Liquids, Solutions, and Interfaces: From Classical Macroscopic Descriptions to Modern Microscopic Details

W. RONALD FAWCETT

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University of California, Davis

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Cover illustration: A Li^+ cation solvated by four tetrahedrally disposed acetonitrile molecules. The Li^+ cation is the principal component of the non-aqueous electrolyte solution used in rechargeable lithium ion batteries found in laptop computers and cell phones. Acetonitrile is often used as one of the solvents in these batteries.

9 8 7 6 5 4 3 2 1

Printed in the United States of America
on acid-free paper

To my three muses,
Zuzana, Natalka, and Tetiana

Time is a never ending Fugue
An Interplay of Slow and Fast
Of Silence . . .
And of Light and Dark
That Flickers with Hypnotic Rhythm

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Preface

This book developed from a series of lectures given to freshmen graduate students specializing in analytical and physical chemistry and chemical engineering at the University of California, Davis. The purpose of these lectures is to introduce the students to modern topics in solution chemistry. Solutions are involved in every practical chemistry laboratory, in chemical analysis, in biochemistry, in clinical chemistry, and in chemical synthesis. When I was a student, solution chemistry occupied a major fraction of physical chemistry textbooks. At that time it dealt mainly with classical thermodynamics, phase equilibria, and non-equilibrium phenomena, especially those related to electrochemistry. Much has happened in the intervening period with the development of important new experimental techniques. At the present time, solutions are examined experimentally *at the molecular level*. In X-ray and nuclear diffraction experiments, the structure of liquids and solutions is described in atomic detail to give the time average of the distribution and orientation of the component molecules and ions. Laser spectroscopy provides a route to the time resolution of molecular events occurring in the femtosecond time range. Non-linear spectroscopic techniques are being used to study the molecular composition and structure of interfaces. Both theory and experiment have seen tremendous advances since the 1950s. The purpose of this book is to bring the student through these developments from the classical macroscopic descriptions to the modern microscopic details.

The subject matter in this monograph falls into three general areas. The first of these involves liquids and solutions at equilibrium. These subjects are discussed in chapters 1–5, and include the thermodynamics of solutions, the structure of liquids, electrolyte solutions, polar solvents, and the spectroscopy of solvation.

An attempt is made to familiarize the student with the fundamental background material together with important aspects of current research in each of these areas. Chapters 6 and 7 deal with non-equilibrium properties of solutions, and the kinetics of reactions in solutions. In the latter chapter, emphasis is placed on fast reactions in solution and femtochemistry. Chapters 8–10 involve important aspects of solutions at interfaces. These include liquids and solutions at interfaces, electrochemical equilibria, and the electrical double layer. This subject matter is of interest to analytical chemists, physical chemists, biochemists, and chemical and environmental engineers.

The material in this book should be suitable for senior undergraduates and graduate students who have completed two semesters or three quarters of chemical thermodynamics and statistical mechanics. A solid background in mathematics and physics is also necessary to understand the subject matter. The instructor will note that detailed derivations of the thermodynamic equations have been given. In the case of quantum mechanics and statistical mechanics, some derivations are not given but instead, the background for the theory is carefully described. In addition, the student is referred to the original literature. The material is arranged in such a way that it may be presented at different levels. Thus, if one wishes to present only the fundamentals of describing the structure of liquids from chapter 2, the material dealing with the statistical mechanical description of liquid systems can be largely avoided. The same comment applies to most of the material in this monograph. Introductions to thermodynamics, statistical thermodynamics, and chemical kinetics are included in chapters 1, 2, and 7, respectively. This material is given to help students review the subject matter from earlier courses in physical chemistry and to introduce the symbols used in this book. General references giving other sources for the material covered in a given chapter, and to compilations of experimental data are listed at the end of each chapter.

As far as possible only SI units have been used in writing equations and presenting experimental data. Angstroms and calories, which still appear in the scientific literature, are avoided. Instead, nanometers and picometers are used for atomic and molecular dimensions, and joules for units of energy. Pressure is discussed in terms of pascals and bars rather than torrs and atmospheres. Equations involving the molecular dipolar properties, namely the dipole moment and polarizability, assume units of coulomb meters and farad square meters, respectively, for these quantities. However, tabulated data are given in the more familiar cgs system with debyes for the dipole moment and cubic nanometers for the polarizability. This follows the usage in most data tabulations at the present time. The connection between the SI and cgs units is explained in chapter 2. The symbols recommended by the International Union of Pure and Applied Chemistry [1] are used as much as possible.

This preface would not be complete without an expression of gratitude to those who made this project possible. First, I am grateful to those who introduced me to the topics discussed in this book during my student years at the University of Toronto. There are many teachers in this group but special mention goes to Professors Frank Wetmore and Mike Dignam in the Department of Chemistry.

Second, I would like to thank my students, especially those at UC Davis who listened to and discussed the lectures on which this book is based. Third, I thank my typists Elizabeth Bogren and Zuzana Kováčová, who patiently and faithfully prepared the manuscript including all the complicated equations. Special thanks are also due to Alex Tikanen and Dmytro Verbovy for their work with the diagrams. Finally, I would like to thank those who reviewed individual chapters including Rafael Andreu, Imre Bako, Bob de Levie, Dennis Evans, Manuel Galan, Douglas Henderson, Andrzej Lasia, Shiraz Markarian, Roger Parsons, Oleg Petrii, Dino Tinti, Nancy True, and Galina Tsirlina. I am especially indebted to Oldřich and Eva Fischer, who have gone through the text with painstaking care and helped to eliminate numerous small errors and to establish a consistent system of symbols. The helpful comments of all those involved in the review process resulted in a significant improvement in this monograph during the long gestation period.

Reference

1. Mills, I.; Cvitaš, T.; Homann, K.; Kallay, N.; Kuchitsu, K. *Quantities, Units, and Symbols in Physical Chemistry*; Blackwell Scientific Publications: Oxford, U.K., 1986.

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Contents

Fundamental Constants

Fundamental Constants		
Velocity of light	c	2.997925×10^{8} m s^{-1}
Fundamental charge	e_0	1.602177×10^{-19} C
Electron rest mass	m_e	9.109390×10^{-31} kg
Proton rest mass	m_p	1.672623×10^{-27} kg
Neutron rest mass	m_n	1.67493×10^{-27} kg
Avogadro constant	N_L	6.022137×10^{23} mol^{-1}
Planck constant	h	6.626076×10^{-34} Js
Boltzmann's constant	k_B	1.380658×10^{-23} J K^{-1}
Gas constant	R	8.314510 J mol^{-1} K^{-1}
Faraday constant	F	96485.3 C mol^{-1}
Permittivity of vacuum	ε_0	8.854188×10^{-12} C^2 N^{-1} m^{-2}
Defined Constants		
Temperature of H_2O freezing	T	273.15 K
Standard acceleration of free fall	g	9.80665 m s^{-2}
Conversion Factors		
Standard atmosphere	atm	101,325 Pa
Thermochemical calorie	cal	4.184 J
Angstrom	Å	100 pm
1 erg		10^{-7} J
1 litre atm		101.325 J
1 eV		1.6022×10^{-19} J
1 C		2.9979×10^{9} esu
1 V		3.3356×10^{-3} esu
1 F		8.9875×10^{11} esu
1 Debye		3.3356×10^{-30} C m
1 Gauss		10^{-4} Tesla

From Cohen and Taylor, *Rev. Mod. Phys.*, 59 (1987) 1121

Liquids, Solutions, and Interfaces

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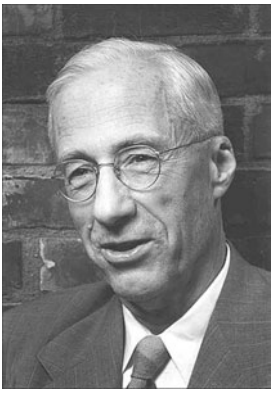
1

The Thermodynamics of Liquid Solutions



Joel Henry Hildebrand

Joel Hildebrand was born in Camden, New Jersey, in 1881. His interest in science developed in high school and he went on to study physics and chemistry at the University of Pennsylvania, obtaining a B.S. degree in 1903. He stayed at Pennsylvania for a doctoral degree in chemistry, which he obtained in 1906. Like several young American scientists of that period, he went to Germany to study the emerging field of physical chemistry. Hildebrand spent a year at the University of Berlin in the laboratory of Walther Nernst and attended lectures given by Nernst and van't Hoff. He then returned to the University of Pennsylvania, where he held the position of instructor in chemistry until 1913. Then, at the invitation of G. N. Lewis, he joined the faculty of the University of California at Berkeley, where he remained for the rest of his scientific career. Hildebrand's main scientific research was in the area of the physical chemistry of liquids and non-electrolyte solutions. He was a major contributor to the theory of regular solutions. Much of his work in this field is summarized in his monograph with Robert Scott, *The Solubility of Non-electrolytes* [1]. He was famous at Berkeley for his lectures, especially to freshman classes. His scientific work was recognized by many awards during his long career, including the Priestley Medal of the American Chemical Society in 1962. Hildebrand was also an avid sportsman and was particularly fond of skiing in the Sierra Nevada mountains. One of his last papers was published in the *Annual Review of Physical Chemistry* in 1981 at the age of 100. He died in 1983.

1.1 Most Liquid Solutions Are Not Ideal

Chemistry in the laboratory very often involves the use of liquid solutions. This is especially true in chemical analysis, where the amount of analyte is easily manipulated when it is dissolved in a solution. Solutions are often the medium for chemical reactions which form the basis of titrations. Other simple analytical procedures are based on absorption spectroscopy, which is used to determine the concentrations of an analyte in solution.

Most liquid solutions, also called liquid mixtures, are non-ideal. This follows from the fact that the components are in intimate contact with one another, and that the forces between the various species are usually not the same. As a result, the physical properties of the solution, for example, the vapor pressure of a given component, are usually not simply related to its concentration. This non-ideality leads to the concept of the activity of a solution component. As far as the analytical chemist is concerned, only concentration is ultimately of interest. Thus, if an analysis is based on the measurement of a physical property which in turn depends on the activity of a component, it is very important that the relationship between activity and concentration be understood for the system in question.

Activity and its relationship to concentration is defined within the context of chemical thermodynamics. Using the laws which govern phase equilibria and the laboratory observations relating to these processes one can develop a detailed understanding of this relationship. In this chapter the macroscopic concepts of chemical thermodynamics which are relevant to solutions are reviewed. In addition, some simple models based on molecular concepts are discussed. The examples chosen are mainly limited to non-electrolyte solutions, especially those involving polar molecules.

1.2 Concentration Units

Concentration of one component in a two-component system can be expressed in several ways: as a weight/weight ratio, as a volume/volume ratio, or as a weight/volume ratio. Physical chemists clearly prefer to express concentration as a weight/weight ratio because then one has the possibility of estimating the number of moles of both components in the solution. In this case, solution composition is independent of temperature and pressure. On the other hand, the analytical chemist prefers to use a weight/volume ratio. This is usually because one component, namely, the analyte, is present at low concentration. Then, one refers to this component as the solute, and the majority component as the solvent. However, in this case the concentration changes when temperature or pressure is changed.

Consider the simple example of a solution of acetonitrile in water formed by mixing 10 g of acetonitrile with 90 g of water. The concentration of acetonitrile can be simply stated as 10% by weight. Another way of expressing the concentration is in terms of the relative number of moles of these molecules. Given that the molecular mass of acetonitrile is 41.04 g, the number of moles of acetonitrile n_B used to form the solution is $10.000/41.04 = 0.2437$. The corresponding number of moles of water n_A is $90.000/18.02 = 4.9945$ where 18.02 is its molecular mass. Thus, one may express the concentration as the mole fraction, x_B, of acetonitrile where

$$x_B = \frac{n_B}{n_A + n_B} = \frac{0.2437}{4.9945 + 0.2437} = 0.0465 \tag{1.2.1}$$

Another commonly used concentration unit in physical chemistry is molality. It is defined as the number of moles of component B per 1000 g of pure component A, which is regarded here as the solvent. In the present case, the molality is

$0.2437 \times 1000/90 = 2.708\,m$. This is still a weight/weight ratio but has units of mol kg^{-1}. The relationship between mole fraction and molality can be written

$$x_B = \frac{m_B}{(1000/M_A) + m_B} \tag{1.2.2}$$

where M_A is the molecular weight of the solvent, that is, component A. In dilute solutions for which $m_B \ll 1000/M_A$ this relationship becomes

$$x_B \cong \frac{m_B M_A}{1000} \qquad \text{(dilute solutions)} \tag{1.2.3}$$

For example, a $0.02\,m$ solution of acetonitrile in water corresponds to a mole fraction x_B equal to 3.6×10^{-4}.

The concentration unit used for analysis is molarity, that is, the number of moles of solute per liter of solution. It should be noted that the molarity involves a weight/volume ratio, and that the volume involved is that of the *total solution*. In order to determine the molarity of the system being considered here, one must know the density of the solution. In general, this property cannot be determined from the densities of the individual components but must be found in an independent experiment. The density of acetonitrile–water solutions as a function of the weight fraction of acetonitrile is shown in fig. 1.1. From these data one finds that the density of the solution made of 10 g acetonitrile and 90 g water is 0.979 g mL^{-1} at 25°C. Thus, the volume of the same solution is 102.15 mL and the corresponding molarity, $0.2437/0.10215 = 2.386$ M. The relationship between the molarity c_B and mole fraction x_B is

$$x_B = \frac{c_B}{(1000\,\rho - c_B M_B)/M_A + c_B} \tag{1.2.4}$$

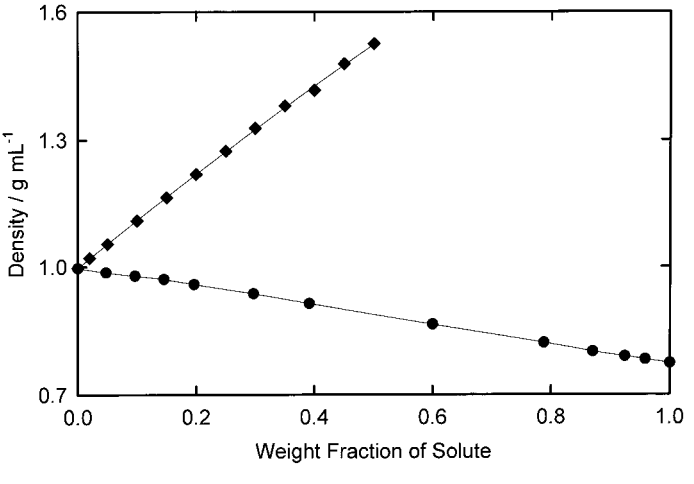


Fig. 1.1 Plots of the density of aqueous solutions of acetonitrile (AcN,●) and sodium hydroxide (◆) against their weight fraction in the solution.

Table 1.1 Concentration of Acetonitrile in Aqueous Solutions Using Different Expressions for the Relative Amounts of Acetonitrile and Water at 25°C

Weight Percent	Mole Fraction/x_B	Molality, m_B/mol kg^{-1}	Molarity, c_B/mol L^{-1}	Solution Density, ρ/g L^{-1}
0.01	4.39×10^{-5}	2.44×10^{-3}	2.44×10^{-3}	0.997
0.1	4.39×10^{-4}	2.44×10^{-2}	2.44×10^{-2}	0.997
1	4.42×10^{-3}	0.246	0.245	0.995
10	0.0465	2.708	2.386	0.979

where ρ is the density of the solution in g mL^{-1}. When the solution is dilute, one may neglect the terms in the denominator involving c_B so that the expression for x_B becomes

$$x_B \cong \frac{c_B M_A}{1000\,\rho_A} \qquad \text{(dilute solutions)} \tag{1.2.5}$$

where ρ_A is the density of the pure solvent A. On comparing equations (1.2.3) and (1.2.5), one sees that for aqueous solutions where $\rho_A \cong 1.0$, the molarity is equal to the molality when the solution is dilute. These calculations are illustrated in table 1.1 for a change in acetonitrile concentration by a factor of 1000 in the range of dilute solutions. It is clear that molality and molarity are equal for dilute aqueous solutions. However, if water is not the solvent, the density of the solution is probably sufficiently different from unity that these quantities are no longer equal. Notice also that the definition of molarity is temperature dependent because the volume of the system depends on temperature. Thus, the analyst should always cite the temperature at which solutions were prepared.

A plot of the density of sodium hydroxide solutions of varying composition is also shown in fig. 1.1. Electrolyte solutions are considerably more dense than water when they are concentrated. The important point to remember about these systems is that their compositions cannot be varied over the whole range because the solute is normally a solid at room temperature. Thus, the range of the weight fraction scale is determined by the solubility of the solid solute. In order to convert from molality to molarity, the solution density must be determined. Density data for common solutions can be found in data compilations such as the Landolt–Börnstein tables.

1.3 Thermodynamic Quantities

The composition of a solution is obviously one of its important properties. In the preceding section various ways of describing the composition of a two-component system were described. Other properties include its volume, V, internal energy, U, and entropy, S. In order to specify any one of these, one must specify not only the amounts of each of the components but also the temperature, T, and pressure, P. These quantities are known as the independent variables of the system. They are

to some extent arbitrary, but nevertheless convenient. If the system possesses more than two components, the number of variables required to be specified to determine any quantity such as V is $N + 2$, where N is the number of components.

Consider first of all the volume of the solution. The volume of any solution may be estimated from the mass of each component and its density. Volume is an *extensive* property, since its value depends on the total amount of solution. A quantity of more fundamental interest is the specific volume, V_s, that is, the volume per gram. It is simply the reciprocal of the density. This is an *intensive* quantity, since its value does not depend on the size of the solution, only on its composition, temperature, and pressure. From the point of view of chemists, an even better way to describe this property is in terms of the molar volume, that is, the volume per mole of solution. For a two-component solution, the molar volume V_m is related to the density as follows:

$$V_m = \frac{M_A x_A + M_B x_B}{\rho} \tag{1.3.1}$$

Notice that the units of this quantity are L mol^{-1} if the density is expressed in g L^{-1}. To calculate the volume from the molar volume one must know the number of moles of each component, n_A and n_B. Thus,

$$V = (n_A + n_B)V_m \tag{1.3.2}$$

where the relative amounts of n_A and n_B are those required to give the mole fractions x_A and x_B.

It was pointed out above that the volume is a function of the number of moles of each component, temperature, and pressure. Thus, one may write for a two-component system

$$V = V(n_A, n_B, T, P) \tag{1.3.3}$$

It follows that the total derivative of the volume dV is given by

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{n_B,T,P} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{n_A,T,P} dn_B + \left(\frac{\partial V}{\partial T}\right)_{n_A,n_B,P} dT + \left(\frac{\partial V}{\partial P}\right)_{n_A,n_B,T} dP \tag{1.3.4}$$

where each partial derivative specifies the change in the volume with a given independent variable, holding the other independent variables constant. It is very important that this specification be made; otherwise one does not know exactly what change is being measured.

The internal energy of the system, U, is defined on the basis of the first law of thermodynamics, which, in simple terms, states that energy cannot be created or destroyed. For a closed system, the gain in internal energy during a process involving a change in the values of its independent variables is equal to the heat gained by the system, q, plus the work done on the system, w. Mathematically, this is expressed as

$$\Delta U = q + w \tag{1.3.5}$$

If the changes in q and w are infinitesimally small, this relationship may be written

$$dU = dq + dw \tag{1.3.6}$$

Furthermore, if the work is limited to pressure–volume changes, then

$$\mathrm{d}U = \mathrm{d}q - P\mathrm{d}V \tag{1.3.7}$$

The relationship $\mathrm{d}w = -P\mathrm{d}V$ reflects the fact that when mechanical work is done on the system, its volume decreases. Otherwise stated, if the volume of the system increases during a change in state, the system must do work against the surrounding pressure, which leads to a net loss in its internal energy.

The second law of thermodynamics states that all spontaneous processes lead to an increase in disorder, which is quantitatively measured by means of the system's entropy, S. For an infinitesimally small process involving a flow of heat into the system, $\mathrm{d}q$, the entropy change, $\mathrm{d}S$, is given by

$$\mathrm{d}S = \frac{\mathrm{d}q}{T} \tag{1.3.8}$$

Combining equations (1.3.7) and (1.3.8), one obtains an important result summarizing the first and second laws in differential form:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \tag{1.3.9}$$

One must remember that this expression applies to a closed system, that is, one in which no matter enters or leaves ($\mathrm{d}n_i = 0$). If one relaxes this condition for a two-component system, then the general expression for the change in internal energy becomes

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \left(\frac{\partial U}{\partial n_\mathrm{A}}\right)_{n_\mathrm{B},S,V} \mathrm{d}n_\mathrm{A} + \left(\frac{\partial U}{\partial n_\mathrm{B}}\right)_{n_\mathrm{A},S,V} dn_\mathrm{B} \tag{1.3.10}$$

where the last two derivatives describe the change in internal energy with the number of moles of each component. Since equation (1.3.10) gives the total differential of U, one arrives at the following definitions of temperature and pressure:

$$T = \left(\frac{\partial U}{\partial S}\right)_{n_\mathrm{A},n_\mathrm{B},V} \tag{1.3.11}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{n_\mathrm{A},n_\mathrm{B},S} \tag{1.3.12}$$

Furthermore, equation (1.3.10) suggests that the internal energy is best described as a function of entropy, volume, and the number of moles of each component, that is

$$U = U(S, V, n_\mathrm{A}, n_\mathrm{B}) \tag{1.3.13}$$

As a result, chemists have introduced other thermodynamic functions so that the properties of a system may be considered with respect to more convenient independent variables, especially temperature and pressure.

The three remaining thermodynamic variables and their definitions are as follows: the enthalpy,

$$H = U + PV \tag{1.3.14}$$

the Helmholtz energy,

$$A = U - TS \tag{1.3.15}$$

and the Gibbs energy,

$$G = U - TS + PV \tag{1.3.16}$$

The differential form of the enthalpy for a closed system may be found by writing the total derivative:

$$\mathrm{d}H = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P \tag{1.3.17}$$

Combining this result with equation (1.3.9), one obtains

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P \tag{1.3.18}$$

For the Helmholtz energy, the corresponding result is

$$\mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V \tag{1.3.19}$$

and for the Gibbs energy

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P \tag{1.3.20}$$

It follows that the Gibbs energy for a closed system is conveniently described as a function of temperature and pressure. Relaxing the condition that the system be closed, the total derivative of G in an open two-component system becomes

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \left(\frac{\partial G}{\partial n_{\mathrm{A}}}\right)_{n_{\mathrm{B}},T,P} \mathrm{d}n_{\mathrm{A}} + \left(\frac{\partial G}{\partial n_{\mathrm{B}}}\right)_{n_{\mathrm{A}},T,P} \mathrm{d}n_{\mathrm{B}} \tag{1.3.21}$$

This is a very important equation in discussing chemical equilibria, and is the starting point for deriving other important results. One sees that the entropy can be defined from the temperature dependence of the Gibbs energy,

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,n_{\mathrm{A}},n_{\mathrm{B}}} \tag{1.3.22}$$

and the volume from the pressure dependence

$$V = +\left(\frac{\partial G}{\partial P}\right)_{T,n_A,n_{\mathrm{B}}} \tag{1.3.23}$$

The thermodynamic variables, U, S, H, A, and G introduced above are extensive quantities like the volume V. Thus, the amount of internal energy in a sulfuric acid solution depends on whether one has 250 mL beaker, a 4 L bottle, or a full railway tank car. Just as for volume, it is necessary to define intensive variables giving the internal energy per gram, U_{s}, or the internal energy per mole, U_{m}. Since the present discussion is concerned with chemistry, we will use only the molar quantities U_{m}, S_{m}, H_{m}, A_{m}, and G_{m} which are defined from the corresponding extensive quantity by equations like equation (1.3.2).

1.4 Partial Molar Quantities

Partial molar quantities are used to describe the change in properties of a multicomponent system when one component is added at constant temperature, pres-

sure, and amounts of all other components. In the present section, partial molar quantities will be considered with respect to the volume of a two-component system. For example, the partial molar volume of component A is defined as

$$\upsilon_A = \left(\frac{\partial V}{\partial n_A}\right)_{n_B, T, P} \tag{1.4.1}$$

and that of B as

$$\upsilon_B = \left(\frac{\partial V}{\partial n_B}\right)_{n_A, T, P} \tag{1.4.2}$$

It follows from equation (1.3.4) that, at constant temperature and pressure, a change in the volume of a two-component solution is given by

$$dV = \upsilon_A \, \mathrm{d}n_A + \upsilon_B \mathrm{d}n_B \tag{1.4.3}$$

This expression may be integrated under conditions that the relative amounts of n_A and n_B, that is, the composition of the solution, do not change:

$$V = \upsilon_A n_A + \upsilon_B n_B \tag{1.4.4}$$

The resulting equation states that the volume of the solution may be calculated given the number of moles of each component and their partial molar volumes. In terms of the molar volume, this equation becomes

$$V_m = \upsilon_A x_A + \upsilon_B x_B \tag{1.4.5}$$

It can be shown that there is a relationship between the partial molar volumes for a given solution composition. Taking the total derivative of the volume on the basis of equation (1.4.4), one obtains at constant temperature and pressure

$$\mathrm{d}V = \upsilon_A \, \mathrm{d}n_A + n_A d\upsilon_A + \upsilon_B \mathrm{d}n_B + n_B \mathrm{d}\upsilon B \tag{1.4.6}$$

Comparing equations (1.4.3) and (1.4.6), one finds that

$$n_A d\upsilon_A + n_B \, d\upsilon_B = 0 \tag{1.4.7}$$

or dividing by the total number of moles, $n_A + n_B$,

$$x_A d\upsilon_A + x_B \, d\upsilon_B = 0 \tag{1.4.8}$$

This equation, which is one example of the Gibbs–Duhem equation, shows that changes in the partial molar volume of one component may be related to changes in the same quantity for the other component. Experimentally, it means that one only has to measure one partial molar volume as a function of composition provided one has a value of the second partial molar volume at a reference point. In order to illustrate this point, equation (1.4.8) is written in a form suitable for calculating υ_A from υ_B:

$$\int d\upsilon_A = -\int \frac{x_B}{x_A} d\upsilon_B \tag{1.4.9}$$

If the reference point for the integration is a solution consisting of pure component A ($x_B = 0$), then the integration constant required is the molar volume of pure component A, and one may write

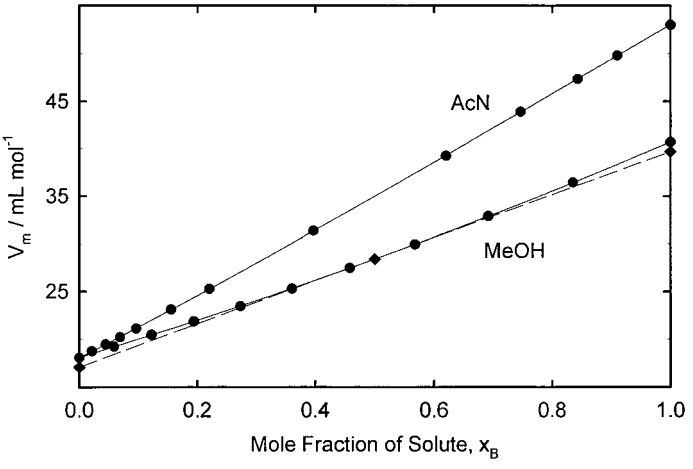


Fig. 1.2 Plots of the molar volume of aqueous solutions of acetonitrile (AcN) and methanol (MeOH) against their mole fraction in solution.

$$\upsilon A - V_{\mathrm{mA}} = -\int_{x_{\mathrm{B}}=0}^{x_{\mathrm{B}}} \frac{x_{\mathrm{B}}}{x_{\mathrm{A}}} \mathrm{d}\upsilon_{\mathrm{B}} \tag{1.4.10}$$

Since the data tabulated in the literature for thermodynamic quantities are intensive, one needs a method of determining partial molar quantities from these data. However, the partial molar quantity involves the first derivative of an extensive quantity such as the volume with respect to the number of moles of a particular component. Although the resulting derivative is intensive in nature, it itself implies that it comes from extensive quantities. The raw data that are used to estimate $\partial V/\partial n_i$ are normally the molar volume V_{m} as a function of the mole fraction of a given component x_i. Thus, it is reasonable to examine the relationship between $\partial V/\partial n_i$ and $\partial V_m/\partial x_i$. A plot of V_{m} against x_{B}, the mole fraction of acetonitrile, is shown in fig. 1.2 using the data given in table 1.2 for the acetonitrile–water system. Considering the relationship between V and V_{m} (equation (1.3.2)),

$$\left(\frac{\partial V_{\mathrm{m}}}{\partial n_{\mathrm{A}}}\right)_{n_{\mathrm{B}}} = \frac{1}{n_{\mathrm{A}} + n_{\mathrm{B}}}\left(\frac{\partial V}{\partial n_{\mathrm{A}}}\right)_{n_{\mathrm{B}}} - \frac{V}{(n_{\mathrm{A}} + n_{\mathrm{B}})^2} \tag{1.4.11}$$

Furthermore,

$$\left(\frac{\partial x_{\mathrm{B}}}{\partial n_{\mathrm{A}}}\right)_{n_{\mathrm{B}}} = \frac{-n_{\mathrm{B}}}{(n_{\mathrm{A}} + n_{\mathrm{B}})^2} \tag{1.4.12}$$

Now dividing equation (1.4.11) by (1.4.12), one obtains the result that

$$\frac{\partial V_{\mathrm{m}}}{\partial x_{\mathrm{B}}} = -\frac{\upsilon_{\mathrm{A}}}{x_{\mathrm{B}}} + \frac{V}{n_{\mathrm{B}}} \tag{1.4.13}$$

This equation is rearranged to give

Table 1.2 Molar Volume Data for the Acetonitrile–Water System at 25°C

Mole Fraction of Acetonitrile x_{AcN}	Molar Volume of the Solution V_m/mL mol^{-1}	Excess Molar Volume V_m^{ex}/mL mol^{-1}	Partial Molar Volumes	
			Acetonitrile υ_{AcN}/ mL mol^{-1}	Water υ_w/mL mol^{-1}
0	18.07	0	—	18.07
0.2	24.56	–0.50	51.83	17.75
0.4	31.48	–0.56	52.51	17.46
0.6	38.60	–0.44	53.03	16.95
0.8	45.85	–0.17	53.08	16.91
1.0	53.01	0	53.01	—

$$V_m = \upsilon_A + x_B \frac{\partial V_m}{\partial x_B} \tag{1.4.14}$$

One may interpret this equation by relating it to the equation for a simple straight line. Referring to fig. 1.2, it follows that a line drawn with a slope equal to $\partial V_m / \partial x_B$ at the point (V_m, x_B) will intersect the V_m axis at υ_A, which is the y intercept. Such a line is shown on the molar volume plot in fig. 1.2 at the point ◆ ($x_B = 0.5$) for the methanol–water system. In a similar way, it is easily shown that

$$V_m = \upsilon_B + x_A \frac{\partial V_m}{\partial x_A} \tag{1.4.15}$$

Since a plot of the molar volume against the mole fraction of B is easily converted to one against the mole fraction of A ($x_A = 1 - x_B$), equation (1.4.15) shows that the intercept on the right-hand ordinate of fig. 1.2 ($x_B = 1$, $x_A = 0$) gives the partial molar volume of component B.

On the basis of the above analysis it has been shown the partial molar quantities are easily obtained from intensive quantities like the molar volume V_m when this quantity is plotted as a function of an intensive composition variable like the mole fraction. The plots in fig. 1.2 show that the molar volume is almost a linear function of the mole fraction of solute. If the curves in fig. 1.2 were actually perfect straight lines, the partial molar volumes would be constant independent of solution composition. Such a situation would arise if the solution were perfectly ideal. In reality, very few solutions are ideal, as will be seen from the discussion in the following section. In order to see more clearly the departure from ideality, one defines and calculates a quantity called the excess molar volume. This quantity is equal to the actual molar volume less the molar volume for the solution if it were ideal. The latter can be considered as the volume of the solution that would be found if the molecules of the two components form a solution without expansion or contraction. Thus, the ideal molar volume can be defined as

$$V_m^{id} = x_A V_{mA} + x_B V_{mB} \tag{1.4.16}$$

and is calculated directly from the molar volumes of the pure components A and B. It follows that the excess molar volume is given by

$$V_m^{ex} = V_m - V_m^{id} = V_m - x_A V_{mA} - x_B V_{mB} \tag{1.4.17}$$

The excess molar volume is also called the molar volume of mixing.

Plots of V_m^{ex} against the mole fraction of solute are shown for the acetonitrile–water and methanol–water systems in fig. 1.3. The V_m^{ex} function focuses attention on the non-ideality of the solution. The plots demonstrate clearly that the behavior of these solutions is not simple. Both systems have negative excess volumes. This indicates that the molecules occupy a smaller volume in solution than they do as pure liquids. Such an observation is undoubtedly due to attractive forces between the two components, which are stronger than the forces between molecules in the pure liquids.

The partial molar volumes may be calculated from the data for the excess molar volume in a manner similar to that used with the molar volume data. On the basis of equation (1.4.17), one may write

$$\frac{\partial V_m^{ex}}{\partial x_B} = \frac{\partial V_m}{\partial x_B} + V_{mA} - V_{mB} \tag{1.4.18}$$

Then substituting equation (1.4.13), one obtains after rearrangement

$$\upsilon_A = V_m - x_B \frac{\partial V_m^{ex}}{\partial x_B} + x_B(V_{mA} - V_{mB}) \tag{1.4.19}$$

Using the definition of V_m^{ex} given by equation (1.4.17), this simplifies to

$$\upsilon_A = V_m^{ex} - x_B \frac{\partial V_m^{ex}}{\partial x_B} + V_{mA} \tag{1.4.20}$$

In a similar way, one may show that

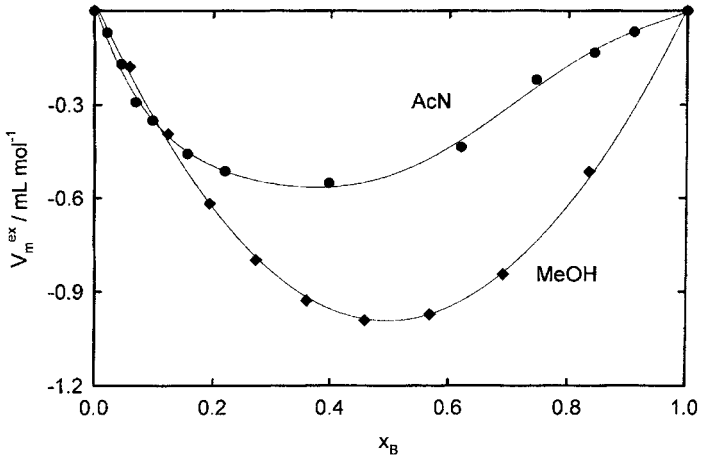


Fig. 1.3 Plots of the excess molar volume for the acetonitrile (AcN)–water and methanol (MeOH)–water systems against the mole fraction of these solutes.

$$\upsilon_B = V_m^{ex} - x_A \frac{\partial V_m^{ex}}{\partial x_A} + V_{mB} \tag{1.4.21}$$

EXAMPLE

The application of equations (1.4.20) and (1.4.21) to determine partial molar volumes in the methanol–water system is now illustrated. The excess molar volume for this system is fairly symmetrical with respect to the mole fraction of methanol, and can be fitted with reasonable accuracy by a cubic equation using least squares. The result is

$$V_m^{ex} = 0.0286 - 4.163x_B + 4.341x_{B^2} - 0.1977x_{B^3} \tag{1.4.22}$$

The resulting curve is shown in fig. 1.3, drawn through the experimental points. On the basis of this analytical expression, one may now write an analytical expression for the first derivative at any point on the curve. This equation is

$$\frac{\partial V_m^{ex}}{\partial x_B} = -4.163 + 8.682x_B - 0.5931x_{B^2} \tag{1.4.23}$$

Now, suppose one wants the values of the partial molar volumes at $x_B = 0.4$. Substituting into equation (1.4.22), one finds that $V_m^{ex} = -0.955$ mL mol^{-1}; similarly, from equation (1.4.23), $\partial V_m^{ex}/\partial x_B = -0.785$ mL mol^{-1}. The molar volume of pure water, V_{mA}, is 18.07 mL mol^{-1}, and that of pure methanol, V_{mB}, 40.72 mL mol^{-1}. Calculating the partial molar volume of water from equation (1.4.20), one obtains

$$\begin{aligned} \upsilon_A &= -0.955 + 0.4 \times 0.785 + 18.07 \\ &= 17.43 \text{ mL mol}^{-1} \end{aligned} \tag{1.4.24}$$

Similarly, from equation (1.4.21) for the partial molar volume of methanol,

$$\begin{aligned} \upsilon_B &= -0.955 - 0.6 \times 0.785 + 40.72 \\ &= 39.29 \text{ mL mol}^{-1} \end{aligned} \tag{1.4.25}$$

These calculations can be carried out for any value of x_B.

Partial molar quantities can be defined for any of the remaining thermodynamic functions including the internal energy U, the enthalpy H, the Helmholtz energy A, and the Gibbs energy G. Those most used in chemistry are the chemical potentials, which are defined from the Gibbs energy for the system. Thus, the chemical potential of component A is defined as

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{n_B,T,P} \tag{1.4.26}$$

and that for component B as

$$\mu_B = \left(\frac{\partial G}{\partial n_B}\right)_{n_A,T,P} \tag{1.4.27}$$

These quantities are connected to the molar Gibbs energy for the solution by the equation

$$G_m = x_A\mu_A + x_B\mu_B \tag{1.4.28}$$

The application of these quantities to understanding physical and chemical equilibria in solutions is investigated in the sections which follow.

1.5 Ideal Solutions—Raoult's Law

The concept of an ideal solution is important in the development of an understanding of the properties of real solutions. In a liquid solution, molecules are in intimate contact with one another so that the question of ideality is determined by the nature of the intermolecular forces. Suppose a solution is formed by mixing two liquids, A and B. Then, the solution is ideal if the intermolecular forces between A and B molecules are no different from those between A and A, or B and B molecules.

An indication of whether or not the above condition for ideality is met is obtained from the vapor pressure of the solution. At a given temperature, the vapor pressure of a pure liquid is a measure of the ability of molecules to escape from the liquid to the gas phase. By studying the vapor pressure of a solution as a function of its composition at constant temperature one may assess the solution's ideality or its degree of departure from ideality. For an ideal solution, the tendency of molecule A to escape is proportional to its mole fraction, that is, to its concentration expressed in terms of the fraction of molecules which are of type A. The proportionality constant must be the vapor pressure of pure component A because this vapor pressure is reached when the mole fraction is unity. This result is Raoult's law, which is expressed mathematically as

$$P_A = P_A^\circ x_A \tag{1.5.1}$$

Similarly, for the other component B,

$$P_B = P_B^\circ x_B \tag{1.5.2}$$

A system which is close to ideal in its behavior is a solution of benzene and toluene. These molecules are very similar in structure so that the intermolecular forces between benzene and toluene do not differ greatly from those between benzene molecules or toluene molecules in each pure liquid. The vapor pressure diagram for this system at 25°C is shown in fig. 1.4. Since toluene has a higher molecular weight, its vapor pressure as a pure liquid is lower (3.25 kPa) than that of benzene (12.69 kPa). The total vapor pressure P_T is obtained by adding those of components A and B, so that

$$P_T = P_A + P_B = P_A^\circ + (P_B^\circ - P_A^\circ)x_B \tag{1.5.3}$$

The total vapor pressure also a linear function of the mole fractions x_A and x_B.

It is clear from the above that Raoult's law defines ideality by relating the properties of the liquid solution to the vapor with which it is in equilibrium. Since one knows how to deal with the thermodynamic properties of ideal gaseous

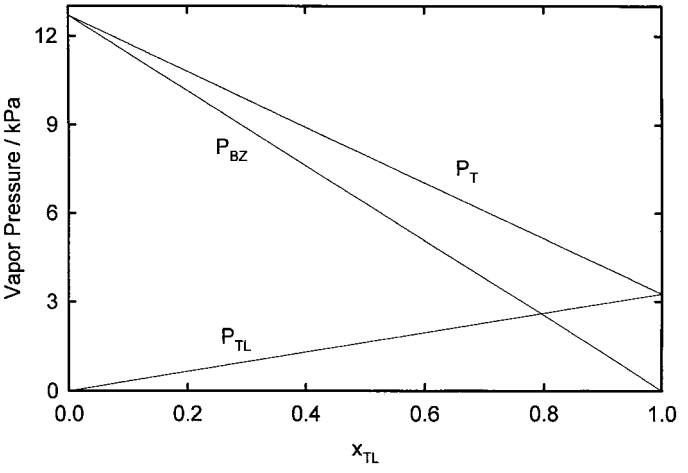


Fig. 1.4 Vapor pressure of benzene, P_{BZ}, and toluene, P_{TL}, and total vapor pressure, P_T, plotted against the mole fraction of toluene x_{TL} for benzene–toluene solutions at 25°C.

solutions, one now has a route to develop the thermodynamics of ideal liquid solutions.

1.6 Thermodynamics of Ideal Solutions

The thermodynamic equations for ideal solutions are derived by considering the equilibrium between a given component in the vapor phase and liquid solution. Thus, for component A in a solution containing two components,

$$A_{liquid} \rightleftharpoons A_{vapor} \tag{1.6.1}$$

The thermodynamic condition for equilibrium is that the chemical potential of A in the liquid phase be equal to that of A in the vapor, that is,

$$\mu_A^s = \mu_A^v \tag{1.6.2}$$

where μ_A^s is the chemical potential of A in the liquid solution, and μ_A^v, that for A in the vapor phase. If one now assumes that the vapor phase behaves ideally, one may write

$$\mu_A^v = \mu_A^{v,\circ} + RT \ln P_A \tag{1.63}$$

where $\mu_A^{v,\circ}$ is the standard chemical potential of A in the vapor phase measured when the partial pressure of A is 1 bar, and P_A, the actual partial pressure of A. Since Raoult's law applies when the liquid solution is ideal, one may also write

$$\mu_A^s = \mu_A^v = \mu_A^{v,\circ} + RT \ln x_A P_A^\circ \tag{1.6.4}$$

where x_A is the mole fraction of A and P_A° the partial pressure of the pure liquid A. Since $\mu_A^{v,\circ}$ and P_A° are constants for any given temperature and pressure, equation (1.6.4) may be rewritten as

$$\mu_A^s = \mu_A^{s,\circ} + RT \ln x_A \tag{1.6.5}$$

where

$$\mu_A^{s,\circ} = \mu_A^{v,\circ} + RT \ln P_A^\circ \tag{1.6.6}$$

Thus, $\mu_A^{s,\circ}$ is the standard chemical potential of component A in the liquid solution, which can be measured when the mole fraction of A is one (pure A). A similar analysis for the other component B leads to the equation

$$\mu_B^s = \mu_B^{s,\circ} + RT \ln x_B \tag{1.6.7}$$

where

$$\mu_B^{s,\circ} = \mu_B^{v,\circ} + RT \ln P_B^\circ \tag{1.6.8}$$

The thermodynamic quantities associated with the mixing of pure liquids to form a solution are important in assessing solution properties. Suppose n_A moles of component A are combined with n_B moles of component B to form a solution. The Gibbs energy change associated with this process is given by

$$\Delta_{mix}G = n_A\mu_A^s + n_B\mu_B^s - n_A\mu_A^{s,\circ} - n_B\mu_B^{s,\circ} \tag{1.6.9}$$

On the basis of equations (1.6.5) and (1.6.7), this may be rewritten as

$$\Delta_{mix}G = n_A RT \ln x_A + n_B RT \ln x_B \tag{1.6.10}$$

Dividing both sides by the total number of moles, $n_A + n_B$, one obtains

$$\Delta_{mix}G_m = x_A RT \ln x_A + x_B RT \ln x_B \tag{1.6.11}$$

where the subscript "m" indicates that the Gibbs energy change is given on a molar (intensive) basis. It is easy to see that this result can be generalized to a multicomponent system with n components by writing

$$\Delta_{mix}G_m = \sum_{i=1}^{n} x_i RT \ln x_i \tag{1.6.12}$$

Since the mole fraction x_i is less than one, its logarithm is negative. Thus, $\Delta_{mix}G_m$ is a negative quantity, indicating that the mixing process is spontaneous, as one would expect.

The entropy change associated with mixing can be obtained by taking the temperature derivative of $\Delta_{mix}G_m$. Accordingly,

$$\Delta_{mix}S_m = -\frac{\partial \Delta_{mix}G_m}{\partial T} = -\sum_{i=1}^{n} x_i R \ln x_i \tag{1.6.13}$$

This quantity is clearly positive, since the mixing process results in an increase in entropy.

On the basis of the definitions of Gibbs energy and enthalpy (equations (1.3.14) and (1.3.16), the enthalpy of mixing is given by

$$\Delta_{\text{mix}} H_{\text{m}} = \Delta_{\text{mix}} G_{\text{m}} + T\Delta_{\text{mix}} S_{\text{m}} \tag{1.6.14}$$

Substituting in equations (1.6.12) and (1.6.13), one obtains

$$\Delta_{\text{mix}} H_{\text{m}} = 0 \tag{1.6.15}$$

This result gives one of the important properties of ideal solutions, namely, that the mixing process does not involve any heat. Since the components of the solution interact with each other in exactly the same manner that they interact with themselves in the pure liquid, mixing is neither exothermic nor endothermic.

By taking the pressure derivative of $\Delta_{\text{mix}} G_{\text{m}}$, one may determine the volume change associated with mixing:

$$\Delta_{\text{mix}} V_{\text{m}} = \frac{\partial \Delta_{\text{mix}} G_{\text{m}}}{\partial P} = 0 \tag{1.6.16}$$

The fact that the volume change associated with mixing the components is zero gives another important property of an ideal solution. On the other hand, a volume change does accompany the formation of most solutions. One example was analyzed above in section 1.4. This change is another reflection of the fact that the energy due to the intermolecular forces between the components changes with solution composition.

In summary, there are three important characteristics of ideal solutions that one should remember in assessing the properties of any non-ideal system: (i) the vapor pressure of each component is proportional to its mole fraction in solution over the whole composition range (Raoult's law); (ii) the enthalpy of mixing is zero; (iii) the volume change associated with mixing is zero. The sections which follow deal with non-ideal solutions.

1.7 Non-Ideal Solutions

Most solutions are non-ideal. This is simply a result of differences in the chemical nature of the molecular components in the solution, and in the way in which they interact with each other. A convenient way of examining intermolecular forces in a pure liquid is in terms of its internal pressure, P_{i}, which is defined as

$$P_{\text{i}} = \left(\frac{\partial U}{\partial V}\right)_T \tag{1.7.1}$$

This quantity was investigated extensively by Hildebrand [1], who showed that the internal pressure is approximately equal to the enthalpy of vaporization divided by the molar volume. Thus,

$$P_{\text{i}} \cong \frac{\Delta_{\text{vap}} H_{\text{m}}}{V_{\text{m}}} \tag{1.7.2}$$

Values of the internal pressure for some commonly used solvents are given in table 1.3. It is apparent that the internal pressure varies considerably from one solvent to another, water having the highest value among those considered.

Table 1.3 Values of Internal Pressure for Some Common Solvents at 25°C

Solvent	Molar Volume $V_m/cm^3\ mol^{-1}$	Enthalpy of Vaporization $\Delta_{vap}H_m/\ kJ\ mol^{-1}$	Internal Pressure $P_i/kJ\ dm^{-3}$
Acetonitrile	52.9	33.2	628
Acetone	74.0	30.8	416
Carbon tetrachloride	97.1	32.4	334
Chloroform	80.7	32.2	399
Dimethylsulfoxide	71.3	52.9	742
Hexane	131.6	31.55	240
Nitrobenzene	102.7	52.5	511
Methanol	40.7	37.43	917
Propylene carbonate	85.2	42.8	502
Water	18.07	43.99	2434

Thus, one has a clear indication that intermolecular forces are significantly different in these liquids. Under these circumstances, a solution formed from two of them would not be ideal and would generally exhibit positive deviations from Raoult's law. It is also obvious that not every pair of liquids formed from those shown in the table are miscible. Thus, a very non-polar solvent such as hexane is immiscible with a very polar one like water. For those which are miscible, the difference in internal pressure gives a good indication of the extent of departure from ideality. A very few systems show a negative deviation from Raoult's law behavior. This occurs when there is a strong attraction between the two molecules forming the solution, a well-known example being the chloroform–acetone system.

An example of a system exhibiting a small positive deviation from Raoult's law is a methanol–water solution (see fig. 1.5). It should be noted that when the concentration of methanol is small ($x_{MeOH} < 0.1$), the vapor pressure of water is close to the value expected on the basis of Raoult's law. Similarly, for a dilute solution of water in methanol ($x_{MeOH} > 0.9$, $x_w < 0.1$), the vapor pressure of methanol is approximately equal to that in an ideal solution. These conditions are often observed in dilute solutions and have important consequences with respect to their thermodynamic properties, as will be seen in the following section.

A much more complex behavior is demonstrated by the acetonitrile–water system [2] (fig. 1.6). The vapor pressure curves show an interesting change in slope at a mole fraction of acetonitrile close to 0.8. However, when the mole fraction of acetonitrile is less than 0.06, the vapor pressure of water is close to the value predicted by Raoult's law.

As mentioned above, a few systems show negative deviations from Raoult's law, a well-known example being the acetone–chloroform system (fig. 1.7). In this case there is attractive interaction between the two components, specifically, between the electron-rich oxygen in acetone, and the hydrogen atom in chloroform. As a result, the escaping tendency of either molecule from the solution is

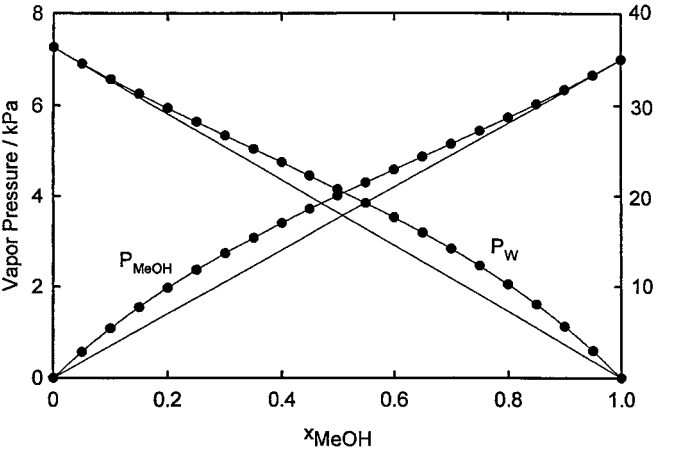


Fig. 1.5 Vapor pressure of methanol and water for methanol–water solutions plotted against the mole fraction of methanol at 40°C. The left-hand ordinate scale gives the vapor pressure of water and the right-hand scale that of methanol.

less than it would be if the chemical interaction did not occur. These systems are similar to those showing positive deviations from Raoult's law in that the vapor pressure of the predominant component approaches ideal behavior when the mole fraction of the minority component is very small, that is, with a mole fraction less than 0.1.

Now we proceed to examine the thermodynamic properties of non-ideal solutions.

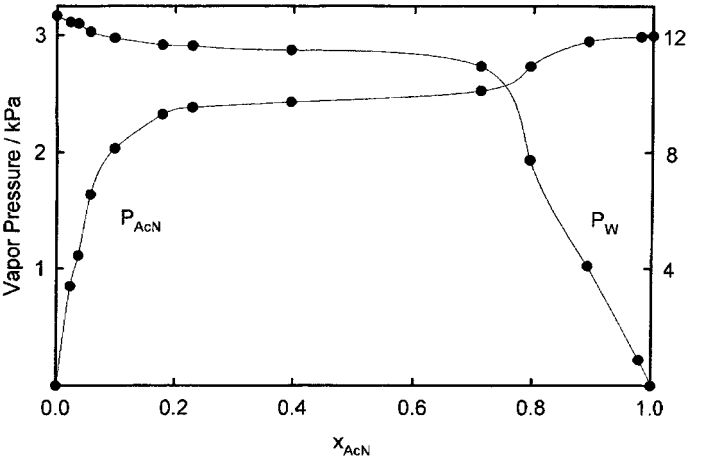


Fig. 1.6 Vapor pressure of acetonitrile and water for acetonitrile–water solutions at 25°C plotted against the mole fraction of acetonitrile. The left-hand ordinate scale gives the vapor pressure of water and the right-hand scale, that of acetonitrile.

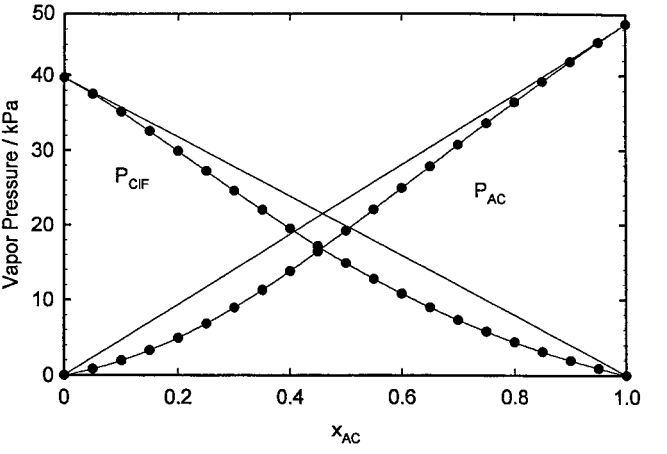


Fig. 1.7 Vapor pressure of acetone and chloroform for acetone–chloroform solutions at 35°C plotted against the mole fraction of acetone.

1.8 Thermodynamics of Non-Ideal Solutions

The starting point for developing the thermodynamics of non-ideal solutions is the same as that for ideal solutions. Thus, one considers the equilibrium between each component in the liquid solution and its vapor. It follows from section 1.6 that one may write in general for component A,

$$\mu_A^s = \mu_A^v = \mu_A^{v,\circ} + RT \ln P_A \tag{1.8.1}$$

This equation states that chemical potentials of component A in the liquid solution and vapor are equal and that each relates to the vapor pressure of A. However, one would like to have a way of relating the chemical potential of A to its mole fraction in solution. This is achieved by relating the vapor pressure of A to its mole fraction in the liquid solution using a correction factor to make the value of P_A predicted by Raoult's law equal to the true value. Thus, one writes

$$P_A = \gamma_A x_A P_A^\circ \tag{1.8.2}$$

where γ_A is the correction factor, known as the *activity coefficient* of A. It is clear that γ_A is greater than unity when the system exhibits positive deviations from Raoult's law, and less than unity when the deviations are negative. Furthermore, the value of γ_A depends on x_A, since the extent of departure varies with solution composition (see figs. 1.5–1.7). Combining equations (1.8.1) and (1.8.2), one obtains

$$\mu_A^s = \mu_A^{s,\circ} + RT \ln \gamma_A x_A \tag{1.8.3}$$

where $\mu_A^{s,\circ}$ is given by equation (1.6.6). It is emphasized that the standard state for this definition of the activity coefficient is based on the properties of pure component A. As the mole fraction of A approaches unity, the activity coefficient γ_A also approaches unity, as can be seen from the vapor pressure plots presented earlier. It is also emphasized that the standard chemical potential has the same

value as it would have in an ideal solution because it only depends on the properties of pure component A. The product $\gamma_A x_A$ is known as the *activity* of component A in solution. Thus, one may also write

$$\mu_A^s = \mu_A^{s,\circ} + RT \ln a_A \tag{1.8.4}$$

where

$$a_A = \gamma_A x_A \tag{1.8.5}$$

In a similar way, one may write for component B,

$$\mu_B^s = \mu_B^{s,\circ} + RT \ln a_B = \mu_B^{s,\circ} + RT \ln \gamma_B x_B \tag{1.8.6}$$

where $\mu_B^{s,\circ}$ is given by equation (1.6.8) and

$$\gamma_B = P_B/(x_B P_B^\circ) \tag{1.8.7}$$

It is interesting to evaluate the thermodynamic functions of mixing for the non-ideal solution. On the basis of equations (1.8.3) and (1.8.6),

$$\Delta_{mix} G = n_A RT \ln \gamma_A x_A + n_B RT \ln \gamma_B x_B \tag{1.8.8}$$

or on a molar basis

$$\Delta_{mix} G_m = x_A RT \ln \gamma_A x_A + x_B RT \ln \gamma_B x_B \tag{1.8.9}$$

In the case of non-ideal solutions the mixing functions are often referred to the value they would have in an ideal solution, $\Delta_{mix} G_m^{id}$, thereby defining the *excess* Gibbs energy of solution formation:

$$\Delta_{mix} G_m^{ex} = \Delta_{mix} G_m - \Delta_{mix} G_m^{id} = x_A RT \ln \gamma_A + x_B RT \ln \gamma_B \tag{1.8.10}$$

In order to calculate the other excess functions one must know the temperature and pressure derivatives of the activity coefficients γ_A and γ_B. The excess entropy of mixing is given by

$$\Delta_{mix} S_m^{ex} = -x_A R \ln \gamma_A - x_A RT \frac{\partial \ln \gamma_A}{\partial T} - x_B R \ln \gamma_B - x_B RT \frac{\partial \ln \gamma_B}{\partial T} \tag{1.8.11}$$

and the excess enthalpy by

$$\Delta_{mix} H_m^{ex} = x_A RT^2 \frac{\partial \ln \gamma_A}{\partial T} - x_B RT^2 \frac{\partial \ln \gamma_B}{\partial T} \tag{1.8.12}$$

Finally, the excess volume of mixing is obtained from the pressure derivatives of the activity coefficients:

$$\Delta_{mix} V_m^{ex} = x_A RT \frac{\partial \ln \gamma_A}{\partial P} + x_B RT \frac{\partial \ln \gamma_B}{\partial P} \tag{1.8.13}$$

EXAMPLE

The vapor pressure of acetonitrile above an acetonitrile–water solution with a mole fraction of 0.395 in acetonitrile is 9.727 kPa at 25°C. The corresponding vapor pressure of water is 2.874 kPa. At the same temperature the vapor

pressures of the pure liquids are 11.983 kPa and 3.166 kPa for acetonitrile and water, respectively. Estimate the Raoult law activity coefficients for each component, the molar Gibbs energy of mixing, and the excess value of this function. The enthalpy of mixing for this solution is 876.1 J mol^{-1}. Estimate the entropy of mixing and its excess value.

The Raoult law activity coefficient for acetonitrile is

$$\gamma_{AcN} = \frac{9.727}{0.395 \times 11.98} = 2.055 \tag{1.8.14}$$

The corresponding quantity for water is

$$\gamma_{w} = \frac{2.874}{0.605 \times 3.166} = 1.500 \tag{1.8.15}$$

The molar Gibbs energy of mixing is

$$\begin{aligned} \Delta_{mix}G_m &= 0.395 \times 2479.4 \times \ln(2.055 \times 0.395) \\ &\quad + 0.605 \times 2479.4 \times \ln(1.500 \times 0.605) \\ &= -349.9 \text{ J mol}^{-1} \end{aligned} \tag{1.8.16}$$

The excess molar Gibbs energy of mixing is

$$\begin{aligned} \Delta_{mix}G_m^{ex} &= 0.395 \times 2479.4 \ln(2.055) + 0.605 \times 2479.4 \ln(1.500) \\ &= 1313.6 \text{ J mol}^{-1} \end{aligned} \tag{1.8.17}$$

The enthalpy of mixing is also the excess enthalpy of mixing because an ideal solution has zero enthalpy of mixing. Now, the entropy of mixing can be calculated:

$$\Delta_{mix}S_m = \frac{\Delta_{mix}H_m - \Delta_{mix}G_m}{T} = \frac{876.1 + 349.9}{298.2} = 4.111 \text{ J K}^{-1} \text{ mol}^{-1} \tag{1.8.18}$$

and

$$\Delta_{mix}S_m^{ex} = \frac{\Delta_{mix}H_m^{ex} - \Delta_{mix}G_m^{ex}}{T} = \frac{876.1 - 1313.6}{298.2} = -1.467 \text{ J K}^{-1} \text{ mol}^{-1} \tag{1.8.19}$$

Values of the excess Gibbs energy, enthalpy, and entropy for the acetonitrile–water system which show significant departures from ideality are shown as a function of solution composition in fig. 1.8. The excess enthalpy is positive over the whole composition range, reaching a maximum value of 1067 J mol^{-1} in the vicinity of an acetonitrile mole fraction equal to 0.7. These data give a direct measure of the endothermic nature of the mixing process. The excess entropy displays a rather complex behavior, being negative at lower concentrations of acetonitrile and positive for values of x_{AcN} greater than 0.7. Excess thermodynamic data such as those shown in fig. 1.8 provide a convenient way of recording the properties of non-ideal solutions and are often found in tables for liquid-vapour equilibria. However, they provide information about the solution as a

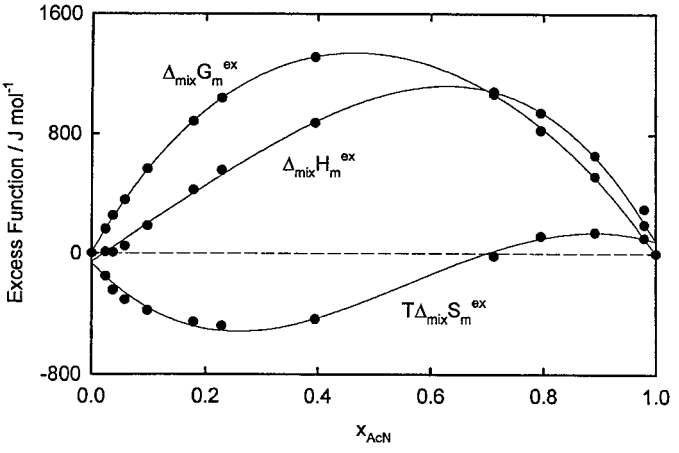


Fig. 1.8 Excess Gibbs energy, enthalpy, and entropy for acetonitrile–water solutions at 25°C plotted against the mole fraction of acetonitrile.

whole, not about the individual components. If one wants the activity coefficients for each component, one must also have vapor pressure data for each component as a function of solution composition.

In assessing the above treatment of non-ideal solutions, it must be kept in mind that it is applicable to a limited number of systems. This follows from the fact that we are often dealing with solutions of solids in liquids, and also because not all liquids are miscible over the whole composition range. Under these circumstances it is not convenient to define the standard state for one component in terms of the pure substance. Thus, for the majority of solutions, the majority component is treated as the solvent and its thermodynamics discussed with respect to its pure state within the context of Raoult's law. The other minority component, which is the solute, is discussed using a standard state based on the properties of an ideally dilute solution. These systems are considered in more detail later in this chapter.

1.9 Regular Solutions

In examining the properties of non-ideal solutions, it became clear that some systems differ from ideality in a manner which could be treated by quite simple statistical mechanical models. The solution non-ideality is often reflected in the experimental observation that the enthalpy of mixing is not zero, so that A–B interactions are different from A–A and B–B interactions. On the basis of his study of the properties of a large number of liquid solutions, Hildebrand [1, 3] introduced the concept of a regular solution. This is a system for which the enthalpy of mixing is non-zero and the entropy of mixing has its ideal value so that ΔS^{ex} is zero. This is equivalent to assuming that the molecules are randomly distributed in the mixture so that the differences in the intermolecular forces which lead to the non-zero value of ΔH^{ex} cannot be large. Guggenheim [4, 5]

discussed strictly regular solutions which have the additional restriction that $\Delta_{\text{mix}} V_{\text{m}}^{\text{ex}}$ be zero. These types of systems are considered in this section.

Consider a mixture of two molecules A and B which are both approximately spherical in shape. As perfect spheres they can pack together in a face-centered cubic lattice to form a liquid with a coordination number c of 12 in each pure liquid. The mixture packs in the same way provided the molecular sizes are not too different, more specifically, provided the molecular volumes do not differ by more than a factor of two [4]. If the free volume between molecules in the mixture does not differ from the sum of those in the two pure liquids used to form the mixture, then the volume of mixing is effectively zero, and the interaction energy experienced by a given molecule in the mixture may be calculated by summing the contributions from nearest neighbors. Mixtures with these properties are *strictly regular*.

Let us now consider how one can estimate the enthalpy of mixing given the enthalpies associated with A–A, A–B, and B–B interactions at the molecular level. If each molecule has c nearest neighbors, then the number of interactions experienced by type A molecules is $cn_{\text{A}}/2$, and the number of B molecules, $cn_{\text{B}}/2$, where the factor of two appears in order to avoid counting the interactions twice. If one defines the number of A–A interactions as n_{AA}, the number of B–B interactions as n_{BB}, and the number of A–B interactions as n_{AB}, it follows that

$$cn_{\text{A}} = 2n_{\text{AA}} + n_{\text{AB}} \tag{1.9.1}$$

and

$$cn_{\text{B}} = 2n_{\text{BB}} + n_{\text{AB}} \tag{1.9.2}$$

By adding these equations, one obtains an expression for twice the total number of interactions in the solution.

Suppose that the enthalpy associated with an A–A interaction is h_{AA}, that with B–B, h_{BB}, and that with an A–B interaction, h_{AB}. Then the enthalpy of n_{A} molecules in pure A associated with intermolecular interactions is

$$H_{\text{A}} = \frac{cn_{\text{A}}}{2} h_{\text{AA}} \tag{1.9.3}$$

Similarly, for pure B,

$$H_{\text{B}} = \frac{cn_{\text{B}}}{2} h_{\text{BB}} \tag{1.9.4}$$

The enthalpy of the solution formed from these pure liquids, associated with intermolecular interactions is

$$H_{\text{sl}} = n_{\text{AA}} h_{\text{AA}} + n_{\text{BB}} h_{\text{BB}} + n_{\text{AB}} h_{\text{AB}} \tag{1.9.5}$$

As a result, the enthalpy of mixing becomes

$$\begin{aligned} \Delta_{\text{mix}} H &= H_{\text{sl}} - H_{\text{A}} - H_{\text{B}} \\ &= n_{\text{A}B} \left(h_{\text{AB}} - \frac{h_{\text{AA}} + h_{\text{BB}}}{2} \right) \end{aligned} \tag{1.9.6}$$

In order to develop this model further one has to obtain an expression for n_{AB} in terms of n_{A} and n_{B}. The assumption used is that the molecular composition

around a given molecule is completely random and therefore reflects the overall solution composition. This is precisely the assumption used by Hildebrand to define a regular solution. Thus, the number n_{AB} can be calculated from the mole fractions defining solution composition, and is given by

$$n_{AB} = cnx_A x_B \tag{1.9.7}$$

where n is the total number of molecules ($n = n_A + n_B$). The enthalpy of mixing can now be expressed as

$$\Delta_{mix}H = cnx_A x_B \Delta h \tag{1.9.8}$$

where

$$\Delta h = h_{AB} - \frac{h_{AA} + h_{BB}}{2} \tag{1.9.9}$$

Since the mixing process is completely random, one may use the value of ΔS_{mix} for an ideal solution, which for the present system is given by

$$\Delta_{mix}S = -n_A R \ln x_A - n_B R \ln x_B \tag{1.9.10}$$

Thus, the expression for the Gibbs energy of mixing becomes

$$\Delta_{mix}G = n_A RT \ln x_A + n_B RT \ln x_B + c(n_A + n_B)x_A x_B \Delta h \tag{1.9.11}$$

One can now derive expressions for the chemical potentials of the individual components. Since the Gibbs energy of the solution is

$$G_{sl} = n_A \mu_A^{s,\circ} + n_B \mu_B^{s,\circ} + \Delta_{mix}G \tag{1.9.12}$$

the chemical potential of A is obtained by differentiating G_{sl} with respect to n_A (equation (1.4.26)):

$$\mu_A = \mu_A^{s,\circ} + RT \ln x_A + cx_B^2 \Delta h \tag{1.9.13}$$

Similarly, one finds for B,

$$\mu_B = \mu_B^{s,\circ} + RT \ln x_B + cx_A^2 \Delta h \tag{1.9.14}$$

Thus, according to the model for a regular solution the activity coefficients γ_A and γ_B are given by

$$\ln \gamma_A = \frac{cx_B^2 \Delta h}{RT} \tag{1.9.15}$$

and

$$\ln \gamma_B = \frac{cx_A^2 \Delta h}{RT} \tag{1.9.16}$$

These quantities, in turn, may be related to the vapor pressure of each component over the solution using equations. (1.8.2) and (1.8.7):

$$P_A = x_A P_A^{\circ} \exp\left(\frac{cx_B^2 \Delta h}{RT}\right) \tag{1.9.17}$$

and

$$P_B = x_B P_B^\circ \exp\left(\frac{c x_A^2 \Delta h}{RT}\right) \tag{1.9.18}$$

A plot of vapor pressure data for a hypothetical system, assuming $c\Delta h/RT$ is unity, is shown in fig. 1.9. The positive deviations from ideality indicate that the mixing process is endothermic. As the parameter Δh is increased, the deviations increase in the positive direction. Obviously, the theory also predicts negative deviations from Raoult's law when Δh is negative, that is, when the mixing process is exothermic. Under these conditions the intermolecular forces between the two species A and B are attractive, and the escaping tendency of each is less than it would be if the solution were ideal ($\Delta h = 0$).

EXAMPLE

Estimate the vapor pressure of the two components in a regular solution for which $c\Delta h/(RT) = 1$ and $x_A = 0.4$ given that the vapor pressure of pure component A is 15.0 kPa and that of pure B, 20.0 kPa. Also calculate the Raoult law activity coefficients. Repeat the calculation for the case that $c\Delta h/(RT) = -1$.

From equation (1.9.17) at $x_A = 0.4$, the vapor pressure of A is

$$P_A = 0.4 \times 15.0 \exp(1 \times 0.36) = 8.60 \text{ kPa} \tag{1.9.19}$$

The vapor pressure of B is

$$P_B = 0.6 \times 20.0 \exp(1 \times 0.16) = 14.08 \text{ kPa} \tag{1.9.20}$$

The activity coefficients are

$$\gamma_A = \frac{P_A}{x_A p_A^\circ} = \frac{8.60}{0.4 \times 15.0} = 1.433 \tag{1.9.21}$$

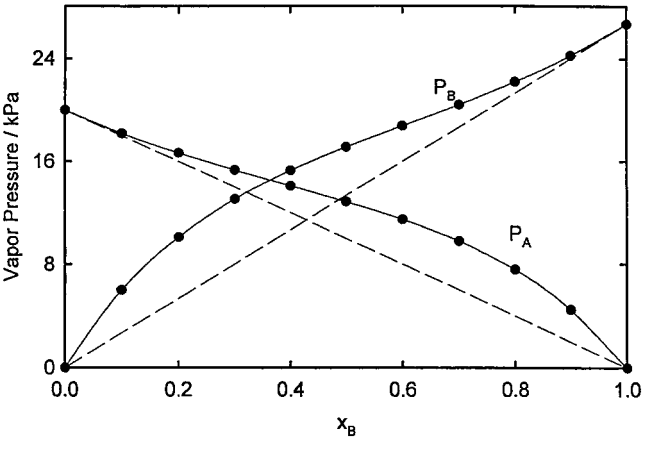


Fig. 1.9 Vapor pressure for a hypothetical regular solution for which $c\Delta h(RT) = 1$ plotted against the mole fraction of component B. The vapor pressure of pure component B is 26.7 kPa, and that of component A, 20.0 kPa. The broken lines show Raoult law behavior.

and

$$\gamma_B = \frac{P_B}{x_B P_B^\circ} = \frac{14.08}{0.6 \times 20.0} = 1.173 \tag{1.9.22}$$

In the case that the mixing process is exothermic and $c\Delta h/(RT) = -1$, the vapor pressures are

$$P_A = 0.4 \times 15.0 \exp(-1 \times 0.36) = 4.19 \text{ kPa} \tag{1.9.23}$$

and

$$P_B = 0.6 \times 20.0 \exp(-1 \times 0.16) = 10.23 \text{ kPa} \tag{1.9.24}$$

The activity coefficients are

$$\gamma_A = \frac{P_A}{x_A P_A^\circ} = \frac{4.19}{0.4 \times 15.0} = 0.698 \tag{1.9.25}$$

and

$$\gamma_A = \frac{P_B}{x_B P_B^\circ} = \frac{10.23}{0.6 \times 20.0} = 0.853 \tag{1.9.26}$$

It is clear that there must be a limit to the endothermicity associated with the mixing process, if a stable solution is to be formed. As the enthalpy of mixing increases at a given composition, eventually a value is reached where the Gibbs energy of mixing is zero. This follows from the fact that the entropy of mixing for a regular solution is constant for fixed solution composition and equal to the ideal value (equation (1.9.10)). Values of $\Delta_{mix}G_m$ for a regular solution as a function of composition for increasing values of $c\Delta h/(RT)$ are shown in fig. 1.10. When this parameter reaches a value of 3, $\Delta_{mix}G_m$ increases over part of the composition

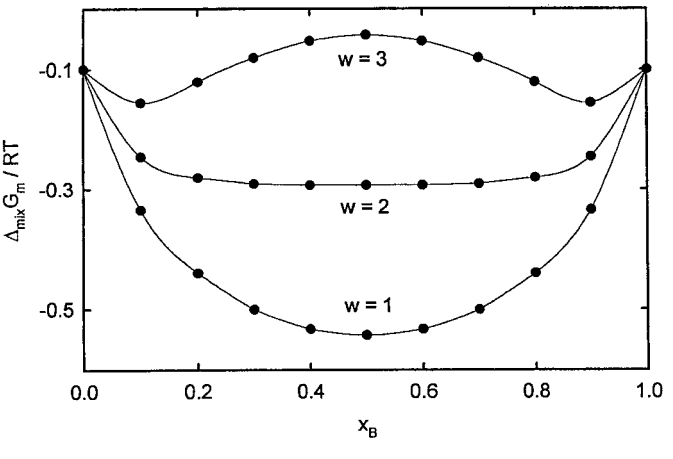


Fig. 1.10 The molar Gibbs energy of mixing in units of RT plotted against the mole fraction of component B for regular solutions with increasing values of the ratio $w = c\Delta h(RT)$.

range; this result indicates that a solution does not form. One may regard the diagrams in this figure as referring to a unique system at different temperatures. Thus, as temperature decreases, and $c\Delta h/(RT)$ increases, one eventually reaches a temperature at which the solution separates into its component liquids. The temperature at which phase separation begins to take place is called the *critical* temperature, and for regular solutions corresponds to $c\Delta h/RT$ equal to 2. It is easily apparent that the value of $\Delta_{\text{mix}}G_{\text{m}}$ is approximately constant over most of the composition range for this value of $c\Delta h/(RT)$.

The critical temperature at which phase separation begins is defined by the conditions [4]

$$\frac{\partial^2[\Delta_{\text{mix}}G_{\text{m}}(RT)]}{\partial x_{\text{B}}^2} = 0 \tag{1.9.27}$$

and

$$\frac{\partial^3[\Delta_{\text{mix}}G_{\text{m}}/(RT)]}{\partial x_{\text{B}}^3} = 0 \tag{1.9.28}$$

In other words, the slope of a plot $\Delta_{\text{mix}}G_{\text{m}}$ against x_{B} must be constant and equal to zero over the composition region where the critical phenomenon is observed. From equation (1.9.11), it follows that

$$\frac{\partial^2[\Delta_{\text{mix}}G_{\text{m}}/(RT)]}{\partial x_{\text{B}}^2} = \frac{1}{x_{\text{A}}} + \frac{1}{x_{\text{B}}} - \frac{2c\Delta h}{RT} = 0 \tag{1.9.29}$$

$$\frac{\partial^3[\Delta_{\text{mix}}G_{\text{m}}/(RT)]}{\partial x_{\text{B}}^3} = \frac{1}{x_{\text{A}}^2} + \frac{1}{x_{\text{B}}^2} = 0 \tag{1.9.30}$$

Thus, at the critical temperature, when $x_{\text{A}} = x_{\text{B}}$,

$$\frac{c\Delta h}{RT} = 2 \tag{1.9.31}$$

At lower temperatures, this ratio is larger, and phase separation occurs.

The important feature of the above treatment, which is also known in statistical mechanics as the Bragg–Williams approximation [6], is that the molecular composition around a given molecule reflects the bulk composition. This cannot be the case in general because of the differences in intermolecular forces between the solution components. Thus, if molecule A interacts more strongly with molecule B than with itself, the local composition of B around A is higher than the average value. Recognition of this fact leads to more complex descriptions of mixing phenomena such as that based on the quasi-chemical or Bethe approximation [5]. However, as soon as one accepts that the local molecular composition is not the same as the average bulk composition, it follows that the entropy of mixing is not given by the ideal value (equation (1.9.10)) and that the solution is no longer regular. The quasi-chemical model and other models for non-ideal molecular solutions have been considered in some detail in the development of theories for molecular liquid solutions but are not considered further here.

1.10 An Empirical Approach to Non-Ideal Solutions

Most real solutions are neither *ideal* nor *regular*. As a result a realistic description of their thermodynamic properties must consider the fact that both the excess enthalpy of mixing, $\Delta_{\text{mix}}H^{\text{ex}}$, and excess entropy, $\Delta_{\text{mix}}S^{\text{ex}}$, are non- zero. Wilson [7] has proposed an empirical description of the excess thermodynamic properties of non-ideal systems which provides an excellent description on the basis of two adjustable parameters. His approach includes systems in which the component molecules have different sizes, and estimates the Gibbs energy of mixing on the basis of the local volume fractions of each component. It is presented here for the case of binary mixtures but can easily be extended to systems with more components.

Consider the solution composed of two molecules A and B. The number of A–A interactions, n_{AA}, with respect to the number of A–B interactions, n_{AB}, is given by the overall ratio of A to B in the solution weighted by factors which account for the enthalpy associated with these interactions, namely, h_{AA} and h_{AB}. Thus, one writes

$$\frac{n_{\text{AA}}}{n_{\text{AB}}} = \frac{n_{\text{A}}}{n_{\text{B}}} \frac{\exp[-h_{\text{AA}}/(RT)]}{\exp[-h_{\text{AB}}/(RT)]} \tag{1.10.1}$$

Similarly, estimating the ratio of the number of B–B interactions to A–B interactions, one obtains

$$\frac{n_{\text{BB}}}{n_{\text{AB}}} = \frac{n_{\text{B}} \exp[-h_{\text{BB}}/(RT)]}{n_{\text{A}} \exp[-h_{\text{AB}}/(RT)]} \tag{1.10.2}$$

The volume fractions of each molecule, ζ_{A} and ζ_{B}, are then defined using these ratios and the molar volumes of the two pure components, V_{mA} and V_{mB}:

$$\zeta_{\text{A}} = \frac{n_{\text{A}} V_{\text{mA}} \exp[-h_{\text{AA}}/(RT)]}{n_{\text{A}} V_{\text{mA}} \exp[-h_{\text{AA}}/(RT)] + n_{\text{B}} V_{\text{mB}} \exp[-h_{\text{AB}}/(RT)]} \tag{1.10.3}$$

and

$$\zeta_{\text{B}} = \frac{n_{\text{B}} V_{\text{mB}} \exp[-h_{\text{BB}}/(RT)]}{n_{\text{A}} V_{\text{mA}} \exp[-h_{\text{AB}}/(RT)] + n_{\text{B}} V_{\text{mB}} \exp[-h_{\text{BB}}/(RT)]} \tag{1.10.4}$$

The Gibbs energy of mixing is then assumed to be

$$\Delta_{\text{mix}}G_{\text{m}} = RTx_{\text{A}} \ln \zeta_{\text{A}} + RTx_{\text{B}} \ln \zeta_{\text{B}} \tag{1.10.5}$$

Subtracting off the Gibbs energy of mixing for the ideal solution (equation (1.6.11)), one obtains for $\Delta_{\text{mix}}G_{\text{m}}^{\text{ex}}$:

$$\Delta_{\text{mix}}G_{\text{m}}^{\text{ex}} = RTx_{\text{A}} \ln(\zeta_{\text{A}}/x_{\text{A}}) + RTx_{\text{B}} \ln(\zeta_{\text{B}}/x_{\text{B}}) \tag{1.10.6}$$

This may be rewritten as

$$\Delta_{\text{mix}}G_{\text{m}}^{\text{ex}} = -RTx_{\text{A}} \ln(1 - r_{\text{BA}}x_{\text{B}}) - RTx_{\text{B}} \ln(1 - r_{\text{AB}}x_{\text{A}}) \tag{1.10.7}$$

where

$$r_{\text{BA}} = 1 - \frac{V_{\text{mB}} \exp[-h_{\text{BB}}/(RT)]}{V_{\text{mA}} \exp[-h_{\text{AB}}/(RT)]} \tag{1.10.8}$$

and

$$r_{AB} = 1 - \frac{V_{mA}\exp[-h_{AA}/(RT)]}{V_{mB}\exp[-h_{AB}/(RT)]} \tag{1.10.9}$$

The parameters r_{AB} and r_{BA} are treated as adjustable and are chosen to obtain a good fit with the experimental data.

One may now derive expressions for the activity coefficients of the two components. On the basis of equation (1.8.10)

$$\Delta_{mix}G^{ex} = n_A RT \ln \gamma_A + n_B RT \ln \gamma_B \tag{1.10.10}$$

so that

$$\frac{\partial\left[\Delta_{mix}G^{ex}/(RT)\right]}{\partial n_A} = \ln \gamma_A + n_A \frac{\partial \ln \gamma_A}{\partial n_A} + n_B \frac{\partial \ln \gamma_B}{\partial n_A} \tag{1.10.11}$$

and

$$\frac{\partial\left[\Delta_{mix}G^{ex}/(RT)\right]}{\partial n_B} = \ln \gamma B + n_A \frac{\partial \ln \gamma_A}{\partial n_B} + n_B \frac{\partial \ln \gamma_B}{\partial n_B} \tag{1.10.12}$$

From the Gibbs–Duhem relationship (see equation (1.4.8) and associated discussion), the last two terms in equations (1.10.11) and (1.10.12) are equal to zero. It follows that the derivatives of $\Delta_{mix}G^{ex}/(RT)$ with respect to n_A and n_B give directly the activity coefficients of components A and B. Thus, differentiating equation (1.10.7) with respect to n_A and simplifying, one obtains

$$\ln \gamma_A = -\ln(1 - r_{BA}x_B) - \frac{x_A x_B r_{BA}}{1 - r_{BA}x_B} + \frac{x_B^2 r_{AB}}{1 - r_{AB}x_A} \tag{1.10.13}$$

In a similar way, the expression for $\ln \gamma_B$ is

$$\ln \gamma_B = -\ln(1 - r_{AB}x_A) - \frac{x_A x_B r_{AB}}{1 - r_{AB}x_A} + \frac{x_A^2 r_{BA}}{1 - r_{BA}x_B} \tag{1.10.14}$$

Wilson [7] demonstrated the effectiveness of this model using data for both binary and ternary systems, one example being the carbon tetrachloride–acetonitrile system. This system shows positive deviations from Raoult's law, as shown from the data for $\Delta_{mix}G_m^{ex}$ presented in fig. 1.11. Wilson [7] found that the best values of the parameters r_{BA} and r_{AB} are 0.6118 and 0.8287 at 25°C, respectively, where B refers to carbon tetrachloride and A to acetonitrile. The fitted curve is also shown in the figure, from which it is clear that there is excellent agreement between the model and experiment.

EXAMPLE

Using Wilson's parameters for the carbon tetrachloride–acetonitrile system, estimate the Raoult law activity coefficients for each component in a equimolar solution. Then estimate the molar Gibbs energy of mixing.

If acetonitrile is component A, then its activity coefficient is given by equation (1.10.13) so that

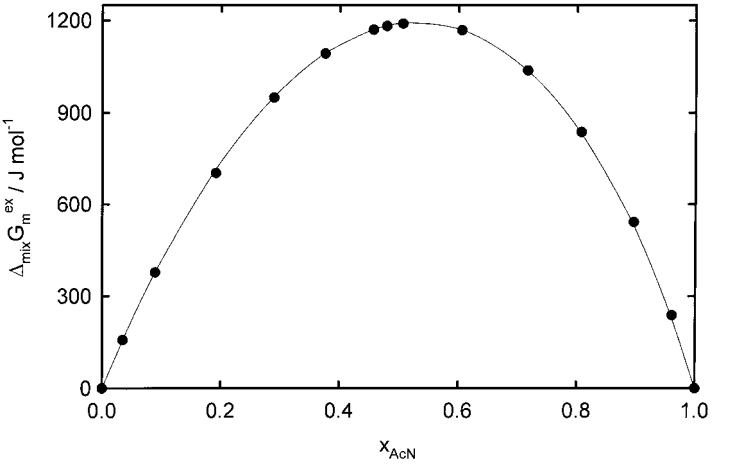


Fig. 1.11 Plot of the excess Gibbs energy of mixing for the carbon tetrachloride–acetonitrile system against the mole fraction of acetonitrile at 45°C. The points show the experimental results and the solid curve was calculated using equation (1.10.7) with the parameters given by Wilson [7] (see text).

$$\ln \gamma_A = -\ln(1 - 0.6118 \times 0.5) - \frac{0.5^2 \times 0.6118}{1 - 0.6118 \times 0.5} + \frac{0.5^2 \times 0.8287}{1 - 0.8287 \times 0.5}$$

$$= 0.3651 - 0.2204 + 0.3538 = 0.4985 \qquad (1.10.15)$$

The value of γ_A is 1.646.

Similarly, for carbon tetrachloride which is component B

$$\ln \gamma_B = -\ln(1 - 0.8287 \times 0.5) - \frac{0.5^2 \times 0.8287}{1 - 0.8287 \times 0.5} + \frac{0.5^2 \times 0.6118}{1 - 0.6118 \times 0.5}$$

$$= 0.5350 - 0.3538 + 0.2204 = 0.4016 \qquad (1.10.16)$$

The value of γ_B is 1.494.

The molar Gibbs energy of mixing is given by equation (1.8.9) so that

$$\Delta_{mix}G_m = 0.5 \times 8.3145 \times 298.2 \ln(1.646 \times 0.5) + 0.5 \times 8.3145 \times 298.2 \ln(1.494 \times 0.5)$$

$$= -603.1 \text{ J mol}^{-1} \qquad (1.10.17)$$

Equation (1.10.7) can also be used to derive expressions for the excess entropy and enthalpy functions. Differentiating this equation with respect to temperature, the expression for $\Delta_{mix}S_m^{ex}$ is

$$\Delta_{mix}S_m^{ex} = Rx_A \ln(1 - r_{BA}x_B) + Rx_B \ln(1 - r_{AB}x_A)$$

$$- \frac{RTx_Ax_B}{1 - r_{BA}x_B}\frac{\partial r_{BA}}{\partial T} - \frac{RT\,x_Ax_B}{1 - r_{AB}x_A}\frac{\partial r_{AB}}{\partial T} \qquad (1.10.18)$$

Combining equations (1.10.7) and (1.10.18), the expression for $\Delta_{\text{mix}}H_{\text{m}}^{\text{ex}}$ is

$$\Delta_{\text{mix}}H_{\text{m}}^{\text{ex}} = -\frac{RT^2\, x_{\text{A}}x_{\text{B}}}{1 - r_{\text{BA}}x_{\text{B}}}\frac{\partial r_{\text{BA}}}{\partial T} - \frac{RT^2\, x_{\text{A}}x_{\text{B}}}{1 - r_{\text{AB}}x_{\text{A}}}\frac{\partial r_{\text{AB}}}{\partial T} \tag{1.10.19}$$

The two derivatives $\partial r_{\text{BA}}/\partial T$ and $\partial r_{\text{AB}}/\partial T$ constitute two additional parameters which are obtained by fitting $\Delta_{\text{mix}}H_{\text{m}}^{\text{ex}}$ data to the model. Obviously, description of the entropy requires four parameters.

The effectiveness of Wilson's model lies in the fact that only two parameters are required to describe the Gibbs energy at a given temperature. Its weakness lies in the fact that there is no clear molecular interpretation of these parameters. Wilson's approach works for a great variety of systems but when the departures from ideality are complex, more detailed models are required. Some extensions of Wilson's work have been discussed by Renon and Prausnitz [8] but they require introduction of more adjustable parameters.

1.11 Ideally Dilute Solutions

For many solutions, it is not possible to vary the composition of the components over the whole range of mole fractions. This is obviously true of solutions made up of a solid and a liquid. For these systems it is better to choose a standard state which is based on the properties of a dilute solution. This leads to the definition of an *ideally dilute solution*. Such a system is easily defined on a molecular basis as one in which the solute molecule only comes in contact with solvent molecules, and never with another solute molecule. In the previous discussion of regular solutions it was concluded that, when the two components are of equal size, the coordination number for the other molecules around a central one is twelve. This suggests that an ideally dilute solution must have a solute mole fraction which is less than 1/13, that is, 0.08.

The above approximate guideline for an ideally dilute solution can only be made more exact by examining vapor pressure data for a specific system. The case of the methanol–water system discussed earlier is used as an illustration. For very dilute solutions, that is, when x_{MeOH} is less than 0.04, the vapor pressure of methanol is linear in its mole fraction. This is the region where Henry's law is obeyed. As the mole fraction increases, the actual vapor pressure falls below that predicted by Henry's law, quite significant deviations being found when x_{MeOH} reaches 0.1. Henry's law for component B in a two-component system of A and B may be expressed as

$$P_{\text{B}} = k_{\text{H}}x_{\text{B}} \tag{1.11.1}$$

where k_{H} is the slope of the Henry law line. Raoult law behavior is also shown in fig. 1.12. For this non-ideal system, which exhibits positive deviations from Raoult's law, the slope of the Raoult law line, which is equal to the vapor pressure of pure methanol, is much less than that for the Henry law line. It should be remembered that in the concentration range over which Henry's law holds for the solute, Raoult's law is valid for the solvent (see fig. 1.5). This fact gives one

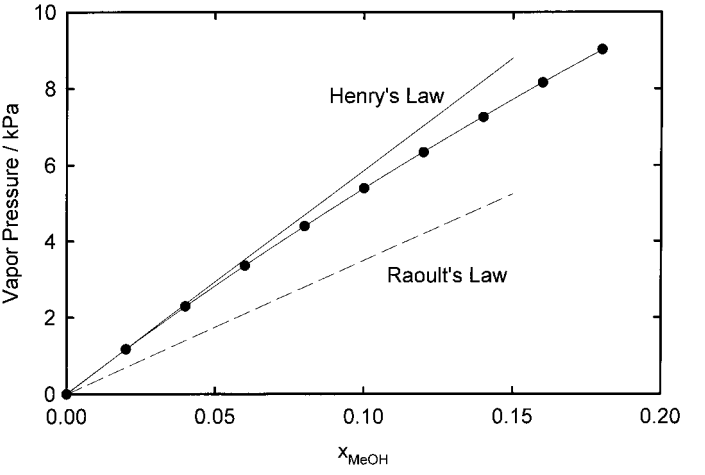


Fig. 1.12 Vapor pressure of methanol for dilute solutions of methanol in water plotted against the mole fraction of methanol. The straight line shows the vapor pressure according to Henry's law, and the broken line, that according to Raoult's law.

another convenient guideline for judging the concentration range for ideally dilute behavior.

The value of the Henry law constant and concentration range over which this law is valid depends very much on the system. This is easily seen by comparing the behavior of the methanol–water and acetonitrile–water systems (figs. 1.5 and 1.6). In the latter case ideally dilute solution behavior is observed for a lower range of mole fractions of the solute, that is, when x_{AcN} is less than 0.03.

The most important application of low concentration behavior of solutes is for solid solutes, especially electrolytes. Electrolyte solutions are examined in detail in chapter 3. Some general thermodynamic methods for describing the properties of very dilute solutions are considered in the following section.

1.12 Thermodynamics of Ideally Dilute Solutions

Just as was done previously, one develops the thermodynamic description of an ideally dilute solution by considering the equilibrium between the dilute solute component in the liquid solution and in the vapor phase. If the minority component is designated B, then one may write its chemical potential as

$$\mu_B^s = \mu_B^v = \mu_B^{v,\circ} + RT \ln P_B \tag{1.12.1}$$

Since Henry's law holds when the solution is ideally dilute, this can be rewritten as

$$\mu_B^s = \mu_B^{s,\bullet} + RT \ln x_B \tag{1.12.2}$$

where

$$\mu_B^{s,\bullet} = \mu_B^{v,\circ} + RT \ln k_H \tag{1.12.3}$$

It should be noted that $\mu_B^{s,\bullet}$ gives the standard chemical potential for the ideally dilute solute in a hypothetical system in which the mole fraction of B is unity. This is obviously a fictitious state which is impossible in reality but whose properties are obtained by extrapolating the Henry's law line to $x_B = 1$ (see fig. 1.12). When Henry's law is not obeyed, an activity coefficient γ_B^H is introduced so that the product $\gamma_B^H k_H x_B$ is equal to the vapor pressure P_B. The activity of the dilute component a_B^H is defined to be $\gamma_B^H x_B$. Thus, the general expression for the concentration dependence of μ_B^s becomes

$$\mu_B^s = \mu_B^{s,\bullet} + RT \ln a_B^H = \mu_B^{s,\bullet} + RT \ln \gamma_B^H x_B \tag{1.12.4}$$

where γ_B^H is the Henry's law activity coefficient on the mole fraction scale.

Because of the inconvenient nature of the standard state defined above, the concentration units used to describe the concentration dependence of the chemical potential are usually different. More convenient choices for concentration are molality and molarity. When the solution is dilute the relationship between mole fraction and molality is quite simple (see equation (1.2.3)). In terms of molality, the expression for the concentration dependence of the chemical potential of component B becomes

$$\mu_B^s = \mu_B^{s,\bullet} + RT \ln m_B \tag{1.12.5}$$

where

$$\mu_B^{s,\bullet} = \mu_B^{v,\circ} + RT \ln\left(\frac{k_H M_A}{1000}\right) \tag{1.12.6}$$

and M_A is the molecular weight of the solvent. Now, the standard chemical potential is that for a hypothetical system which obeys Henry's law for a solute concentration of 1 *m*. For the methanol–water system, x_B is equal to 0.018 at this concentration. Not only is this a dilute solution by the criteria that have been discussed here, but it is also a system which approximately obeys Henry's law on the basis of the data shown in fig. 1.12. It should be emphasized that this will not always be the case, significant departures from Henry's law being observed for very low concentrations for some systems, for example, acetonitrile–water mixtures.

When the dilute system does not obey Henry's law, one introduces an activity coefficient as above to correct to the experimentally observed value. Thus, in general, one may write

$$P_B = \frac{\gamma_B^H k_H M_A}{1000} m_B \tag{1.12.7}$$

where γ_B^H is the Henry's law activity coefficient for component B on the molality scale. Then, on the basis of equation (1.12.1), the chemical potential of component B may be written

$$\mu_B^s = \mu_B^{s,\bullet} + RT \ln a_B^H = \mu_B^{s,\bullet} + RT \ln \gamma_B^H m_B \tag{1.12.8}$$

where a_B^H is the activity of B on the molality scale with the standard state defined according to Henry's law (equation (1.12.6)).

Alternatively, one may use molarity as the concentration unit. In this case, one must know the density of the solution to order to relate mole fraction to molarity. For very dilute solutions, using equation (1.2.5), the concentration dependence of the chemical potential is given by

$$\mu_B^s = \mu_B^{s,\bullet} + RT \ln c_B \tag{1.12.9}$$

where

$$\mu_B^{s,\bullet} = \mu_B^{v,\circ} + RT \ln \frac{k_H M_A}{1000 \rho_A} \tag{1.12.10}$$

ρ_A being the density of the solvent. When the system does not obey Henry's law, one introduces an activity coefficient, γ_B^H which is the multiplicative correction factor required to make the vapor pressure of B predicted by Henry's law equal to that observed experimentally. Thus, γ_B^H is defined by the equation

$$P_B = \frac{\gamma^H k_H M_A}{1000 \rho_A} c_B \tag{1.12.11}$$

and the expression for the concentration dependence of μ_B^s becomes

$$\mu_B^s = \mu_B^{s,\bullet} + RT \ln a_B^H = \mu_B^{s,\bullet} + RT \ln \gamma_B^H c_B \tag{1.12.12}$$

EXAMPLE

Carbon–tetrachloride–benzene solutions can be regarded as regular with an enthalpy parameter $c\Delta h$ equal to 324 J mol^{-1} at 25°C. Given that the vapor pressure of pure carbon tetrachloride is 14.13 kPa, determine the Henry's law constant for this component by examining its vapor pressure at mole fractions in the range 0.001 to 0.1. Then estimate the Henry's law activity coefficient at a mole fraction of 0.1 on the mole fraction and molality scales.

From the theory for regular solutions, the Raoult law activity coefficient for component B in a solution of A and B is

$$\ln \gamma_B^R = \frac{c\Delta h x_A^2}{RT} \tag{1.12.13}$$

Values of γ_B^R were estimated for values of x_B in the range 0.001 to 0.005 and are recorded in the following table. Then, the partial pressure of B (carbon tetrachloride) was estimated using the relationship

$$P_B = \gamma_B^R P_B^\circ x_B \tag{1.12.14}$$

Finally, the ratio P_B/x_B was also calculated.

x_B	γ_B^R	P_B / Pa	$P_B/100x_B$	m_B
0.001	1.139	16.1	161	0.013
0.002	1.139	32.1	161	0.026
0.003	1.139	48.3	161	0.039
0.004	1.138	64.4	161	0.051
0.005	1.138	80.4	161	0.064

It is clear from these results that the Henry's law constant is 16,100 Pa.

At $x_B = 0.1$, P_B is equal to 1571 Pa. Henry's law predicts that P_A is 1610 Pa. Therefore, the Henry's law activity coefficient is 0.976.

The molality is easily calculated from the mole fraction using the relationship

$$m_B = \frac{1000 x_B}{M_A x_A} \tag{1.12.15}$$

where M_A is the molecular mass of benzene (78.1). Values of the molality for the dilute solutions are also recorded in the table. The Henry's law constant on this scale is 1253 Pa kg mol^{-1}. A mole fraction of 0.1 in carbon tetrachloride corresponds to a molality of 1.42 m. Thus, the predicted vapor pressure by Henry's law is 1780 Pa. As a result the Henry's law activity coefficient is 0.883.

On the basis of the above, the definitions of the standard state (equations (1.12.3), (1.12.6), and (1.12.10)) and of the activity coefficient γ_B^H (equations (1.12.4), (1.12.7), and (1.12.11)) depend on the choice of concentration units used for the dilute solution component. It is emphasized that one must always state the concentration units in defining these two quantities. This point is further illustrated in table 1.4, where activity coefficients for the components in dilute aqueous solutions of methanol are tabulated. Notice first of all that the molality of methanol has reached 6.2 m when the mole fraction is 0.1. This is due to the difference between the molecular mass of water (18 g) and that of methanol (32 g). On the basis of the Raoult law activity coefficients the behavior of water is ideal over most of this concentration range, the activity coefficient being 1.000 to four

Table 1.4 Raoult Law and Henry Law Activity Coefficients for Dilute Solutions of Methanol in Water at 40°C

Methanol Concentration		Activity Coefficients			
		Raoult's Law		Henry's Law*	
x_{MeOH}	m_{MeOH} /mol kg^{-1}	γ^R_{MeOH}	γ^R_w	γ^H_{MeOH} (x = s.s)	γ^H_{MeOH} (m = s.s)
0.0001	0.006	1.7054	1.000	1.000	1.000
0.0002	0.011	1.704	1.000	1.000	1.000
0.0005	0.028	1.704	1.000	1.000	1.000
0.001	0.056	1.704	1.000	1.000	1.000
0.002	0.111	1.702	1.000	0.999	1.000
0.005	0.279	1.696	1.000	0.996	0.997
0.01	0.561	1.687	1.000	0.990	0.987
0.02	1.133	1.669	1.000	0.979	0.967
0.05	2.921	1.618	1.001	0.949	0.908
0.1	6.167	1.539	1.005	0.903	0.819

*The first column gives the Henry law activity coefficient for methanol on the basis of a standard state of $x_{MeOH} = 1$ and the second on the basis of a standard state of $m_{MeOH} = 1$.

significant figures up to a mole fraction of 0.02. At the same time, the behavior of methanol with respect to Raoult's law is non-ideal over the range considered. Since deviations from ideal behavior are positive (see fig. 1.5), the Raoult law activity coefficient for methanol is greater than one; in addition, it changes significantly in this concentration range, decreasing steadily in magnitude as the mole fraction increases. On the other hand, the values of γ^{H}_{MeOH} are unity at the lowest concentrations in the region where Henry's law holds. As concentration increases, these activity coefficients fall below unity and differ according to the choice of standard state. By multiplying the concentration in particular units by the appropriate activity coefficient, one obtains the Henry law activity. For instance when $x_{MeOH} = 0.1$, the activity of methanol on the mole fraction scale is 9.90×10^{-3}. On the molality scale, the activity is 0.554 mol kg^{-1} of water. By multiplying the latter quantity by $M_A/1000$, that is, 0.018 kg mol^{-1} for water, one obtains approximately the activity on the mole fraction scale (see equation (1.2.3)).

The results recorded in table 1.4 emphasize the necessity of clearly stating the standard conditions for defining activity coefficients in liquid solutions. As stated above, the molality scale is preferred to the mole fraction scale for most systems, especially those which are not miscible over the whole composition range. The molality scale is preferred over the molarity scale because the definition of solution concentration is independent of temperature and pressure. On the other hand, the molarity concentration scale is so popular in chemistry that one often finds activity coefficients also recorded in the literature using a Henry's law scale on the basis of molarity. This is especially true of electrolyte solutions, which are always non-ideal. When one recognizes that the majority of solutions involve solid solutes, the importance of the Henry's law definition of the standard state becomes clear. These solutes usually have a negligible vapor pressure for the conditions that the solutions are used. Thus, a question arises regarding determination of the activity of non-volatile solutes. This is dealt with in the following section.

1.13 Experimental Determination of Solution Activities

In order to determine the activity of a component in solution, one must measure its vapor pressure. In the case of volatile liquids such as those discussed in most of this chapter, vapor pressure measurement is not a problem so that very accurate determination of activity is possible over the whole composition range for which a solution is formed. However, many solutes, for example, most solids, have negligible vapor pressures. Under these circumstances, one makes use of the Gibbs–Duhem relationship between the activities of the two-components in solution. Since the vapor pressure of the solvent can be measured, its activity can be determined, and then used to estimate the activity of the solute.

On the basis of equation (1.4.28), for any infinitesimal change in a two-component system, one may write

$$dG_m = x_A d\mu_A + \mu_A dx_A + x_B d\mu_B + \mu_B dx_B \tag{1.13.1}$$

From the first and second laws of thermodynamics for this system (equation (1.3.21)), one has

$$dG_m = -S_m dT + V_m dP + \mu_A dx_A + \mu_B dx_B \tag{1.13.2}$$

Therefore, in general, one may write

$$S_m dT - V_m dP + x_A d\mu_A + x_B d\mu_B = 0 \tag{1.13.3}$$

and at constant temperature and pressure

$$x_A d\mu_A + x_B \, d\mu_B = 0 \tag{1.13.4}$$

This is the form of the Gibbs–Duhem equation needed to relate the activity of component B in solution to that of component A. Choosing the Raoult law activity for the solvent A, and the Henry law activity for the solute B, equation (1.13.4) may be rewritten as

$$d\left(\ln a_B^H\right) = -\frac{x_A}{x_B} d(\ln a_A^R) \tag{1.13.5}$$

In the limit of very dilute solutions, both activity coefficients approach unity so that the activity of A can be replaced by x_A, and the activity of B by its molality (assuming that one has chosen molality as the concentration unit). However, as x_B becomes very small the ratio x_A/x_B becomes very large. Thus, in practice, one may not choose the infinitely dilute solution as a reference point but instead a very dilute solution for which Henry's law is valid. Then, integrating equation (1.13.5) between this very dilute concentration designated m_1, to any other concentration m_2, one obtains

$$\ln a_B^H = \ln \gamma_B^H m_2 = \ln m_1 - \int_1^2 \frac{x_A}{x_B} d\left(\ln a_A^R\right) \tag{1.13.6}$$

An example of application of the Gibbs–Duhem relationship to determination of the activity coefficients of sucrose in aqueous solutions is shown in table 1.5. Sucrose ($C_{12}H_{22}O_{11}$) has a very high molecular mass (342 g) compared to water so that solutions with very low solute mole fractions have relatively high molalities. By measuring the water vapor pressure as a function of sucrose concentration down to very low concentrations, one is able to determine its activity coefficient and thus its activity on the Raoult law scale. It should be noted that the vapor pressure of water begins to depart from ideal behavior at a quite low sucrose mole fraction (0.005). By carrying out the integration defined by equation (1.13.6) one is able to calculate the Henry's law activity for sucrose and, thus, the activity coefficients given in table 1.5.

It should be noted that the values of γ^H quickly become non-unity and are greater than one. This is indicative of strong attractive solute–solvent interactions and negative deviations from Raoult law behavior. In the case of the methanol–water system for which positive deviations from Raoult's law is observed (table 1.4), the Henry law activity coefficients are less than one.

The above procedure for determining activity coefficients for solid solutes is often applied to electrolytes. This important class of solutes always behaves non-ideally. The properties of electrolyte solutions are considered in detail in chapter 3.

Table 1.5 Activity Coefficient Data for Sucrose and Water as Determined from Water Vapor Pressure Measurements for Their Solutions at 25°C

Concentration of Sucrose		Activity Coefficients	
Mole Fraction	Molality /mol kg^{-1}	Water (Raoult's Law) γ_w^R	Sucrose (Henry's Law) γ_s^H
1×10^{-4}	5.6×10^{-3}	1.000	1.000
1×10^{-3}	0.056	1.000	1.001
5×10^{-3}	0.279	0.9999	1.042
0.02	1.134	0.998	1.206
0.04	2.315	0.990	1.52
0.07	4.182	0.968	2.15
0.1	6.173	0.939	2.91

1.14 Concluding Remarks

The material in this chapter explains the relationship between the concentration of a solution component and its activity. The activity is monitored through the vapor pressure of the components, which are volatile for most of the examples considered. Thus, it is very easy to understand why the activity of a given component can also be defined as its *escaping tendency*. It is obvious from the fact that most solutions are non-ideal that the relationship between activity and concentration is not simple. When the solution is very dilute, Henry's law holds for the solute and Raoult's law for the solvent. Then the activity is proportional to the concentration over a finite concentration range which must be determined for each system.

A review of chemical thermodynamics, especially as it relates to the properties of liquid solutions, has also been presented. Partial molar quantities such as the chemical potential are an important feature of the treatment of this subject. It is often the case that the activity and chemical potential of one quantity is relatively easy to determine directly by experiment, whereas that of another component is not. Under these circumstances, the change in chemical potential of one component can be related to that of another through the Gibbs–Duhem equation. This relationship and its use in estimating thermodynamic properties are extremely important in solution chemistry.

Two simple models for non-ideal solutions have been discussed. These are the Hildebrand–Guggenheim model for regular solutions, and Wilson's empirical approach to non-ideal solutions. They give the flavor of the subject but represent only a very small fraction of the theoretical work done in this area. The extension of the model for regular solutions using the quasi-chemical approximation was mentioned earlier. In this way, the approximation that the distribution of molecules is random in solution is relaxed. Another subject which has been examined in detail in the literature is solutions with strong association. This association is often due to hydrogen bonding and therefore is important in understanding the properties of solutions formed with water and the alcohols. Polymer solutions

have also been considered and their thermodynamic properties derived. More details regarding this subject and an introduction to the original literature in this field can be found in the monographs by Prigogine [9] and Marcus [10].

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Problems

1. The density of $LiClO_4$ solutions in dimethylsulfoxide at 25°C is given by

$$\rho = 1.0965 + 6.204 \times 10^{-2}c$$

where ρ is the density in g $mL^{-1}$and c, the concentration of $LiC1O_4$ in M. Calculate the molality and mole fraction of the solute for solutions with concentrations of 0.1, 0.2, and 0.5 M.

2. The following density data are reported for the carbon tetrachloride–acetonitrile system at 25°C.

Mole Fraction Acetonitrile	Density /g mL^{-1}
0	1.5844
0.1657	1.5066
0.3145	1.4248
0.4406	1.3441
0.5498	1.2640
0.6473	1.1827
0.7348	1.1003
0.8113	1.0194

0.8797	0.9390
0.9430	0.8575
1.0000	0.7766

Calculate the excess molar volume for the solution and partial molar volumes of the two components at mole fractions equal to 0, 0.2, 0.4, 0.6, 0.8, and 1.0. Use the appropriate numerical interpolation and differentiation techniques (see appendix C).

3 The following results are reported for the carbon tetrachloride–acetonitrile system at 45°C.

Mole Fraction CCl_4		Total Vapor Presure
Liquid	Vapor	/kPa
0	0	27.783
0.0347	0.1801	33.062
0.1914	0.4603	44.796
0.3752	0.5429	48.604
0.4790	0.5684	49.274
0.6049	0.5936	49.466
0.8069	0.6470	48.362
0.9609	0.8001	41.908
1.000	1.000	34.501

Use an interpolation method to obtain the values of the mole fraction of CCl_4 in the vapor and the total vapor pressure for values of the mole fraction in the liquid phase equal to 0.2, 0.4, 0.6, and 0.8. Then calculate the vapor pressure and the activity coefficient of each component for the same values. Finally estimate the molar Gibbs energy of mixing on the Raoult law scale at these four points.

4. The following data are reported for the molar enthalpy of mixing for the system discussed in question 3.

Mole Fraction of CCl_4 Liquid	$\Delta_{mix}H_m$ /J mol^{-1}
0	0
0.128	414
0.317	745
0.407	862
0.419	858
0.631	930
0.821	736
1.0	0

Determine the value of $\Delta_{mix}H_m$ at x_{CCl_4} equal to 0.2, 0.4, 0.6, and 0.8. Combine these data with those obtained in question 3 to prepare a plot of $\Delta_{mix}G_m$, $\Delta_{mix}H_m$, and $T\Delta_{mix}S_m$ against x_{CCl_4}.

5. Calculate the excess Gibbs energy, entropy, and enthalpy of mixing for the carbon tetrachloride–acetonitrile system discussed in questions 3 and 4. Prepare a plot of these data and compare the results with those obtained in the previous question.

6. The following data are available for solutions of acetone and chloroform at 50°C.

Mole Fraction of Acetone		Total Pressure
Liquid	Vapor	/kPa
0	0	69.5
0.10	0.071	66.0
0.20	1.165	63.2
0.30	0.279	61.7
0.38	0.380	61.1
0.40	0.408	61.3
0.50	0.550	62.5
0.60	0.684	65.2
0.70	0.789	68.1
0.80	0.890	72.0
0.90	0.955	76.8
1.00	1.000	81.6

Calculate the Raoult law activity coefficients of both components and plot them as a function of the mole fraction of acetone. Determine the range of composition with respect to acetone that the solution can be regarded as regular. Calculate the enthalpy parameter for acetone–chloroform interactions on the basis of a one-parameter least-squares fit of the data in this range using an appropriate plot.

7. J. J. Van Laar gave a useful semiempirical equation for the molar excess Gibbs energy of solutions,

$$\Delta_{\text{mix}}G_{\text{m}}^{\text{ex}} = \frac{b_{12}x_1x_2}{b_1x_1 + b_2x_2}$$

where b_{12}, b_1, and b_2 are characteristic constants. Show that the Van Laar relation implies that

$$\left(\frac{1}{\ln \gamma_1}\right)^{1/2} = \frac{\sqrt{A_{12}}}{B_{12}}\frac{x_1}{x_2} + \frac{1}{\sqrt{A_{12}}}$$

$$\left(\frac{1}{\ln \gamma_2}\right)^{1/2} = \frac{\sqrt{B_{12}}}{A_{12}}\frac{x_2}{x_1} + \frac{1}{\sqrt{B_{12}}}$$

where $A_{12} = b_{12}/(b_2RT)$ and $B_{12} = b_{12}/(b, RT)$

8. The following vapor pressure data are found for methanol–water solutions at 40°C.

xMeOH	P_{MeOH}/kPa
0.04	2.1
0.08	4.3
0.12	6.4
0.2	9.9
0.4	17.2
0.6	23.3
0.8	29.3
1.0	36.0

Calculate the Raoult law and Henry law activity coefficients for methanol on the mole fraction scale.

2

The Structure of Liquids

Douglas James Henderson

Douglas (Doug) Henderson was born in Calgary, Alberta, Canada in 1934. He grew up in Vancouver, British Columbia and attended the University of British Columbia where he obtained a bachelor's degree in mathematics in 1956. Henderson then went to the University of Utah in Salt Lake City to work with Henry Eyring on the theory of liquids. He obtained his Ph.D. in physics under Eyring's direction in 1961. After leaving graduate school he held faculty positions at universities in both the United States and Canada. During 1966–67, Henderson was an invited scientist at the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Melbourne, Australia. There he began a long and very successful collaboration with John Barker. One of the major results of their work was the perturbation theory of liquids, some of which was outlined in *Reviews of Modern Physics* in 1976 in their well-known paper "What is liquid? Understanding the states of matter" [1]. Barker and Henderson moved together to the IBM Almaden Research Center in San Jose, California as research scientists in 1969. Henderson's research interests in the statistical mechanics of condensed phases involve many aspects, an important one in recent years being the electrical double layer. He was instrumental in bringing our understanding of interfacial phenomena at polarizable interfaces beyond the primitive level. He is currently professor of chemistry at Brigham Young University in Provo, Utah. His career is noteworthy for the international collaborations which he has established in many countries where research in statistical mechanics is carried out. He has published over 400 papers in this area. In addition, he has won numerous awards for his scientific work, the most recent being the Hildebrand Award of the American Chemical Society in 1999 for his work on the structure of liquids.

2.1 What Is a Liquid?

It is well known from studies of the properties of matter that the liquid state is much more complex than either the gaseous or solid states. Studies of the properties of gases quickly lead to the ideal gas law, which describes the properties of real gases at low pressures and high temperatures. This success is clearly due to

the fact that the molecules in a dilute gas are far from one another so that the effects of intermolecular forces and of the finite volume occupied by the gas molecules are negligible. As the pressure of a gas is increased and its temperature lowered, the effects of non-ideality become apparent, and the equation of state becomes more complex. These changes are those required to convert the gas to a liquid. As the molecules come closer together, the influence of intermolecular forces becomes greater and the free volume available for the gas molecules is significantly reduced because of the space occupied by the molecules themselves. The statistical mechanical description of a gas relies upon the concept that the molecules are in constant movement with trajectories determined by collisions with the walls of the container and with other molecules. The probability of finding another molecule in the immediate vicinity of a given molecule is extremely low and does not vary significantly with distance from the reference molecule.

On the other hand, solids are characterized by a very ordered structure in which each ion or molecule is surrounded by a fixed number of neighbors whose nature and orientation are determined by the interparticle forces in the crystal. These may be chiefly ion–ion interactions, as in an ionic crystal, or intermolecular forces, as in a molecular crystal. Because of the high state of order in crystals it is a reasonably straightforward problem to calculate their thermodynamic properties on the basis of quite simple statistical mechanical models.

One way of conceptualizing a liquid is as a very disordered solid. If one disrupts the structure of the nearest neighbors around a reference molecule in a molecular crystal, the effect of the disruption extends quite far. As a result, there is some local order around the reference point but the extent of order falls off rapidly with distance so that at distances equivalent to four or five molecular diameters the system does not possess order with respect to the reference point. Theories of the liquid state based on an approach involving disordered solids were pursued from the 1930s to the 1960s but did not meet with much success. On the other hand, the liquid may be regarded as an extremely imperfect gas. In this approach, which has been quite successful, the statistical mechanical techniques used to describe the properties of non-ideal gases are extended to liquids.

Considerable advances have been made since the 1950s in developing the theory of liquids [G1, G2]. The purpose of this chapter is to give an introduction to this subject, outlining the main theoretical and experimental topics. Rigorous development of the theory is not possible without appealing to more sophisticated mathematics. However, an understanding of the basic concepts involved in this subject is helpful, not only in reading further in the area of liquid structure, but also in developing the other topics considered in this monograph.

Liquids may be classified according to the intermolecular (or interatomic) forces existing between the components. In this way, seven different kinds of liquids may be identified:

1. The simplest liquids are those formed by the inert gases, He, Ne, Ar, etc. These atoms interact via van der Waals forces and strongly repel each other at short interatomic distances.

2. Homonuclear diatomic molecules such as H_2, N_2, and Cl_2 form the second group. They are similar to the first in that they do not possess a dipole moment but have electrical quadrupole moments and are not spherical.
3. Liquid metals such as Hg make up the third group. Because of the mobility of electrons in metals, these systems have long-range coulombic forces, and are "softer" with respect to short-range repulsive forces. In addition, electrical screening effects are important in liquid metals.
4. Molten salts are systems in which the components are ions but which are electrically neutral on a local scale. Coulombic forces are long range in molten salts and electrical screening is important. The complexity of these systems depends on the nature of the ions, that is, whether they are monoatomic or polyatomic. For polyatomic ions, other electrostatic forces may be involved.
5. Aprotic polar liquids such as dimethyl sulfoxide and acetonitrile make up another group. These molecules have high dipole moments, so that dipole–dipole interactions are an important part of the description of intermolecular forces.
6. Another group is composed of protic polar liquids such as water and the alcohols. In these systems, hydrogen bonding adds a further complication to the description of intermolecular forces.
7. Finally, non-polar molecular liquids, such as carbon tetrachloride and the hydrocarbons, form a group. Many of these systems possess no permanent dipole moment so that the intermolecular forces are similar to those existing in simple atomic liquids such as liquid argon. However, internal modes of motion are important in describing the properties of the molecular liquid.

Chemists are obviously concerned mainly with liquids in the last three groups. However, they are the most difficult to model from the point of view of theory. Much of the theoretical effort has been directed to understanding the properties of the simplest liquids, namely, the inert gases. In the following sections, the statistical mechanical approach developed to understand liquid properties is outlined. The purpose of this subject is to establish a connection between the properties of the individual atoms or molecules in the liquid and the bulk properties of the system. An important part of this development is the experimental study of liquid structure which is also outlined in the following discussion.

2.2 The Statistical Thermodynamics of Liquids

Statistical thermodynamics uses statistical arguments to develop a connection between the properties of individual molecules in a system and its bulk thermodynamic properties. For instance, consider a mole of water molecules at 25°C and standard pressure (1 bar). The thermodynamic state of the system has been defined on the basis of the number of molecules, the temperature, and the pressure. In order to relate the macroscopic thermodynamic properties such as U, G, H and A to the properties of the individual molecules, one would have to solve the Schrödinger wave equation (SWE) for a system composed of 6×10^{23} interacting water molecules. This is an impossible task at present but if it were possible, one would obtain a wave function, Ψ_j, and an energy, ϵ_j, for the system. Moreover,