

**SOLUTIONS AND
SOLUBILITIES
PART II**

MICHAEL R.J.DACK

**TECHNIQUES
OF CHEMISTRY
VOLUME VIII**

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TECHNIQUES OF CHEMISTRY

VOLUME VIII

SOLUTIONS AND SOLUBILITIES

Edited by

MICHAEL R. J. DACK

Research School of Chemistry
The Australian National University
Canberra, Australia

PART II



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ARNOLD WEISSBERGER, *Editor*

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ARNOLD WEISSBERGER, *Editor*

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SOLUTIONS AND SOLUBILITIES, in Two Parts

Edited by Michael R. J. Dack

AUTHORS OF PART II

E. B. BAGLEY

Northern Regional Research Laboratory, Agricultural Research Service, U. S. Department of Agriculture, Peoria, Illinois

ALLAN F. M. BARTON

Department of Chemistry, Victoria University of Wellington, Wellington, New Zealand

HENRY A. BENT

Department of Chemistry, North Carolina State University, Raleigh, North Carolina

MICHAEL R. J. DACK

Research School of Chemistry, The Australian National University, Canberra, Australia

CHARLES A. ECKERT

Department of Chemical Engineering, School of Chemical Sciences, University of Illinois, Urbana, Illinois

FORREST W. GETZEN

Department of Chemistry, North Carolina State University, Raleigh, North Carolina

GABRIELLO ILLUMINATI

Centro di Studio sui Meccanismi di Reazione, Department of Organic Chemistry, The University of Rome, Rome, Italy

DIGBY D. MACDONALD

*Department of Chemistry, Victoria University of Wellington,
Wellington, New Zealand*

J. M. SCIGLIANO

Monsanto Company, St. Louis, Missouri

RALPH ZINGARO

*Department of Chemistry, Texas A & M University, College Station,
Texas*

INTRODUCTION TO THE SERIES

Techniques of Chemistry is the successor to the Technique of Organic Chemistry Series and its companion—Technique of Inorganic Chemistry. Because many of the methods are employed in all branches of chemical science, the division into techniques for organic and inorganic chemistry has become increasingly artificial. Accordingly, the new series reflects the wider application of techniques, and the component volumes for the most part provide complete treatments of the methods covered. Volumes in which limited areas of application are discussed can easily be recognized by their titles.

Like its predecessors, the series is devoted to a comprehensive presentation of the respective techniques. The authors give the theoretical background for an understanding of the various methods and operations and describe the techniques and tools, their modifications, their merits and limitations, and their handling. It is hoped that the series will contribute to a better understanding and a more rational and effective application of the respective techniques.

Authors and editors hope that readers will find the volumes in this series useful and will communicate to them any criticisms and suggestions for improvements.

ARNOLD WEISSBERGER

*Research Laboratories
Eastman Kodak Company
Rochester, New York*

PREFACE

Most chemical processes of industrial and biological importance occur in solution. The role of solvent is so great that million-fold rate changes take place in some reactions simply by changing the reaction medium. Our bodies contain some 65 to 70% water which acts as a lubricant, as an aid to digestion, and more specifically, as a stabilizing factor to the double helix conformation of DNA. But what do we know about the detailed structure of water and the other solvents? What happens at a microscopic and macroscopic level when species are dissolved in these solvents? How can we investigate such phenomena?

It would be presumptuous to suppose that *Solutions and Solubilities* answers all these questions. The title itself is so all-embracing that a book many times its size could only discuss the many facets of the subject in a superficial manner. Specialized topics such as electrochemistry, photochemistry in solution, the electron in solution, and molten salts were all considered for inclusion in the volume. The fact that they, and other topics, have been omitted does not downgrade their importance to solution chemistry. In the selection of topics, we have attempted to cut across traditional divisions in chemistry, and provide the basis for integrated lecture courses at graduate level. Each chapter contains a wealth of background material on its subject and, justifying the volume's place in the *Techniques of Chemistry* series, describes the most recent experimental procedures. We have been especially fortunate with our contributing authors, so many of whom are recognized leaders in their field of study. To them, a debt of gratitude is owed for the care and enthusiasm with which they entered this project.

The advice and encouragement of Professors R. P. Bell, K. J. Laidler, and R. W. Taft during the planning stage of the volume are gratefully acknowledged. It is also a pleasure to acknowledge the innumerable suggestions made by colleagues over the years which have undoubtedly helped to remedy some of my own inadequacies and gaps of knowledge. Production of *Solutions and Solubilities* is testimony to the help freely given by Dr. Arnold Weissberger, and to the patience and skill of staff at John Wiley & Sons.

MICHAEL R. J. DACK

Canberra, Australia
August 1974



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INTRODUCTION TO THEORIES OF SOLUTIONS AND APPLICATIONS TO PHASE EQUILIBRIA

Charles A. Eckert

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1 INTRODUCTION

The purpose of this chapter is to demonstrate some of the practical, experimental, and calculational methods used in treating liquid solutions. It is aimed at workers in the field of the chemical sciences who make or interpret experimental measurements concerning the behavior of liquid solutions or make estimates of the behavior of liquid solutions. This work will not go

deeply into the most theoretical aspects of the structure of liquids, nor will it attempt to describe all possible experimental techniques. Rather, the emphasis will be on the mathematical description of nonionic solutions, and the applications to phase equilibria.*

Ultimately, the goal of workers in the field of solution thermodynamics is to predict as many thermodynamic properties as possible for mixtures from the very minimum number of readily accessible experimental data—if possible, from pure-component data only. The power of solution thermodynamics is that it provides a framework within which to apply models of the liquid state in an attempt to make predictions of properties. Moreover, it provides relationships with which a very maximum of information can be extracted from a relatively small number of experimental data.

Modern treatments of solution thermodynamics invariably involve what is called molecular thermodynamics. Molecular thermodynamics constitutes a means for going beyond the limitations of classical thermodynamics in solving chemical problems, in particular many of the problems of phase equilibria. In spite of the many accomplishments of classical thermodynamics, it can be applied usefully only to the relationships between properties. It offers no source other than experiment for the initial properties needed in a given procedure. On the other hand, molecular thermodynamics surpasses the classical treatment by relating macroscopic thermodynamic properties to fundamental molecular properties based on the results of chemical physics. By using a microscopic approach, it is frequently possible to start with independently known physicochemical properties and from these to estimate P - V - T properties, enthalpies, entropies, free energies, and especially fugacities. The purpose of establishing such relationships is to facilitate meaningful correlations for calculating from a minimum of experimental determinations such phase-equilibrium data as are needed either for the design of chemical processes or for laboratory applications.

The starting point for all understanding of fluid-phase behavior does come from classical thermodynamics, and this is the condition of equilibrium, that the chemical potential μ for any component i is equal in all phases in equilibrium. That is,

$$\mu_i' = \mu_i'' = \mu_i''' \quad (9.1)$$

where ' , '' , ''' represent phases in equilibrium. Chemical engineers have frequently found it more convenient to work with the fugacity rather than the chemical potential. The fugacity f is expressed as

*This chapter is a logical extension of Ben-Naim's discussion of ideal solutions (Chapter II).

$$f_i = f_i^0 \exp\left(\frac{\mu_i - \mu_i^0}{RT}\right), \quad (9.2)$$

where f_i^0 is the arbitrary reference-state fugacity corresponding to the reference-state chemical potential μ_i^0 . Most often this normalization is achieved by assuming that the system approaches ideal-gas behavior in the limit of zero pressure:

$$\lim_{P \rightarrow 0} \frac{f_i}{p_i} = 1, \quad (9.3)$$

where p_i is the partial pressure of i . The fugacity has the enormous advantage of going to the limit of the pressure at very low pressures, whereas the chemical potential blows up in the limit of zero pressure for a gas. We may then rewrite (9.1) as the condition of equilibrium,

$$f_i' = f_i'' = f_i''' \quad (9.4)$$

and the whole problem of phase equilibrium revolves around the evaluation of the fugacities in each of the phases, and how they can be related to measurable variables such as the temperature T , the pressure P , and the composition of each component, generally expressed as a mole fraction (x for liquids, y for vapors). We intend to establish from both classical and molecular thermodynamics the functionality of the fugacity's dependence on the measurable variables. We describe both empirical and theoretical models of the liquid and their application to phase-equilibrium problems.

2 MATHEMATICAL DESCRIPTION OF SOLUTION BEHAVIOR

A specific mathematical framework is required, within which to characterize solution properties, for quantitative predictions and correlations. As mentioned above, this framework is provided most conveniently by representation not in terms of the chemical potentials, but rather in terms of the fugacities of individual components in solution. The resulting formulation is first expressed as an ideal case, and then deviations from that ideal case are correlated in terms of a derived variable, the activity coefficient. The basic equation for all solution behavior, the Gibbs-Duhem expression, may be shown to relate activity coefficients and fugacities as well as chemical potentials, and as a result all correlations of solution behavior are expressed most conveniently as specific solutions of this differential equation. The form for these solutions, as well as a convenient form for modeling the behavior of liquid mixtures, is provided by

the excess thermodynamic functions. The derivation of these, along with a number of useful specific examples, is discussed below.

Ideal and Real Solutions

The ideal solution is defined for the liquid state as Raoult's (or Henry's) law. At modest pressures, this is expressed as

$$f_i = x f_i^0 \quad (9.5)$$

where f_i = fugacity of component i in the solution.

x_i = mole fraction of component i in the solution

f_i^0 = reference-state fugacity.

The choice of the reference state is quite arbitrary; it must be chosen as some specific temperature, pressure, and composition. Utility dictates that the temperature chosen must always be the system temperature. As long as pressures are low (atmospheric or below), the pressure has a negligible effect (the rigorous effect of pressure and the Poynting correction for higher pressures are discussed below). For most normal liquid mixtures of nonelectrolytes, the reference state is chosen as the pure liquid at the system temperature and its own vapor pressure. Let us now assume that the gas phase is ideal (at low pressures), so that the reference fugacity f_i^0 is in effect the saturation pressure P_i^s . Then for a mixture following Raoult's law, the partial pressure (or fugacity) of any species is given by

$$p_i = x_i P_i^s, \quad (9.6)$$

or the vapor composition expressed as a mole fraction y_i is

$$y_i = \frac{x_i P_i^s}{P}. \quad (9.7)$$

The behavior of a binary system obeying Raoult's law is shown schematically in Fig. 9.1.

Unlike the gas phase, very few liquid solutions ever behave ideally, and only a few special cases, such as mixtures of optical isomers, even approach it closely. Deviations from the ideal case are given in terms of an activity coefficient γ , defined as

$$\gamma_i \equiv \frac{f_i}{x_i f_i^0}, \quad (9.8)$$

where γ is generally a function of P , T , and composition. The proper

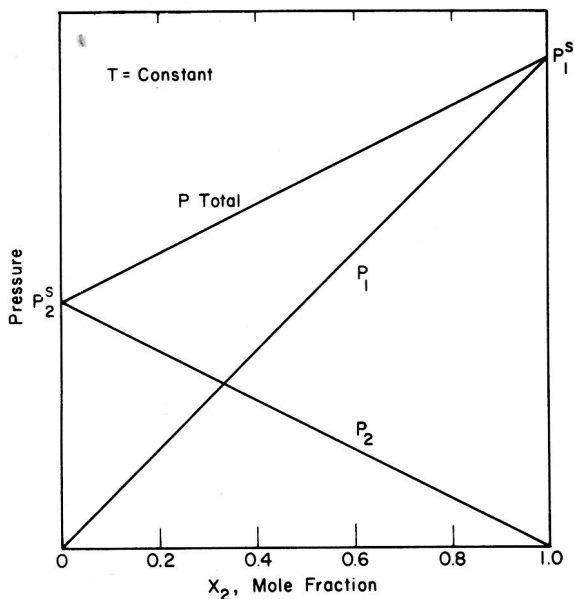


Fig. 9.1. Partial pressures and total pressure in a binary mixture obeying Raoult's law.

establishment of this functionality enables fugacities in liquid mixtures to be calculated. Partial pressures and vapor compositions are then given (still assuming low pressures) as

$$p_i = y_i P = x_i \gamma_i P_i^s \quad (9.9)$$

With the usual definition given above for the reference state, it can be seen that the activity coefficients approach unity for the pure species, and for a Raoult's-law solution they are always unity.

When the observed activity coefficients are greater than unity, the solution is said to exhibit positive deviations from Raoult's law. This is the usual case, and all solutions where dispersion or van der Waals forces dominate exhibit positive deviations from Raoult's law. An example of such a system with modest deviations is shown in Figs. 9.2 and 9.3. Strong positive deviations are also typical of solutions that are termed *associated*. An associated solution is one in which one (or more) of the components undergoes exceptionally strong self-interactions, but which exhibits only normal intermolecular potentials with the other components. Outstanding examples of such behavior are solutions of alcohols in hydrocarbons, where the alcohols hydrogen-bond strongly with themselves, but not with hydrocarbons. As a result, dilution of the alcohol by

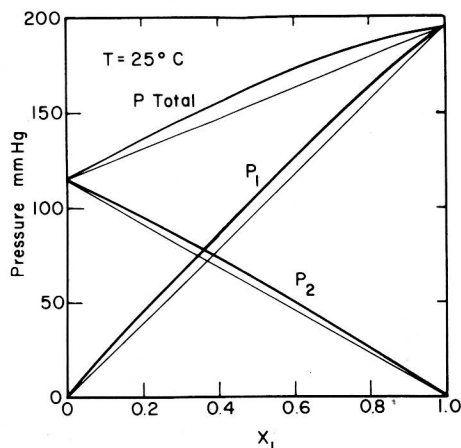


Fig. 9.2. Partial pressures and total pressure for a system showing moderate positive deviations from Raoult's law: chloroform-carbon tetrachloride.

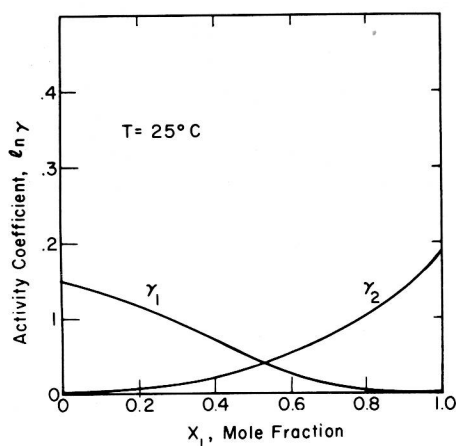


Fig. 9.3. Activity coefficients in the chloroform-carbon tetrachloride system.

the hydrocarbon causes disruption of the hydrogen bonding, and this increases the volatility, or fugacity, of the alcohol to well above the ideal case.

On the other hand, negative deviations from Raoult's law are defined by activity coefficients of less than unity; an example of modest negative deviations is given by the chloroform-benzene system shown in Figs. 9.4 and 9.5. Frequently, but not always, strong negative deviations from Raoult's law are attributable to the phenomenon known as *solvation*. Solvated solutions occur when the unlike-pair intermolecular forces are markedly stronger than the