quaternary solution. The point  $S$  will therefore represent the *solute composition* of the solution. So long as only one phase is present, the removal of water will not change the solute composition of the solution, since the relative proportions of  $A$ ,  $B$ , and  $C$  in the solution are unchanged. However, when the point representing the composition of the solution reaches the solubility surface of  $A$  in the prism, further removal of water will, under equilibrium conditions, result in the precipitation of  $A$  and will change the solute composition of the solution along a straight line directly away from  $A$  in Figure 9.8. As long as the solution remains saturated with respect to  $A$  the point representing its composition must remain on the solubility surface of  $A$ . When the solute composition of the solution reaches the point  $j$ , the solution will be saturated with respect to  $C$  as well as  $A$ . With further removal of water,  $C$  will be precipitated as well as  $A$  and the solute composition of the solution will be constrained to remain on the line  $e'q'$  common to the fields of  $A$  and  $C$ . The composition of the whole solids will be represented by a succession of points along the line  $AC$ , from  $A$  toward  $C$ . The representative point for the whole solids, the point  $S$ , and the point representing the solute composition of the solution must, of course, be collinear. When the solute composition reaches the point  $q'$ , the solution will be saturated with respect to  $B$ , as well as  $A$  and  $C$ ; the composition of the whole solids will then have reached the point  $m$ . Further removal of water will result in the simultaneous precipitation of  $A$ ,  $B$ , and  $C$ , but the composition of the liquid will be constrained to remain at  $q'$  until the dehydration is complete.

The similarity of the pattern of this course of crystallization to that discussed in Section 8.2 is striking. It is apparent that the composition variable *water* in the isothermal dehydration (removal of water) of the four-component system plays the same role as the variable *temperature* in the cooling (removal of heat) of a three-component system; the logic used to decide the course of crystallization is the same for both cases.

### 9.6 Poly-component Compounds in the System $A-B-C-W$

The foregoing discussion was limited, for simplicity, to systems having only the pure components as solid phases. The extension to include binary, ternary, and quaternary compounds does not introduce serious complications. For example, typical phase diagrams for systems having a ternary compound  $A \cdot B \cdot C$  are represented in Figures 9.9, 9.10, and 9.11. These diagrams differ from Figures 9.3 and 9.8 in having a fourth solubility field, for the compound  $A \cdot B \cdot C$ . In these diagrams composition is represented

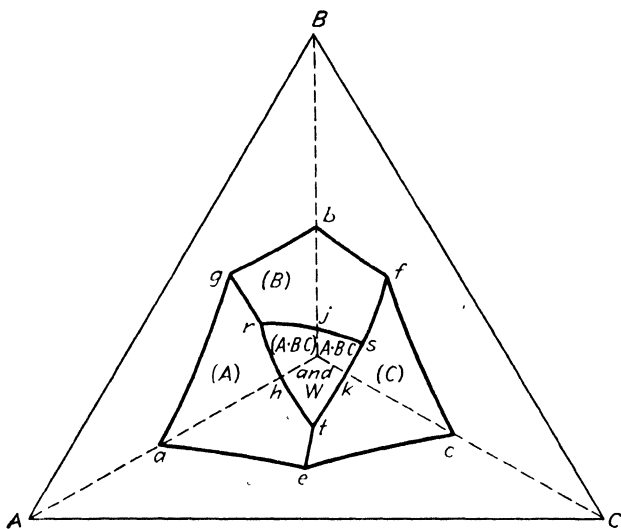


FIG. 9.9 The vertical projection of the tetrahedral diagram for a system having a ternary compound

on a mole scale, so that the composition of the compound  $A \cdot B \cdot C$  is represented by the center of the triangular base.

In Figure 9.9 is shown the vertical projection of the tetrahedral diagram for the system  $A-B-C-W$ . The point  $A \cdot B \cdot C$  is coincident with the projection of the apex  $W$  of the tetrahedron. As in Figure 9.3 the periphery of the projected solubility fields,  $agbfcea$ , gives complete information about solubilities in the three-component systems  $A-B-W$ ,  $B-C-W$ , and  $C-A-W$ . It is apparent from Figure 9.9 that the compound  $A \cdot B \cdot C$ , when added to water, can form a saturated solution without decomposing, since it is

seen from the projection that the line  $W \cdot A \cdot B \cdot C$  in the tetrahedron intersects the solubility surface of  $A \cdot B \cdot C$ . (Compare the case of astracanite and water, Section 6.3.) The line  $rs$  gives the projections of the compositions of solutions simultaneously saturated with respect to  $B$  and  $A \cdot B \cdot C$ ; the line  $st$ , with respect to  $C$  and  $A \cdot B \cdot C$ ; the line  $tr$ , with respect to  $A$  and  $A \cdot B \cdot C$ . The invariant point  $r$  represents the projection of the solute composition of the solution simultaneously saturated with respect to  $A$ ,  $B$ , and  $A \cdot B \cdot C$ ; the invariant point  $s$ , with respect to  $B$ ,  $C$ , and  $A \cdot B \cdot C$ ; the invariant point  $t$ , with respect to  $C$ ,  $A$ , and  $A \cdot B \cdot C$ .

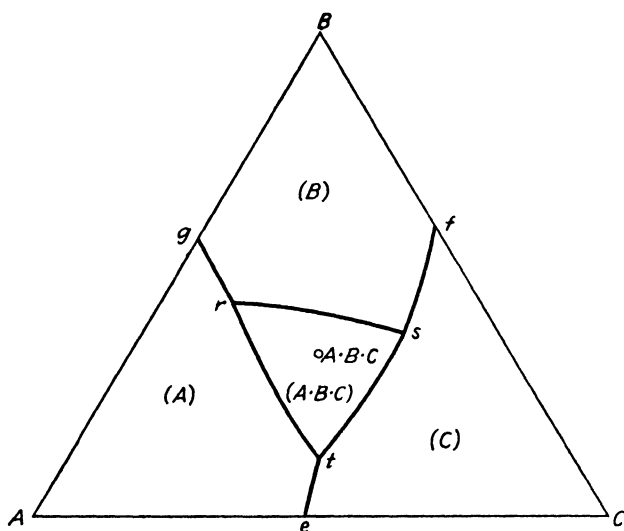


FIG. 9.10 The vertical projection of the prismatic diagram for a system having a ternary compound which dissolves in water without decomposition.

The point  $h$ , the intersection of the line  $tr$  with the straight line joining  $A$  and  $A \cdot B \cdot C$ , is the projection of the composition of the solution simultaneously saturated with respect to  $A$  and  $A \cdot B \cdot C$  in the three-component system  $A - A \cdot B \cdot C - W$ . Similarly  $j$  and  $k$  are the projections of the compositions of the invariant solutions in the three-component systems  $B - A \cdot B \cdot C - W$  and  $C - A \cdot B \cdot C - W$ , respectively. The line  $gr$  is the projection of the compositions of the univariant four-component solutions saturated with respect to  $A$  and  $B$ ; the line  $fs$ , with respect to  $B$  and  $C$ ; the line  $et$ , with respect to  $C$  and  $A$ .

In Figure 9.10 is shown the vertical projection of the prismatic diagram corresponding to the tetrahedral diagram of Figure 9.9. The invariant points and univariant lines are lettered identically in the two diagrams. It is interesting to compare Figure 9.10 with Figure 8.13, the diagram for a three-component system having a ternary compound which melts congruently. It is apparent that the course of crystallization during isothermal evaporation will follow a pattern similar to that which obtains during the cooling of a melt in the system  $A\text{-}B\text{-}C$  of Figure 8.13.

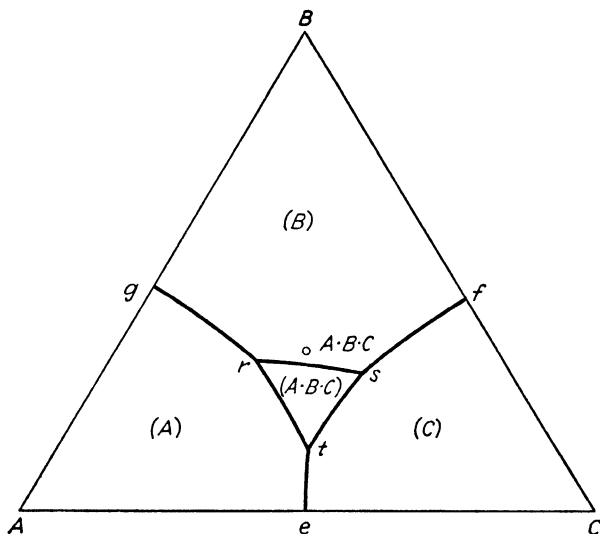


FIG. 9.11 The vertical projection of the prismatic diagram for a system having a ternary compound which undergoes decomposition on being dissolved in water.

If a four-component system  $A\text{-}B\text{-}C\text{-}W$  has a ternary compound  $A\cdot B\cdot C$  which decomposes on forming a saturated solution with water to give a second solid phase, then it is clear that a vertical line through  $A\cdot B\cdot C$  cannot intersect its solubility surface in the prismatic diagram. Such a case is illustrated by Figure 9.11, in which the point  $A\cdot B\cdot C$  lies outside the solubility field of  $A\cdot B\cdot C$ . In this particular case the second solid, formed on adding water to  $A\cdot B\cdot C$ , will be  $B$  and the solute composition of the saturated solution will be the intersection of the line  $rs$  with the prolongation of the straight line drawn from  $B$  through  $A\cdot B\cdot C$ .

### 9.7 Graphical Representation of the Anhydrous Composition of a System Consisting of Water and Two Reciprocal Salt Pairs

As defined earlier, reciprocal salt pairs comply with the metathetical equation  $AX + BY = BX + AY$ , in which  $A$  and  $B$  represent cations and  $X$  and  $Y$  represent anions. The anhydrous composition of any simple salt, poly-component salt, or solution of such salts in the system  $AX$ - $BY$ - $W$  can be expressed in terms of any three of the simple salts, say  $AX$ ,  $BY$ , and  $BX$ . Such compositions can therefore be represented on a triangle having  $AX$ ,  $BY$ , and  $BX$  as the apices. The salt  $AY$  would have to be represented by a point lying outside the triangle, since it consists of *positive* quantities of  $AX$  and  $BY$ , but a *negative* quantity of

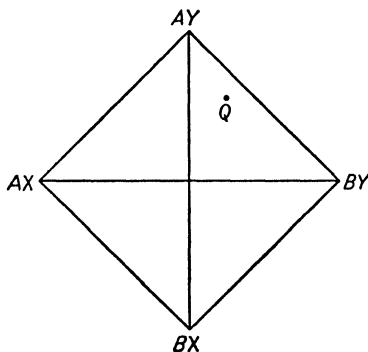


FIG. 9.12 Quadrilateral representation of composition in systems of reciprocal salt pairs.

$BX$  (that is,  $AY = AX + BY - BX$ ). This is shown in Figure 9.12; for convenience the second triangle  $AX$ - $AY$ - $BY$  has been completed. All possible combinations of the four simple salts can then be represented within the confines of the quadrilateral  $AX$ - $AY$ - $BY$ - $BX$  (see Section 8.7). Furthermore, drawing the line  $AY$ - $BX$  completes the symmetry of the figure and shows that any of the sets of components,  $AX$ - $BY$ - $BX$ ,  $AY$ - $BX$ - $AX$ ,  $BY$ - $AX$ - $AY$ , or  $BX$ - $AY$ - $BY$ , may be used to represent anhydrous compositions within the quadrilateral; it should be noted that any point representing anhydrous composition lies within two of these four triangles, *e.g.*, the point  $Q$  lies within the triangles  $BY$ - $AX$ - $AY$  and  $BX$ - $AY$ - $BY$  and therefore this composition can

be expressed in terms of positive quantities of either of these sets of constituents. The proportion of water can be shown by constructing either a prism or a pyramid on the quadrilateral base.

### 9.8 Aqueous Reciprocal Salt Pair Systems. The Pyramidal Solid Diagram and Its Projection

This type of diagram, in which the anhydrous composition is shown on the square base (see Section 9.7) and water as the vertical apex of a pyramid, is analogous to the regular tetrahedron discussed in Section 9.3. Although the projections of pyramidal diagrams have been used by many investigators, they are less useful

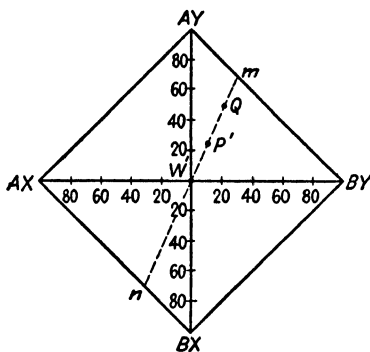


FIG. 9.13 Vertical projection of a pyramidal diagram.  $Q$  = solute composition;  $P'$  = vertical projection of solution composition.

than the projections of prismatic diagrams (Section 9.9) and have been included here only for completeness.

The four slant sides of the pyramid can be used to represent the phase diagrams of the four three-component systems  $AX$ - $AY$ - $W$ ,  $AY$ - $BY$ - $W$ ,  $BY$ - $BX$ - $W$ , and  $BX$ - $AX$ - $W$ . The vertical projections of these sides on the base are the correspondingly lettered triangles of Figure 9.13; the vertical projection of  $W$  is designated as  $W'$ . With respect to the four three-component systems the point  $W'$  represents the projection of  $W$ ; with respect to the four-component system it can represent not only the projection of  $W$  but also the solute composition of a solution containing equal proportions of  $AX$  and  $BY$  or equal proportions of  $AY$  and  $BX$ .

The method of obtaining the projection on the base of the pyramid of a point  $P$  within the pyramid can now be shown. Let the point  $P$  represent the composition  $a\%$  of  $AX$ ,  $b\%$  of  $AY$ ,  $c\%$  of  $BY$ , and  $w\%$  of water. The anhydrous composition of this system,  $Q$ , will obviously lie in the triangle  $AX-AY-BY$ ; if  $c$  is greater than  $a$ , the anhydrous composition will lie within the smaller triangle  $W'-AY-BY$ . It will be convenient to define  $a'$ ,  $b'$ , and  $c'$  as the percentages of  $AX$ ,  $AY$ , and  $BY$  respectively in the anhydrous salts. Thus  $a' = 100a/(a + b + c)$ ;  $b' = 100b/(a + b + c)$ ;  $c' = 100c/(a + b + c)$ ;  $a' + b' + c' = 100$ . The conventional method of representing composition on a diagram of this type is through scales on the mutually orthogonal diagonals, with  $W'$  as the origin, as shown in Figure 9.13. In plotting the point representing the solute composition it is necessary to appreciate that on this diagram the point  $W'$  can represent equal proportions of  $AX$  and  $BY$ . If  $c > a$ , and therefore  $c' > a'$ , the solute composition will lie in the first quadrant and can be represented as positive quantities of  $AY$ ,  $BY$ , and  $W'$ ,

$$\begin{aligned} a'\% \text{ of } AX + b'\% \text{ of } AY + c'\% \text{ of } BY &= a'\% \text{ of } AX \\ &+ a'\% \text{ of } BY + b'\% \text{ of } AY + (c' - a')\% \text{ of } BY \\ &= a'\% \text{ of } W' + b'\% \text{ of } AY + (c' - a')\% \text{ of } BY \end{aligned}$$

The first quadrant is identical with the right-angled isosceles triangle of Figure 6.1; the ordinate of the solute composition,  $Q$ , is therefore  $b'$  and the abscissa is  $c' - a'$ . If  $a$  had been greater than  $c$ ,  $Q$  would have fallen in the second quadrant and the abscissa would have been  $a' - c'$  on the scale  $W'-AX$ .

Since the system  $P$  consists of  $w\%$  of water and  $(a + b + c)\%$  of salts having the composition  $Q$ , it is clear that in the solid diagram  $W$ ,  $P$ , and  $Q$  must be collinear in order to satisfy the proportioning rule. Thus  $P'$ , the vertical projection of  $P$ , will lie on the line  $W'Q$  of Figure 9.13. It is convenient to consider the vertical plane cutting the pyramid through the points  $W$ ,  $W'$ , and  $Q$ , shown in Figure 9.14. Both  $P$  and its vertical projection  $P'$  will, of course, lie on this plane. The ratio  $W'P'/W'Q = (a + b + c)/(a + b + c + w) = (a + b + c)/100$ . The coordinates of  $Q$  in Figure 9.13 are  $b'$  and  $c' - a'$ ; the coordinates of  $P'$  will therefore be  $b'(a + b + c)/100$  and  $(c' - a')(a + b + c)/100$ . By eliminating  $a'$ ,  $b'$ , and  $c'$  in terms of  $a$ ,  $b$ , and  $c$ , the coordinates of  $P'$  are seen to be simply  $b$  and  $c - a$ . Experimental

points can be plotted in this way, but it must be realized that a point such as  $P'$  does not alone define the composition of the solution explicitly. To define the composition completely, additional information would be required, *e.g.*, the percentage of either  $AX$  or  $BY$ , or the total percentage of salts,  $a + b + c$ , or the percentage of water,  $w = 100 - a - b - c$ .

The vertical projection of the pyramidal diagram for the system  $\text{Na}_2\text{SO}_4$ - $\text{KCl}$ - $\text{H}_2\text{O}$  is shown in Figure 9.15. The reciprocal salt pair relation in this system is  $\text{Na}_2\text{SO}_4 + 2\text{KCl} = 2\text{NaCl} + \text{K}_2\text{SO}_4$ . It is therefore convenient to express the proportions of the various salts in terms of equivalents, rather

than moles or grams; the scale readings refer to percentages by equivalents,  $\frac{1}{2}\text{Na}_2\text{SO}_4$ ,  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\frac{1}{2}\text{K}_2\text{SO}_4$ . At  $0^\circ\text{C}$  and 1 atm this system has five solubility fields showing saturation with respect

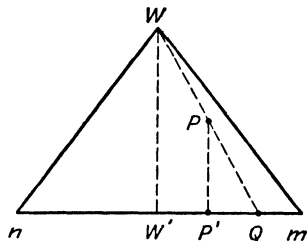


FIG. 9.14 Vertical plane through the pyramid  $AX$ - $AY$ - $BY$ - $BX$ - $W$ .

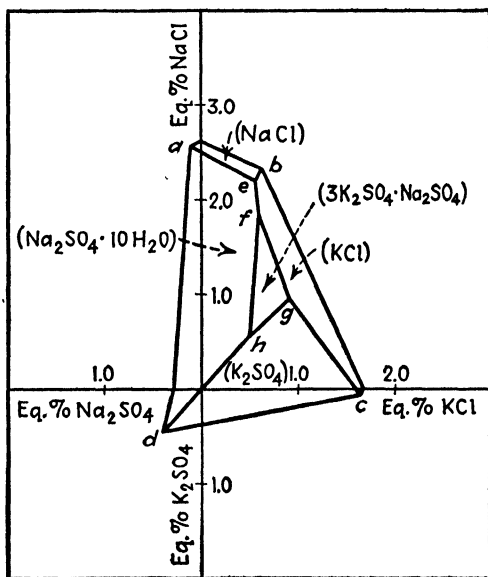


FIG. 9.15 The vertical projection of the pyramidal diagram for the system  $\text{Na}_2\text{SO}_4$ - $\text{KCl}$ - $\text{H}_2\text{O}$  at  $0^\circ\text{C}$ .

to halite ( $\text{NaCl}$ ), sylvite ( $\text{KCl}$ ), arcanite ( $\text{K}_2\text{SO}_4$ ), Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), and glaserite ( $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ ).

### 9.9 Aqueous Reciprocal Salt Pair Systems. The Prismatic Solid Diagram and Its Projection

In the prismatic diagram for a four-component system of water and reciprocal salt pairs, the anhydrous composition can be shown on a square base and the proportion of water by a vertical coordinate. The vertical projection of the prismatic diagram for the system  $\text{Na}_2\text{SO}_4\text{-KCl-H}_2\text{O}$  at  $0^\circ\text{C}$  and 1 atm is shown in Figure 9.16. In this projection the composition of the hydrate Glauber's salt is coincident with the point representing sodium sulfate. Since the four three-component diagrams involving water appear on the four corresponding vertical sides of the prism, the vertical projections of these diagrams will form the four sides of the square base. The four ternary invariant points,  $a$ ,  $b$ ,  $c$ ,  $d$ , and the four quaternary invariant points,  $e$ ,  $f$ ,  $g$ ,  $h$ , are designated in the same way in Figures 9.15 and 9.16.

The compositions shown in Figure 9.16 are anhydrous compositions, expressed as percentages by equivalents. Two methods of plotting compositions will be illustrated by reference to the quaternary solution saturated with respect to halite, sylvite, and Glauber's salt; the composition of this solution,  $e$ , is 8.79% halite, 1.68% sylvite, 0.67% arcanite, and 88.9% water, by equivalents. The corresponding anhydrous composition is 79.0% halite, 15.0% sylvite, and 6.0% arcanite, by equivalents. In the first method of plotting  $e$  the composition is considered in terms of the right-angled isosceles triangle  $\text{NaCl-KCl-K}_2\text{SO}_4$ ; the vertical coordinate is 79%, the horizontal (to the left) 6.0%. The second method is based on the procedure used to obtain the coordinates of  $Q$  in Figure 9.13; the coordinates of  $e$  in the triangle  $\text{NaCl-O-KCl}$  will be 15% on the  $\text{O-KCl}$  axis and  $79.0 - 6.0 = 73.0\%$  on the  $\text{O-NaCl}$  axis.

The course of crystallization during the isothermal evaporation of a solution in the system  $\text{Na}_2\text{SO}_4\text{-KCl-H}_2\text{O}$  can be readily followed by means of Figure 9.16. Consider a solution made up of 65 equivalents of sodium sulfate, 10 equivalents of halite, 25 equivalents of sylvite, and sufficient water to dissolve all the salts. The anhydrous composition of this solution is represented by the point  $s$ . This point lies within the field of Glauber's salt,

which will be the first solid to form on evaporation, under equilibrium conditions. The composition of the resulting solution will follow the path  $st$ , directly away from  $\text{Na}_2\text{SO}_4$  (the anhydrous composition of Glauber's salt). When the solution attains the composition  $t$  it will be saturated with respect to arcanite as well as Glauber's salt. During further evaporation both arcanite and Glauber's salt will be deposited and the solution composition will be constrained to follow the path  $th$ ; the composition of the whole solids will follow the path  $\text{Na}_2\text{SO}_4-v$ . When its composition reaches

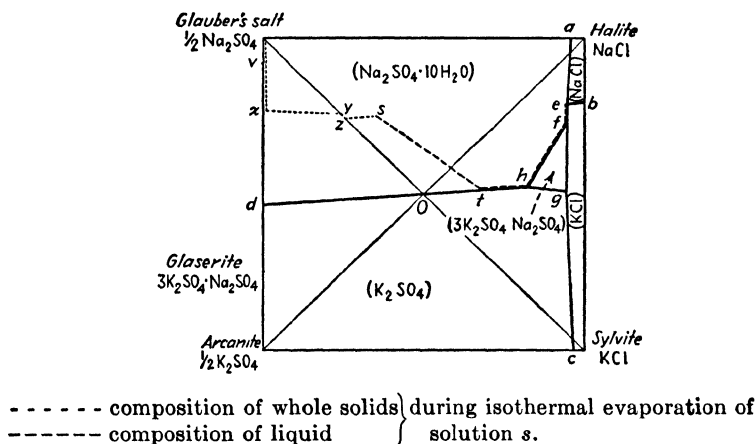


FIG. 9.16 Vertical projection of the prismatic diagram for the system  $\text{Na}_2\text{SO}_4\text{-KCl-H}_2\text{O}$  at  $0^\circ\text{C}$  and 1 atm.

$h$  the solution will be saturated with respect to glaserite as well as Glauber's salt and arcanite. At constant temperature and pressure the system of four phases will be invariant, hence the composition (and amount) of the solution will remain fixed while Glauber's salt and arcanite react to form glaserite and water vapor. The arcanite will be completely used up before the Glauber's salt, leaving a solid mixture of Glauber's salt and glaserite having the composition  $v$ ; the system will then be univariant. With further removal of water the composition of the solution will follow the path  $hf$ , while the composition of the solids will follow the path  $vx$ . When the composition of the solution reaches  $f$ , it will be saturated with respect to sylvite as well as Glauber's salt and glaserite. The system will again be invariant; while the composition of the solution remains fixed at  $f$ , the composition of the whole solids will follow the path  $xy$ , since the reaction under invariant condi-

tions will be the addition of new solids of composition  $f$  to the solids previously present, of composition  $x$ . Since  $f$  lies outside the triangle having the apices Glauber's salt, glaserite, and sylvite and remote from the glaserite apex, it is apparent that glaserite will be resorbed while Glauber's salt and sylvite are being deposited. When the composition of the whole solids reaches the line  $\text{Na}_2\text{SO}_4$ - $\text{KCl}$  (at the point  $y$ ) the glaserite will be completely resorbed. The system will then be univariant. With further removal of water the composition of the solution will follow the path  $fe$ , while the composition of the whole solids will follow the path  $yz$ . When its composition reaches  $e$  the solution will be saturated with respect to halite as well as Glauber's salt and sylvite; the system will once more be invariant. While the composition of the solution remains fixed at  $e$ , the composition of the whole solids will follow the path  $zs$ , corresponding to the addition of new solids of composition  $e$  to the solids of composition  $z$  already present. When the composition of the whole solids reaches  $s$ , the last of the invariant liquid  $e$  will have vanished; the system will then consist of a mixture of the solids Glauber's salt, sylvite, and halite.

### 9.10 The System $\text{NaCl-NH}_4\text{HCO}_3\text{-H}_2\text{O}$

This system is of interest because of its relation to the Solway and Schlösing processes for the industrial production of sodium bicarbonate. The reaction of interest is the reciprocal salt pair conversion  $\text{NaCl} + \text{NH}_4\text{HCO}_3 = \text{NaHCO}_3 + \text{NH}_4\text{Cl}$ .

In Figure 9.17 is given the vertical projection of the prismatic diagram for the system  $\text{NaCl-NH}_4\text{HCO}_3\text{-H}_2\text{O}$  at  $15^\circ\text{C}$  and a total pressure of 1 atm. An aqueous solution of ammonium bicarbonate can exist in equilibrium with a gaseous solution composed of ammonia, carbon dioxide, and water vapor; the vapor in contact with a stable aqueous solution saturated with respect to ammonium bicarbonate must therefore contain these three gases in the relative proportions determined by the equilibrium constant. The data for Figure 9.17 were determined under the condition that the atmosphere in contact with the solution contained an excess of carbon dioxide sufficient to make the sum of the partial pressures 1 atm. This condition does not increase the number of components above four, since neither the proportion of ammonia nor the proportion of carbon dioxide admits of independent variation; these proportions are controlled by the two conditions, (1)

the mass law equation for the dissociation of ammonium bicarbonate in a saturated solution,  $p_{\text{NH}_3} \cdot p_{\text{CO}_2} \cdot p_{\text{H}_2\text{O}} = K_p$  and (2) the imposed condition,  $p_{\text{NH}_3} + p_{\text{CO}_2} + p_{\text{H}_2\text{O}} = 1$  atm (see Section 1.4).

If it is desired to make sodium bicarbonate from the ingredients sodium chloride and ammonium bicarbonate, it is clear from Figure 9.17 that the anhydrous composition of the initial system will lie on the diagonal line  $\text{NaCl-NH}_4\text{HCO}_3$ . This diagonal passes through the fields of sodium chloride, sodium bicarbonate, and ammonium bicarbonate. If sodium bicarbonate is to be the first solid produced, the initial anhydrous composition must fall within the limits 98%  $\text{NaCl}$ , 2%  $\text{NH}_4\text{HCO}_3$  (by equivalents or moles)

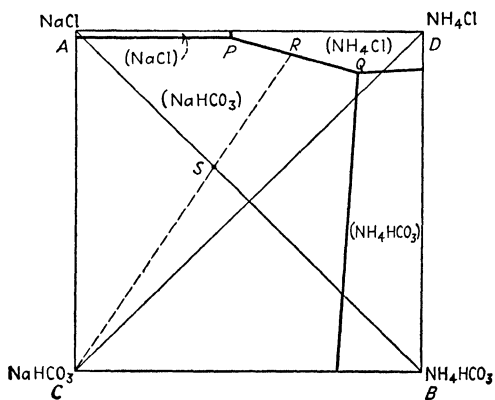


FIG. 9.17 The vertical projection of the prismatic diagram for the system  $\text{NaCl-NH}_4\text{HCO}_3\text{-H}_2\text{O}$  at  $15^\circ\text{C}$  and 1 atm. total pressure.

and 23%  $\text{NaCl}$ , 77%  $\text{NH}_4\text{HCO}_3$ , *i.e.*, on that portion of the diagonal lying in the field of sodium bicarbonate. Furthermore, if sodium bicarbonate is to be the *only* solid produced, the anhydrous composition of the liquid must remain inside the boundaries of the field of sodium bicarbonate.

If the initial anhydrous composition of the system is represented by the point  $S$ , 60 mole per cent  $\text{NaCl}$ , 40 mole per cent  $\text{NH}_4\text{HCO}_3$ , dehydration of the solution will result in the precipitation of sodium bicarbonate and the anhydrous composition of the solution will follow the path  $SR$ . When the anhydrous composition has reached  $R$ , further dehydration would result in the precipitation of ammonium chloride as well as sodium bicarbonate; consequently, if

ammonium chloride is not to be precipitated, the point *R* marks the limit of the path of the anhydrous composition of the solution. The maximum amount of pure solid sodium bicarbonate which can be obtained by dehydration of the initial system is  $SR/CR$  of the initial salts. The proportion of initial salts converted into pure solid sodium bicarbonate is clearly dependent on the relative amounts of sodium chloride and ammonium bicarbonate initially taken. This is shown by the curve *A* of Figure 9.18. The maximum yield on this basis is seen to be obtained from a starting material containing 52 mole per cent NaCl, 48 mole per cent

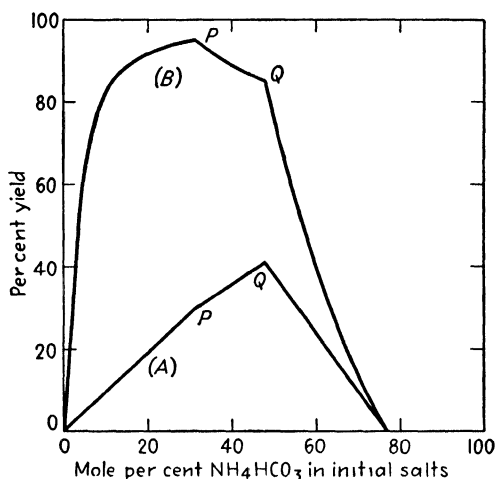


FIG. 9.18 Per cent yield of sodium bicarbonate at 15°C. (A) Moles formed per 100 moles of initial salts; (B) moles formed per 100 moles of ammonium bicarbonate in initial salts.

$\text{NH}_4\text{HCO}_3$ ; the final anhydrous composition of the solution in this case is given by the point *Q* of Figure 9.17.

Generally the ammonium bicarbonate is more costly than the sodium chloride. It is therefore of interest to calculate the yield of sodium bicarbonate in terms of the ammonium bicarbonate usefully converted. This yield is given by the relation

$$\frac{\text{Moles NaHCO}_3 \text{ produced}}{\text{Moles NH}_4\text{HCO}_3 \text{ initially taken}} = \frac{\text{moles NaHCO}_3 \text{ produced}}{\text{moles of initial salts}} \times \frac{\text{moles of initial salts}}{\text{moles NH}_4\text{HCO}_3 \text{ initially taken}}$$

For the system  $S$  referred to above, the yield of sodium bicarbonate per mole of ammonium bicarbonate initially taken would thus be  $(SR/CR)(AB/AS)$ . This yield is also dependent on the relative amounts of sodium chloride and ammonium bicarbonate taken initially; it is greatest for the case in which the final solution has the anhydrous composition  $P$ , that is, in which the starting material is 31.4 mole per cent  $\text{NH}_4\text{HCO}_3$ , 68.6 mole per cent  $\text{NaCl}$ . This is shown by the curve  $B$  of Figure 9.18.

### EXERCISES

1. Assuming equilibrium, trace the paths of the representative points of the liquid and the whole solids during the crystallization at  $15^\circ\text{C}$  of the solutions (a) having the anhydrous composition  $S$  of Figure 9.17, (b) having the anhydrous composition 40%  $\text{NaCl}$ , 60%  $\text{NH}_4\text{HCO}_3$ , by equivalents.
2. Assuming equilibrium, trace the paths of the representative points of the liquid and the whole solids during the crystallization at  $0^\circ\text{C}$  of a solution having the anhydrous composition 60% potassium chloride, 20% potassium sulfate, 20% sodium sulfate, by equivalents.
3. It is required to prepare pure glaserite by evaporation at  $0^\circ\text{C}$  of an aqueous solution made up from Glauber's salt, potassium chloride, and sodium chloride. State the proportions (by equivalents) of these three salts in the solution which would give the greatest yield of pure glaserite.
4. On the field boundary lines of Figure 9.16 draw arrows indicating the direction of increasing proportion of water in the univariant solutions (cf. Section 8.4).



## APPENDIXES

In the preceding chapters the principles of phase equilibria were treated without introducing formal thermodynamics. For the benefit of the reader who is conversant with chemical thermodynamics, the Appendixes will serve to extend and correlate the treatment. The thermodynamic relations required for the consideration of phase equilibria are developed in numerous texts. These relations will not be derived here, but reference will be made to the appropriate equations in the Second Edition of "Introduction to Chemical Thermodynamics" by Luke E. Steiner, McGraw-Hill Book Company, Inc., New York, 1948.



## APPENDIX I

### THE THERMODYNAMIC DERIVATION OF THE PHASE RULE

If variations in such conditions as gravitational field, electrical fields, etc., are excluded (see Section 1.2), the properties of a stable phase will be single-valued functions of the independent variables, the temperature,  $T$ , the pressure,  $P$ , and the number of moles,  $n_1, n_2, \dots, n_c$ , of each of the  $\mathcal{C}$  components of the phase. The only properties concerned in chemical equilibrium are those which are independent of the amount of the phase; such properties are called *intensive* (the volume of a phase is an extensive property, the specific volume an intensive property). The intensive properties of a stable phase will be single-valued functions of  $T$ ,  $P$ , and  $\mathcal{C} - 1$  composition variables (*e.g.*, the mole fractions of any  $\mathcal{C} - 1$  of the components of that phase), a total of  $\mathcal{C} + 1$  in all.

For a system having a total of  $\mathcal{C}$  components in  $\mathcal{O}$  *isolated* phases ( $\phi, \phi', \phi'', \dots$ ), which respectively consist of  $\mathcal{C}', \mathcal{C}'', \mathcal{C}''', \dots$  of these components, the independent variables affecting the intensive properties of each phase will be as follows:

|           |                                                                                                                                                       |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------|
| Phase':   | $T', P'$ , and $\mathcal{C}' - 1$ mole fractions, a total<br><div style="text-align: right;">of <math>\mathcal{C}' + 1</math> variables</div>         |
| Phase'':  | $T'', P''$ , and $\mathcal{C}'' - 1$ mole fractions, a total<br><div style="text-align: right;">of <math>\mathcal{C}'' + 1</math> variables</div>     |
| Phase''': | $T''', P'''$ , and $\mathcal{C}''' - 1$ mole fractions, a total<br><div style="text-align: right;">of <math>\mathcal{C}''' + 1</math> variables</div> |
| Etc.      |                                                                                                                                                       |

The total number of independent variables for the  $\mathcal{O}$  phases will be  $\mathcal{O} + \mathcal{C}' + \mathcal{C}'' + \mathcal{C}''' + \dots$ .

For the  $\mathcal{O}$  phases to *coexist in equilibrium* it is necessary and sufficient that both the temperature and the pressure be uniform throughout the system and that the partial molal free energy of each component be the same in every phase containing that component [Steiner's equation (17.35)]. The partial molal free energy of component  $i$ ,  $\bar{F}_i$ , in the notation of Lewis and Randall, is identical

with  $\mu_i$ , the (molal) chemical potential of Gibbs. The latter symbol will be used in this derivation.

For the  $\mathcal{O}$  phases to *remain* in equilibrium over a range of conditions it is necessary and sufficient that

$$dT' = dT'' = dT''' = \dots \quad (1)$$

$$dP' = dP'' = dP''' = \dots \quad (2)$$

and that  $d\mu$  for each component be the same in all phases which can exist in equilibrium with respect to the transfer of that component.

Let  $\mathcal{O}_1$  be the number of phases which can exist in equilibrium with respect to the transfer of component 1. The equality of the  $d\mu_1$ 's in the  $\mathcal{O}_1$  phases will give rise to  $\mathcal{O}_1 - 1$  independent relations among pairs of the  $d\mu_1$ 's. For example, if four of the phases can exist in equilibrium with respect to the transfer of component 1, then  $d\mu_1' = d\mu_1'' = d\mu_1''' = d\mu_1''''$ , and there will be three independent relations, such as the set

$$d\mu_1' = d\mu_1'' \quad (3)$$

$$d\mu_1' = d\mu_1''' \quad (4)$$

$$d\mu_1' = d\mu_1'''' \quad (5)$$

If this set is chosen, the relations  $d\mu_1'' = d\mu_1'''$ ,  $d\mu_1'' = d\mu_1''''$ , and  $d\mu_1''' = d\mu_1''''$  are not independent.

The chemical potential of a component in any phase is an intensive property of that phase and is therefore a function of the temperature, the pressure, and the mole fractions of all but one of the components of that phase. Thus

$$\mu_1' = f(T', P', N_1', N_2', \dots) \quad \mathcal{C}' + 1 \text{ variables} \quad (6)$$

and

$$d\mu_1' = f(dT', dP', dN_1', dN_2', \dots) \quad \mathcal{C}' + 1 \text{ variables} \quad (7)$$

Similarly

$$d\mu_1'' = f(dT'', dP'', dN_1'', dN_2'', \dots) \quad \mathcal{C}'' + 1 \text{ variables} \quad (8)$$

From equations (3), (7), and (8),

$$f(dT', dP', dN_1', dN_2', \dots) = f(dT'', dP'', dN_1'', dN_2'', \dots) \quad (9)$$

It is evident that for each independent relation between a pair of  $d\mu_1$ 's there will be one relation, such as (9), among the temperature, pressure, and composition variations of the phases. Therefore, since there are  $\mathcal{O}_1 - 1$  independent relations of type (3)

among the  $d\mu_1$ 's, there will be  $\mathcal{P}_1 - 1$  relations of type (9) among the temperature, pressure, and composition variations.

Similarly, if  $\mathcal{P}_2$  be the number of phases which can exist in equilibrium with respect to the transfer of component 2, there will be  $\mathcal{P}_2 - 1$  relations among the temperature, pressure, and composition variations. For a total of  $\mathcal{C}$  components there will be

$$(\mathcal{P}_1 - 1) + (\mathcal{P}_2 - 1) + \cdots + (\mathcal{P}_c - 1) \\ = \mathcal{P}_1 + \mathcal{P}_2 + \cdots + \mathcal{P}_c - \mathcal{C} \quad (10)$$

relations among the temperature, pressure, and composition variations of the system.

It was shown above that the total number of independent variations for the  $\mathcal{P}$  *isolated* phases is  $\mathcal{P} + \mathcal{C}' + \mathcal{C}'' + \mathcal{C}''' + \cdots$ . The thermodynamic requirements for persistence of equilibrium introduce a number of relations among these variations, *viz.*,  $\mathcal{P} - 1$  relations from equation (1),  $\mathcal{P} - 1$  relations from equation (2), and  $\mathcal{P}_1 + \mathcal{P}_2 + \cdots + \mathcal{P}_c - \mathcal{C}$  from (10). The number of independent variations compatible with the persistence of the equilibrium (*i.e.*, the number of degrees of freedom,  $\mathfrak{F}$ ) will be equal to the total number of independent variations for the system of isolated phases *less* the number of independent restrictive relations demanded by the persistence of equilibrium, *i.e.*,

$$\mathfrak{F} = \mathcal{P} + \mathcal{C}' + \mathcal{C}'' + \mathcal{C}''' + \cdots - [(\mathcal{P} - 1) + (\mathcal{P} - 1) + \mathcal{P}_1 \\ + \mathcal{P}_2 + \mathcal{P}_3 + \cdots + \mathcal{P}_c - \mathcal{C}] \\ = \mathcal{C} + 2 - \mathcal{P} + (\mathcal{C}' + \mathcal{C}'' + \mathcal{C}''' + \cdots) - (\mathcal{P}_1 + \mathcal{P}_2 + \mathcal{P}_3 \\ + \cdots + \mathcal{P}_c) \quad (11)$$

It can be readily shown that the two terms in brackets are identical by constructing an array showing the components of each phase; these are indicated by crosses in the sample array below.

|                   | Component           |                     |                     |                       |
|-------------------|---------------------|---------------------|---------------------|-----------------------|
|                   | 1                   | 2                   | 3                   |                       |
| Phase'            | ×                   | ×                   | ×                   | $\mathcal{C}' = 3$    |
| Phase''           | ×                   | ×                   |                     | $\mathcal{C}'' = 2$   |
| Phase'''          |                     |                     | ×                   | $\mathcal{C}''' = 1$  |
| Phase''''         |                     |                     | ×                   | $\mathcal{C}'''' = 1$ |
| $\mathcal{P} = 4$ | $\mathcal{P}_1 = 2$ | $\mathcal{P}_2 = 2$ | $\mathcal{P}_3 = 3$ |                       |

It is evident that  $\mathfrak{C}' + \mathfrak{C}'' + \mathfrak{C}''' + \mathfrak{C}'''' = \mathfrak{P}_1 + \mathfrak{P}_2 + \mathfrak{P}_3 = \text{total number of crosses in the whole array.}$

Thus, regardless of the number of components present in any particular phase or of the number of phases in which any particular component appears, the number of degrees of freedom is given by the relation

$$\mathfrak{F} = \mathfrak{C} + 2 - \mathfrak{P}$$

## APPENDIX II

### FREE ENERGY-COMPOSITION CURVES FOR TWO-COMPONENT SYSTEMS

#### II.1 Free Energy Changes for Spontaneous Processes

The thermodynamic criterion for the spontaneity of any process occurring at constant temperature and pressure is that the free energy,  $F$ , of the system shall decrease during the spontaneous process. This criterion is conveniently expressed by the relation  $dF_{P,T} < 0$  [Steiner's equation (10.32)].

The statement that undercooled water is metastable with respect to the formation of ice implies that the free energy of undercooled water is greater than the free energy of the same weight of ice at the same temperature and pressure. Also, it is evident that the free energy of a supersaturated solution is greater than the free energy of a system consisting of solute and the saturated solution and having the same over-all composition and weight (at the same temperature and pressure).

#### II.2 The Free Energy-Composition Curve for a Mixture at Constant Temperature and Pressure

As mentioned in Chapter 4, decane and water are immiscible liquids. If  $F_1$  is the free energy of 1 mole of water and  $F_2$  the free energy of 1 mole of decane, then the free energy of a mixture of  $n_1$  moles of water and  $n_2$  moles of decane will be given by the relation  $F = n_1 F_1 + n_2 F_2$ . The total number of moles in the mixture is  $n_1 + n_2$  and hence  $F$ , the molar free energy of the mixture, will be given by the relation

$$F = \frac{F}{n_1 + n_2} = N_1 F_1 + N_2 F_2 \quad (12)$$

in which  $N_1$  and  $N_2$  are the mole fractions of water and decane, respectively;  $N_1 = n_1/(n_1 + n_2)$  and  $N_2 = n_2/(n_1 + n_2)$ . Since  $N_1 + N_2 = 1$ , it follows that

$$F = F_1 - N_2(F_1 - F_2) \quad (13)$$

From equation (13) it is evident that  $F$  for the mixture is a linear function of  $N_2$  (or of  $N_1$ ) for the mixture and lies on the straight line joining  $F_1$  and  $F_2$  on the molar free energy-mole fraction diagram. This is shown in Figure II.1. The ordinate of the point  $g$  (at the abscissa  $N_2$ ) on the straight line joining  $F_1$  and  $F_2$  is equal to  $F_1 - F_1j$ . From similar triangles  $F_1j = F_1k$  ( $kg/kF_2$ ) =  $(F_1 - F_2) N_2/1$ . Thus the ordinate of  $g = F_1 - N_2(F_1 - F_2) = F$ .

Let  $F'$  be the molar free energy of a solution composed of  $n'_1$  moles of component 1 and  $n'_2$  moles of component 2. Then let  $F''$  be the molar free energy of a solution composed of  $n''_1$  moles

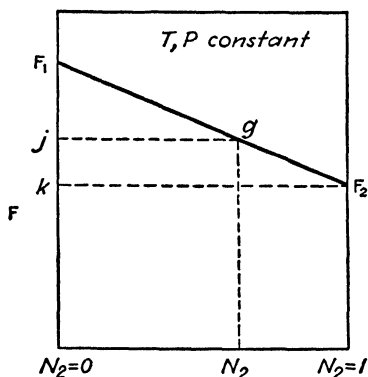


FIG. II.1 Molar free energy-mole fraction diagram for a mixture of two components.

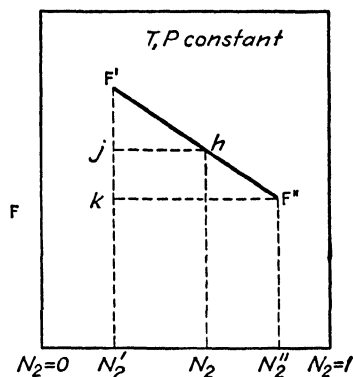


FIG. II.2 Molar free energy-mole fraction diagram for a mixture of two solutions.

of component 1 and  $n''_2$  moles of component 2. The free energy of a mixture of these two solutions,  $F$ , will be given by the relation

$$F = (n'_1 + n'_2)F' + (n''_1 + n''_2)F''$$

The molar free energy of the mixture will be given by the relation

$$\begin{aligned} F &= \frac{(n'_1 + n'_2)F' + (n''_1 + n''_2)F''}{n'_1 + n'_2 + n''_1 + n''_2} \\ &= \frac{(n'_1 + n'_2 + n''_1 + n''_2)F' - (n''_1 + n''_2)F' + (n''_1 + n''_2)F''}{n'_1 + n'_2 + n''_1 + n''_2} \\ &= F' - \frac{n''_1 + n''_2}{n'_1 + n'_2 + n''_1 + n''_2} (F' - F'') \end{aligned} \quad (14)$$

In Figure II.2 the ordinate of the point  $h$  (at the abscissa  $N_2$ ) on the straight line joining  $F'$  and  $F''$  can be shown, by the method used in the previous paragraph, to be equal to

$$F' - \frac{N_2 - N_2'}{N_2'' - N_2'} (F' - F'') \quad (15)$$

The coefficients of  $(F' - F'')$  in (14) and (15) can be shown to be identical by substituting  $N_2 = (n_2' + n_2'')/(n_1' + n_2' + n_1'' + n_2'')$ ,  $N_2' = n_2'/(n_1' + n_2')$ , and  $N_2'' = n_2''/(n_1'' + n_2'')$ . Thus the ordinate of  $h$  is seen to be the molar free energy of the mixture; in general, the molar free energy of a mixture of two phases of over-all composition  $N_2$  is the ordinate at  $N_2$  on the straight line joining the molar free energies of the two phases.

### II.3 The Free Energy-Composition Curve for a Solution at Constant Temperature and Pressure

Alcohol and water in any proportion will form a solution on being mixed (under ordinary conditions). The process of dissolution is spontaneous and hence the molar free energy of the

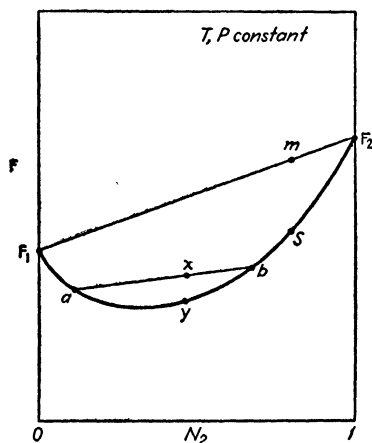


FIG. II.3 Molar free energy-mole fraction diagram for a system in which the two components are completely miscible.

solution will be less than the calculated molar free energy of a mechanical mixture of the alcohol and water. For example, if  $m$  in Figure II.3 is the calculated free energy of the mechanical

mixture, then the molar free energy of the solution will lie directly below  $m$ , say at the point  $s$ . It is evident that the molar free energy-mole fraction curve for any solution will lie below the straight line through  $F_1$  and  $F_2$ .

If any two solutions of alcohol and water having the compositions  $a$  and  $b$  are mixed, they will spontaneously form a solution of intermediate composition. The molar free energy of this solution, say  $y$ , must therefore be less than the calculated molar free energy,  $x$ , of the mechanical mixture of the solutions  $a$  and  $b$ . It is evident from this last consideration that all points on the curve between  $a$  and  $b$  must lie below the chord  $ab$ . The molar free energy-mole fraction curve for a solution must therefore have the property that any chord to the curve lies above that portion of the curve. This form of curve is known as a *festoon*.

## II.4 Partial Molal Free Energies

If  $F$  is the free energy of a solution containing  $n_1$  moles of component 1 and  $n_2$  moles of component 2, the partial molal free energy of component 1 in the solution is defined as  $\bar{F}_1 = (dF/dn_1)_{T,P,n_2}$  and the partial molal free energy of component 2 as  $\bar{F}_2 = (dF/dn_2)_{T,P,n_1}$ . More briefly, these equations may be written  $\bar{F}_1 = \partial F/\partial n_1 = \mu_1$  and  $\bar{F}_2 = \partial F/\partial n_2 = \mu_2$  [Steiner's equation (18.10)]. It can be shown that

$$(n_1 + n_2)\bar{F}_1 = N_2(\partial F/\partial N_1) + F \quad [\text{Steiner's equation (18.34)}]$$

and that

$$(n_1 + n_2)\bar{F}_2 = N_1(\partial F/\partial N_2) + F \quad [\text{Steiner's equation (18.35)}]$$

Hence

$$\bar{F}_1 = N_2 \frac{\partial F}{\partial N_1} + F = F - N_2 \frac{\partial F}{\partial N_2}$$

and

$$\bar{F}_2 = N_1 \frac{\partial F}{\partial N_2} + F$$

For the solution  $y$  of Figure II.4,  $\partial F/\partial N_2$  is the slope of the tangent to the molar free energy curve at that composition. Let the intercepts of this tangent with the ordinates at  $N_2 = 0$  and  $N_2 = 1$  be  $A$  and  $B$ , respectively. It can be seen that  $RA = Ry$

times the slope of the tangent, that is,  $RA = N_2(\partial F/\partial N_2)$ . Since the ordinate of  $R$  is equal to  $F$ , the molar free energy of the solution  $y$ , it follows that  $A = F - N_2(\partial F/\partial N_2) = \bar{F}_1 = \mu_1$ .

Similarly,  $BS = yS$  times the slope of the tangent, that is,  $BS = N_1(\partial F/\partial N_2)$ , and hence  $B = F + N_1(\partial F/\partial N_2) = \bar{F}_2 = \mu_2$ . The partial molal free energies of the components 1 and 2 in a solution are therefore given by the intercepts, at the ordinates  $N_1 = 1$  and  $N_2 = 1$ , of the tangent to the molar free energy-mole fraction curve at the composition of the solution. It should be clear from the definition of  $\mu_i$ , viz.,  $\mu_i = \partial F/\partial n_i$ , that for a pure substance  $i$ ,  $\mu_i = F_i$ .

## II.5 Free Energy Curves and Solubility

In Figure II.5 is shown a typical molar free energy curve,  $Dst$ , for a solution (a festoon). If  $s$  represents the composition and molar free energy of the solution saturated with respect to pure component 2, then the chemical potential of component 2 in the solution  $s$  must be identical with the chemical potential of component 2 in the pure substance 2, i.e.,  $\mu_2$  for this solution must be identical with  $\mu_2$  for the pure substance 2 ( $= F_2$ ). But  $\mu_2$  for the solution  $s$  is the intercept  $B$  of the tangent at  $s$  and therefore in this case  $B$  is coincident with  $F_2$ . The portion of the molar free energy curve to the right of  $s$  has been dotted to indicate that supersaturated solutions are metastable with respect to the formation of a mixture of component 2 and its saturated solution  $s$ . This metastability is shown graphically, in that the portion  $st$  of the molar free energy curve lies above the line  $sB$ , the molar free energy curve for mixtures of component 2 and its saturated solution.

In Figure II.6 is shown a molar free energy-composition curve of a type associated with aqueous systems in which the salt can

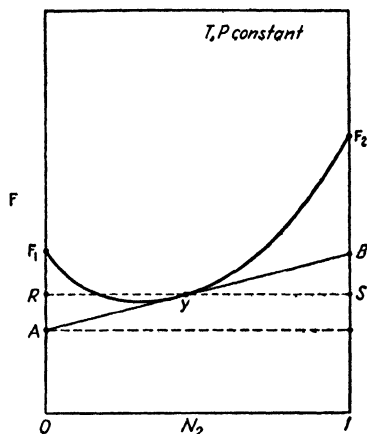


FIG. II.4 Graphical relation of the chemical potentials of the components in a solution to the molar free energy-mole fraction curve for the solution.

form a hydrate. Under the conditions of temperature and pressure chosen, the hydrate is the stable saturating phase (*cf.* the system sodium sulfate-water at 25°C and 1 atm). The point  $H$  represents the composition and molar free energy of the hydrate. The point  $s$  represents the molar free energy of the solution saturated with respect to the hydrate. The tangent to the molar free energy curve  $Dst'$  at the point  $s$  must pass through the point  $H$  in order to satisfy the condition that for saturation the chemical potential of the hydrate in the solution be identical with the chemical potential of the pure hydrate, *i.e.*, the molar free energy of the hydrate.

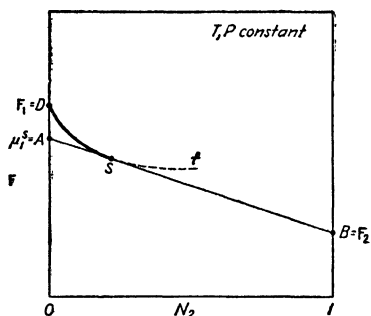


FIG. II.5 Free-energy relations for a solution saturated with respect to component 2.

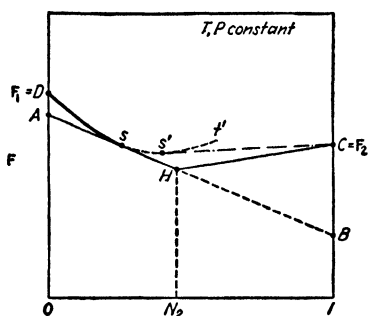


FIG. II.6 Free-energy relations for a solution saturated with respect to a binary compound.

The point  $B$  in Figure II.6 represents the chemical potential of anhydrous component 2 in the solution  $s$ ; it quite evidently does not have the same value as the chemical potential of the hydrate in the solution. The (metastable) solubility of the anhydrous salt at this temperature and pressure will be greater than that of the hydrate (*cf.* Section 3.12). The solution  $s$  will therefore be unsaturated with respect to the anhydrous salt; it follows that the dissolution of anhydrous salt in solution  $s$  would be a spontaneous process. The increase in the free energy of the solution on dissolution of the anhydrous salt must be less than the free energy of the anhydrous salt which dissolves; therefore the chemical potential of the anhydrous salt in solution  $s$  must be less than the molar

free energy of the anhydrous salt. The latter quantity is indicated by the point  $C$ , lying above the point  $B$ . Furthermore the point  $C$  must be the intercept (at  $N_2 = 1$ ) of the tangent to the molar free energy curve at the point  $s'$ , representing the composition and molar free energy of the metastable solution saturated with respect to the anhydrous salt. The fact that the curve  $Dst'$  is a festoon also shows that the point  $C$  must lie above the point  $B$ .

It is seen from Figure II.6 that in its most stable condition the system will consist of the phase or mixture of phases having the lowest molar free energy, *viz.*, an unsaturated solution, if the over-all composition lies between  $D$  and  $s$ ; a mixture of solution  $s$

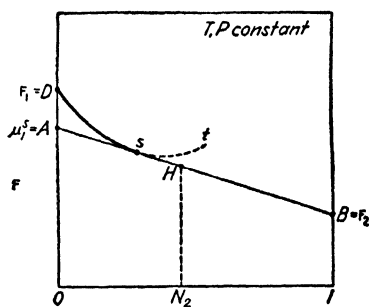


FIG. II.7 Free-energy relations for a solution simultaneously saturated with respect to a binary compound and component 2 (at the transition temperature of the binary compound).

and hydrate  $H$  if it lies between  $s$  and  $H$ ; the pure hydrate if the over-all composition is that of the hydrate; a mixture of the hydrate and the anhydrous salt if it lies between  $H$  and  $C$ . It can also be seen that a solution supersaturated with respect to pure component 2 (molar free energy on the curve  $s't'$ ) is less stable than a mixture of solution  $s'$  and component 2 (molar free energy curve  $s'C$ ).

In Figure II.7 is shown the form of the free energy-composition curve at the transition temperature of a hydrate, the temperature at which the hydrate and anhydrous salt have a common saturated solution (*cf.* the system sodium sulfate-water at 32.384°C and 1 atm). At the transition temperature the chemical potential of the hydrate in the saturated solution  $s$  must be identical with the molar free energy of the hydrate,  $H$ , and the chemical potential



the chemical potential of component 2 must be the same in the two phases ( $\mu_2' = \mu_2''$ ). The two molar free energy curves must therefore have a common tangent at the points  $s'$  and  $s''$ ;  $A = \mu_1' = \mu_1''$  and  $B = \mu_2' = \mu_2''$ . It is evident that a mixture of the two phases  $s'$  and  $s''$ , with molar free energy lying on the line  $s's''$ , will be more stable than a single solution of intermediate composition.

While only a few typical molar free energy-composition curves have been discussed, the principles set forth will serve as a guide in the treatment of other systems.



## INDEX

### A

Allotropes, 13, 91  
 Ammonia, homogeneous equilibrium  
     with nitrogen and hydrogen, 1*ff*  
 Astracanite, 101*ff*.  
 Azeotropes, 83*ff*.

### B

Binary compounds, congruently  
     melting, 62, 134  
     incongruently melting, 63, 136  
     with ternary but not binary field,  
         145  
 Binodal curve, 120  
 Boiling point, determination of, 36  
     maximum, 40  
     of pure substances, 21

### C

Chemical potential (*see* Free energy,  
     partial molal)  
 Components, choice of, 6, 153  
     definition of, 5, 6  
     number of, 6, 155, 176  
 Composition, anhydrous, 161, 170  
     elementary, 5  
     solute, 166, 169  
     in terms of equivalents, 173  
     in terms of phases, 5, 42  
 Congruent melting point, 40, 77, 134,  
     144  
 Conjugate phases, 38  
 Conjugate solutions, 68, 120, 122  
     free energy relations for, 194  
 Consolute temperature, 69  
 Constituents, 4  
     phase, 5, 41, 42  
     solution, 41

Cristobalite, 28  
 Critical solution temperature, 69  
 Critical temperature and pressure,  
     20  
 Crystallization, fractional, 73, 78

### D

Degrees of freedom, 7, 101, 185  
 Description of a system, 41  
 Dissociation pressure of hydrates,  
     51, 52, 54  
 Distillation, fractional, 79*ff*.  
     steam, 60  
 Division of diagram, binary, 63, 72  
     ternary, 134, 148, 150  
 Double decomposition, 154

### E

Enantiotropes, 27  
 Equilibrium, conditions affecting,  
     2, 7  
     definition of, 2  
     effect on, of composition, 3, 8  
         of pressure, 3, 7, 35  
         of temperature, 3, 7, 34  
     homogeneous, 1*ff*.  
 Eutectic composition, determina-  
     tion of, 48  
 Eutectic line, binary, in ternary  
     diagram, 130  
 Eutectic point, binary, 38, 57  
     in ternary diagram, 118, 130  
     ternary, 118, 130, 144  
 Eutectic temperature, determina-  
     tion of, 58  
 Evaporation, isothermal, 104, 165,  
     174, 177

## F

- Fractionating columns, 80  
 Free energy, changes in, for spontaneous processes, 187, 190  
   metastability and, 187, 192  
   of mixture, 187  
   partial molal, 183, 190  
   of solution, 189  
 Freezing points, effect of pressure on, 14  
   of pure substances, determination of, 14  
   of solutions, determination of, 35  
   of water, 13

## G

- Glauber's salt, 6*ff.*, 31*ff.*, 102*ff.*, 173

## H

- Heat of solution, 34  
 Hydrolysis, effect of, on number of components, 154

## I

- Ice, 13*ff.*  
 Incongruent melting point, 40  
 Incongruent transition point, 40, 146  
 Invariant point, quaternary, 160, 168, 173  
   ternary, 130, 144  
 Isomers, 12

## J

- Jänecke's representation of composition, 163, 165

## L

- Liquid crystals, 12, 93  
 Liquidus curve, 57, 73

## M

- Melting points, congruent, 40, 77, 134, 144  
   effect of pressure on, 14  
   incongruent, 40, 136, 150  
   mixed, 59  
   of pure substances, determination of, 14  
 Melting range, 15, 59  
 Metastability, 18, 24-30, 49, 52, 54, 111  
   free energy and, 192  
 Metathetical reactions, 154  
 Monotropes, 26

## P

- Phase constituents, 5, 41, 42  
 Phase rule, 10  
   thermodynamic derivation of, 183  
 Phases, definition of, 4  
 Plait point, 120, 126  
 Polymers, 12  
 Polymorphs, 12  
 Prism, square, 173  
   triangular, 129, 163  
 Projection, of pyramidal diagram, 171  
   of square prismatic diagram, 173  
   of tetrahedral diagram, 160, 167  
   of triangular prismatic diagram, 130, 165, 169  
 Proportioning rule, 41, 44, 97  
 Pyramid, representation of composition by, 171

## Q

- Quadrilateral, representation of composition by, 148, 170  
 Quadruple points, in system sodium sulfate-water, 54  
   in ternary systems, 108  
 Quartz, 28

## R

- Raoult's law, 86  
 Reciprocal salt pairs, 154, 155, 170, 173, 176  
 Reference curves, 121, 122  
 Resorption, 139, 142, 176

## S

- Salt pairs, reciprocal (*see* Reciprocal salt pairs)  
 Schlösing process, 176  
 Solid solutions, 70  
 Solidus curve, 57, 73  
 Solubility, determination of, 31  
   effect on, of pressure, 35  
   of temperature, 34  
   metastable, 53, 192  
   relation of free energy to, 191  
 Solute ratio, 111  
 Solway process, 176  
 Sublimation, 22
- Systems, one-component:  
   menthol, 27  
   phosphorus, 25, 54  
   silica, 28  
   sulfur, 23  
   tin, 28  
   water, 13*ff.*
- two-component:  
   åkermanite-velardeñite ( $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ), 77  
   albite-anorthite ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), 75  
   aniline-water, 124  
   anorthite-velardeñite ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ), 58, 60  
   benzene-ethanol, 83, 84  
   benzhydrol-benzene, 64  
   bismuth-cadmium, 57  
   calcium chloride-water, 52  
   chloroform-acetone, 83-85  
   chloroform-benzene, 78  
   copper-magnesium, 62

## Systems, two component:

- copper-silver, 91  
 copper sulfate-water, 154  
 decane-water, 61  
*p*-dibromobenzene - *p*-chlorobromobenzene, 75  
 ethanol-water, 84  
 1-ethylpiperidine-water, 69  
 isobutyl alcohol-water, 89  
 lead-thallium, 77  
 lithium chloride-potassium chloride, 58  
 magnesium-cadmium, 72  
 naphthalene-menthol, 58  
 nickel-cobalt, 71  
 phenol-water, 75  
 platinum-gold, 73  
 silver-tin, 93  
 sodium sulfate-silver sulfate, 73  
 sodium sulfate-water, 7, 31*ff.*  
 thallium nitrate-potassium nitrate, 91  
*m*-toluidine-glycerol, 70  
 zinc sulfate-water, 52

## three-component:

- ammonium sulfate-potassium sulfate-water, 122  
 copper sulfate-water, 154  
 diethyl ether-ethyl alcohol-water, 119  
 lime-alumina-silica ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ), 150  
 phenol-water-aniline, 124  
 sodium sulfate-magnesium sulfate-water, 101*ff.*  
 sodium sulfate-sodium chloride-sodium fluoride, 115, 133  
 sodium sulfate-sodium chloride- $\text{Na}_2\text{SO}_4 \cdot \text{NaF}$ , 115, 129, 131  
 velardeñite - anorthite -  $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3 \cdot (2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - 3\text{CaO} \cdot 5\text{Al}_2\text{O}_3)$ , 148

## four-component:

- sodium bicarbonate-ammonium chloride-water (sodium chloride-ammonium bicarbonate-water), 176

**Systems, four-component:**

sodium chloride-potassium sulfate-water (sodium sulfate-potassium chloride-water), 173

**T**

Temperature-time curves, 47

Ternary compounds, congruently melting, 144

Ternary eutectic, 118, 130, 144

Tetrahedron, representation of composition by, 158

Thermal analysis, 47

Tie lines, 38, 103, 130

Transition, allotropic, 12, 24, 91  
incongruent, 40, 146

Transition interval of astracanite, 108, 112

Transition point, 40  
ternary, 144

Transition temperature, effect on, of pressure, 24

Transition temperature, effect on, of solution composition, 108  
free energy relations at, 193

Triangle, representation of composition by, 97*ff.*

Tridymite, 28

Triple point, 23  
metastable, 25

**V**

Vapor pressure, effect of temperature on, 19

of metastable phase, 18  
of mixtures of immiscible liquids, 60, 89

partial, 86

of pure substances, determination of, 16

of saturated solutions, 49, 54

of supersaturated solutions, 49

Variance of system (*see* Degrees of freedom)











