



Dense Phase Carbon Dioxide

FOOD AND PHARMACEUTICAL APPLICATIONS

EDITED BY **MURAT O. BALABAN** | **GIOVANNA FERRENTINO**



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Food and Pharmaceutical Applications

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Preface

There are social evolutionary theories that propose that a critical factor in the progress and advancement of human societies was, is, and will be the production of, and access to, adequate food supplies. Despite the accelerating increase in the internationalization of food trade, the supply chain is far from perfect. Improvement in the production, processing, storage, and distribution of food is still an unfinished business.

Yet consumers worldwide are becoming more sophisticated and knowledgeable. Foods that used to be local or regional are now coming to be known worldwide. Consumers demand more, and expect more. Safe food is the primary expectation, but still people all over the world experience food poisoning with unacceptable human and economic consequences. Consumers also demand and expect “better” foods. Quality expectations in terms of nutritional value and sensory attributes are getting more stringent. At the same time, there is fierce competition in the marketplace with thousands of new products being introduced every year, and thousands failing and being replaced. This creates serious economic pressures to reduce cost, to increase production, processing, and distribution efficiency, and to optimize their integration. On top of all this, there is a growing concern about the effect of human activities, including agriculture and food production, on the environment, with its consequences on the sustainability of these endeavors.

This is a complex scene where the players (the food industry, regulatory agencies, scientists, and consumers) have sometimes cooperating and sometimes adversarial roles. Yet, our overall objectives are the same: to provide a safe, excellent-quality (in terms of nutritional value and sensory properties), affordable, convenient, optimally distributed, readily available, and sustainable food supply.

In this complex, sometimes conflicting, and ever-changing environment, the introduction of new technologies, new methods, and new products is becoming even more challenging. The food industry, with its dependence on volume sales and its small profit margin, is conservative and reluctant to change. Yet the changing needs of the marketplace, and increasing and conflicting pressures from consumers, are felt best by the industry. The increasing adoption of nonthermal technologies is therefore an indication that they fulfill a need, a niche in the marketplace.

Dense phase carbon dioxide (DPCD) is a nonthermal method of food processing. Its application is quite different from, for example, supercritical extraction with CO₂. In extraction, the typical solubility of materials in CO₂

is in the order of 1%. This requires large volumes of CO₂ to be used. In contrast, processing with DPCD requires much less CO₂. The typical solubility of CO₂ in many types of liquid foods is in the order of 5%. Even if more CO₂ was added, the excess would not dissolve and therefore would not be effective in, for example, microbial reduction or enzyme inactivation. The pressures used are at least one order of magnitude less than those typically used in ultra-high pressure (UHP) processing. There is no noticeable temperature increase with DPCD due to pressurization. The small weight percentage of CO₂ used assures this. The typical process temperatures are less than 40°C.

DPCD temporarily reduces the pH of the liquid foods with effects on microorganisms and enzymes. Because oxygen is removed from the environment, and because temperature is not high during the short process time (typically about 5 min in continuous systems), nutrients, antioxidant activity, and vitamins are preserved much better than in the case of thermal treatments. The economics of the operation have been studied, and look promising. Although the capital and operating costs are still higher than those of thermal treatments, they are much lower than those of other nonthermal technologies (e.g., UHP operations).

With all its potential for safe foods without nutrient or quality loss, DPCD still has not achieved commercial operation status. A significant number of scientific publications demonstrate its effectiveness against microorganisms and enzymes, and the rate of increase of publications is accelerating. Some of those recent publications are excellent reviews of the technology and its applications. Yet there has been no book that brought together this increasing body of knowledge. This book benefits from the experience and knowledge of individual and groups of international scientists and members of the industry. The editors are indebted to the contributors: the book could not have become a reality without their expertise, experience, and willingness to contribute to this effort.

On behalf of all authors, the editors hope that this book would benefit researchers working in the area of DPCD, and in other nonthermal or traditional technologies with the potential to be used in conjunction with DPCD. We also hope that the industry, the regulatory agencies, and, most importantly, consumers would find interesting and useful information in the book. We believe that DPCD will find its niche in the safe and minimal processing of foods, and will take its place among other commercial nonthermal food- and pharmaceutical-processing operations.

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1

Introduction to Dense Phase Carbon Dioxide Technology

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Abstract: The introduction aims to bring together accumulated knowledge in the areas of supercritical and dense phase CO₂ technology. A summary is given of the areas covered by the book's chapters. Recognized experts in their fields discuss the following topics: solubility of CO₂ in liquids; the effects of supercritical and dense phase CO₂ on microorganisms, including vegetative cells and spores; the application of supercritical and dense phase CO₂ on juices, beverages, and dairy products; progress in the use of pressurized CO₂ in pharmaceuticals. Finally an outlook regarding the future of the technology is presented.

Keywords: overview; dense phase; carbon dioxide; nonthermal processing.

Nonthermal technologies have gained increasing importance in recent years as potentially valuable processes to replace or complement the traditional technologies, currently used for preserving foods and other biological materials. Traditionally, many foods are thermally processed by subjecting them to a temperature range from 60°C to more than 100°C for few seconds to several minutes (Jay 1992). During thermal treatments, heat transferred to the food kills vegetative cells of microorganisms, yeast, and molds, and also inactivates spores depending on the severity of the applied conditions. This process also inactivates many undesirable enzymes in foods that cause quality loss. However, thermal treatment may cause unwanted reactions leading to undesirable changes or formation of by-products in the food.

Thermally processed foods can undergo organoleptic changes and a cooked flavor accompanied by a loss of vitamins, essential nutrients, and flavors.

Increased consumer demand for safe, nutritious, fresh-like food products with a high organoleptic quality and an extended shelf life resulted in the concept of preserving foods using nonthermal methods.

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During nonthermal processing, the temperature of the food is held below temperatures normally used in thermal processing. Therefore, the quality degradation expected from high temperatures is reduced and some vitamins, essential nutrients, and flavors are expected to undergo minimal or no changes (Barbosa-Cánovas 1998). High hydrostatic pressure (HHP), dense phase carbon dioxide (DPCD), oscillating magnetic fields, high-intensity pulsed electric fields, intense light pulses, irradiation, cold plasma, chemicals, biochemicals, and hurdle technology are some of the possibilities in the area of nonthermal technologies. Compared to traditional techniques, these avoid drawbacks such as loss of flavors and nutrients, production of undesirable side reactions, as well as changes in physical, mechanical, and optical properties of the food treated.

The use of dense phase carbon dioxide (DPCD) has been proposed as an alternative nonthermal pasteurization technique for foods (Spilimbergo *et al.* 2002), for the first time in the 1950s by Fraser (1951) and Foster *et al.* (1962) who reported the disruption of bacterial cells by the rapid decompression of carbon dioxide (CO₂) from a pressure of 500 lbf/in² (about 3.45 MPa) to ambient pressure. DPCD involves mostly the supercritical state of CO₂, but may also involve subcritical gases and sometimes liquids under pressure. In the DPCD technique, food is contacted with (pressurized) sub- or supercritical CO₂ for a certain amount of time in batch, semibatch, or continuous equipment. The DPCD technique presents some advantages over HHP due to its milder process conditions. The pressures applied are much lower (generally <30 MPa) compared to those used in HHP (300–1200 MPa). In addition, capital expenditure is considerably lower. In 1969 Swift & Co. (Chicago, IL) obtained the first US patent for food product pasteurization with CO₂ at “super atmospheric” pressure. Since 1980, others demonstrated the bacteriostatic action and inhibitory effect of CO₂ on the growth and metabolism of some microorganisms. *Pseudomonas* was found to be very sensitive while other types, such as *Lactobacillus* and *Clostridium*, were less sensitive. However, it was with the work published by Kamihira *et al.* (1987) that the inhibitory effect of CO₂ under pressure started to be addressed systematically. These authors tested the sterilizing effect of CO₂ in supercritical, liquid and gaseous phase on wet and dry *Escherichia coli*, *Staphylococcus aureus* and conidia of *Aspergillus niger* by using a supercritical fluid extraction apparatus. Since then, many studies investigated the effects of CO₂ on pathogenic and spoilage organisms, vegetative cells and spores, yeasts and molds, and enzymes. It has been proven that this technique can be considered a cold pasteurization method that affects microorganisms and enzymes, using CO₂ under pressures below 50 MPa without exposing foods to the adverse effects of heat. Thus foods retain their physical, nutritional and sensory qualities.

DPCD pasteurization of liquid foods is operational and almost ready to be employed on a commercial scale. Most of the commercialization efforts

have been performed so far by Praxair Inc. (Burr Ridge, IL, US). Based on the technology, licensed from the University of Florida (Balaban *et al.* 1995; Balaban 2004a, b), Praxair developed a continuous process system which utilizes the DPCD as a nonthermal process alternative to thermal pasteurization (Connery *et al.* 2005). This system has been registered under the trademark "Better Than Fresh (BTF)." Praxair constructed four mobile BTF units for processing about 1.5L/min of liquid foods for demonstration purposes. In addition, a commercial-scale unit of 150L/min has also been constructed (Connery *et al.* 2005) and tested in an orange juice-processing plant in Florida. For the continuous treatment of liquid foods, pilot-scale equipment was also manufactured by Mitsubishi Kakoki Co. (Tokyo, Japan) on behalf of and according to the patents owned by Shimadzu Co. (Kyoto, Japan) (Osajima *et al.* 1997, 1999a, b). This equipment consisted of a vessel of 5.8L through which CO₂ and liquid foodstuff were simultaneously pumped at maximum flow rates of 3.0kg/h and 20kg/h, respectively. In 2003, the apparatus was made available only to research laboratories in Japan (private communication, Shimadzu Belgium). At the moment, we have no information available on further commercialization efforts of Shimadzu in the field of DPCD processing for liquid foods. On the basis of their own patent (Sims 2000), PoroCrit LLC (Berkeley, CA, US) also developed a membrane contactor consisting of several hollow-fiber membrane modules for the continuous DPCD pasteurization of liquid foods, mainly beverages, juices, milk, and wine.

As for all non-thermal technologies, the most important issue involved in the commercialization of DPCD process is the regulatory approval. Foods processed thermally or nonthermally must comply with the safety regulations set forth by the US Food and Drug Administration prior to being marketed or consumed. For example, the regulations for thermally processed low-acid canned foods are contained in Title 21, Part 113 of the US Code of Federal Regulations, entitled "Thermally Processed Low-Acid Foods Packaged in Hermetically Sealed Containers." The regulations in Title 21 were established to evaluate (1) the adequacy of the equipment and procedures to perform safe processing operations, (2) the adequacy of record keeping proving safe operation, (3) justification of the adequacy of process time and temperature used, and (d) the qualifications of supervisory staff responsible for thermal-processing and container closure operations (Teixeira 1992). However, the validation of DPCD as a nonthermal method and the determination of compliance regulations necessary for commercialization are complex and challenging. The progress in the validation needs to be encouraged to address the regulatory needs in the near future.

This volume attempts to bring together the accumulated knowledge in the area of DPCD. Experts in many areas have contributed to this book regarding the following topics:

- Solubility of CO₂ in liquids, both from a thermodynamics–theoretical perspective, including models, and from an experimental approach. This is critical because the accumulated evidence points to the critical contribution of dissolved (and saturated) CO₂ to microbial inactivation.
- Effects of DPCD on microorganisms, including vegetative cells and spores; kinetics of microbial inactivation with DPCD; and inactivation of certain enzymes with DPCD. This area is very important because, first and foremost, a new technology must prove the safety of the foods that are processed using it.
- Application of DPCD on juices, beverages, and dairy products. There is a growing body of work in this area, reporting on effects on microorganisms, and especially on quality attributes and nutritional contents. If DPCD applications are to be successful, the organoleptic and nutritional quality of foods processed using DPCD must be known.
- Progress in the use of pressurized CO₂ in pharmaceuticals. This is a well-developed area, with many applications. It also opens up the exciting field of treatment of solids and powders with DPCD.
- An overview of the current technology. This chapter is written by experts in the industry, who have been involved with the design, development, and commercialization efforts of DPCD. Their hands-on views are very valuable.
- An outlook regarding the future of DPCD technology.

It is sincerely hoped that the reader will find the book valuable in bringing information, research results, and most importantly an extensive bibliography in the nonthermal field of DPCD.

2

Thermodynamics of Solutions of CO₂ with Effects of Pressure and Temperature

Sara Spilimbergo and Ireneo Kikic

Abstract: Knowledge of the thermodynamics of CO₂ solutions under pressure is fundamental to the investigation of both the inactivation mechanism and the efficiency of the process as a function of the process parameters of temperature and pressure. In order to evaluate the properties of the solutions during DPCD treatment, it is essential to have reliable high-pressure experimental data and accurate thermodynamic models over a broad range of conditions. A large number of experimental and theoretical studies have been conducted on CO₂ solubility in pure water; however, the literature lacks studies concerning the phase behavior of CO₂-water solutions or CO₂-solid components in food applications. In the present chapter, a general survey of the published knowledge concerning the thermodynamics of CO₂-water phase systems under pressure is given focusing on both the theoretical aspects and the applications, for electrolyte and non-electrolyte models.

Keywords: thermodynamic model; liquid-vapor phase equilibria; equation of state.

2.1 Introduction

The phase behaviour of the system carbon dioxide (CO₂) + water is of great industrial and scientific interest. For instance, in the petroleum industry many natural gases contain acidic gases which have to be removed, such as CO₂ and hydrogen sulphide. Another industrial application is the decontamination of wastewater streams containing dissolved acidic gases. The capture of CO₂, a greenhouse gas, has become a great concern: different storage techniques have been considered such as the storage of CO₂ in deep saline reservoirs. Also, in geochemical applications, especially in the analysis of CO₂-bearing fluid inclusions in minerals, the accurate description of solubility of CO₂ in pure-water solutions is required. Recently, the increasing attention to CO₂ processing in food applications, in particular in

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microbial inactivation of food products at low temperature compared to the traditional thermal treatments, makes the knowledge of a CO₂-water phase system under pressure fundamental to investigate both the inactivation mechanism and the efficiency of the process as a function of the operating parameters of temperature and pressure.

Therefore, it is essential to have reliable high-pressure experimental data and an accurate thermodynamic model over a broad range of conditions to evaluate the solubility in different conditions. For most of these applications, temperatures (T) up to 100°C and pressures (P) up to 100 MPa are particularly relevant.

A large number of experimental and theoretical studies have been conducted on CO₂ solubility in pure water. However, to the best of our knowledge, literature lacks studies concerning phase behaviour of CO₂-liquid solutions or CO₂-solid components in food applications. The objective of the present chapter is to give a general survey of the published knowledge concerning the thermodynamics of CO₂-water phase systems under pressure, focusing on the theoretical aspects and the applications, for both electrolyte and non-electrolyte models.

2.2 Thermodynamics of liquid-vapour phase equilibria

According to the second law of thermodynamics, the total Gibbs energy of a closed system at constant temperature and pressure is minimum at equilibrium. If this condition is combined with the condition that the total number of moles of component i is constant in a closed system,

$$\sum_{\alpha} n_i^{\alpha} = \text{constant} \quad (2.1)$$

Where n_i^{α} is the number of moles of component i in phase α , it can be derived that for a system of Π phases and N components, the equilibrium conditions expressed in terms of chemical potential (μ_i) are as follows (Smith *et al.* 2005):

$$\mu_i^{\alpha} = \mu_i^{\beta} = \dots = \mu_i^{\Pi} \quad (2.2)$$

for $i = 1$ to N .

The chemical potential of component i in phase α is defined by

$$\mu_i^{\alpha} = \left(\frac{\partial \left(\sum_i n_i^{\alpha} g^{\alpha} \right)}{\partial n_i^{\alpha}} \right)_{P, T, n_{j \neq i}^{\alpha}} \quad (2.3)$$

where g is the molar Gibbs energy. Since μ_i^{α} is a function of P , T and $(N-1)$ mole fractions (the additional condition $\sum_i x_i^{\alpha} = 1$ makes one of the mole

fractions a dependent variable), Equation (2.2) represents $N(\Pi - 1)$ equations in $2 + \Pi(N - 1)$ variables. Therefore the number of degrees of freedom F is

$$F = 2 + \Pi(N - 1) - N(\Pi - 1) = 2 - \Pi + N \quad (2.4)$$

Equation (2.4) is the *phase rule* of Gibbs. According to this rule a state with Π phases in a system with N components is determined (all intensive thermodynamic properties can be calculated) if the values of F variables are fixed, provided that g values of all phases as functions of pressure, temperature and composition are known.

For practical applications (calculation of the composition of phases) the explicit dependence of chemical potentials on composition, temperature and pressure is needed. For this reason auxiliary functions such as the fugacity coefficient and the activity coefficient are used. These functions are closely related to the Gibbs energy and assume the ideal gas and the ideal solution behaviour in the reference state.

The fugacity of component i in a mixture \hat{f}_i is defined by

$$d\mu_i \equiv RT \ln \hat{f}_i \quad (2.5a)$$

at constant T (where the symbol $\hat{}$ indicates the value of the quantity in a mixture) with

$$\lim_{P \rightarrow 0} \frac{\hat{f}_i}{P_i} = 1 \quad (2.5b)$$

According to this definition, \hat{f}_i is equal to the partial pressure P_i in the case of an ideal gas. The fugacity coefficient $\hat{\phi}_i$ is defined by

$$\hat{\phi}_i = \frac{\hat{f}_i}{P_i} \quad (2.6)$$

and is a measure for the deviation from ideal gas behaviour.

The fugacity coefficient ($\hat{\phi}_i$) can be calculated from an equation of state by one of the following expressions (Prausnitz *et al.* 1999):

$$\ln \hat{\phi}_i = \frac{1}{RT} \int_0^P \left(\bar{v}_i - \frac{RT}{P} \right) dP \quad (2.7)$$

$$RT \ln \hat{\phi}_i = \frac{1}{RT} \int_{V=\infty}^V \left[\frac{RT}{V} - \left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_{j \neq i}} \right] dV + RT \ln \left(\frac{\sum_i n_i RT}{PV} \right) \quad (2.8)$$

According to Equation (2.5a), the equilibrium relation Equation (2.2) can be replaced by

$$\hat{f}_i^\alpha = \hat{f}_i^\beta = \dots = \hat{f}_i^\pi \quad (2.9)$$

for $i = 1$ to N .

This approach for the calculation of the fugacities in mixtures can be used for gaseous and condensed phases. This approach followed for all the phases at equilibrium is named the $\hat{\phi} - \hat{\phi}$ method since the fugacities of both phases are calculated with Equation (2.7) or (2.8) using an equation of state.

However, the calculation of the integral in Equation (2.8) needs an equation of state for the description of volumetric properties of the phase considered from low density (ideal gas) to the actual density of the phase. For this reason an alternative method for the calculation of the fugacities in condensed-phase mixtures is proposed. In this case, the reference is not the behaviour of an ideal gas mixture (that normally is far away from that of a solid or liquid mixture) but that of an 'ideal mixture'. Excess functions are defined to describe the departure of the properties of a real mixture from the ideal behaviour.

It is very useful from a practical point of view to define as 'ideal' the behaviour of a mixture when it is possible to predict it from the knowledge of the properties of the pure components involved at the same temperature and pressure.

The activity a_i is defined as the ratio of \hat{f}_i and the fugacity of component i in the standard state at the same P and T :

$$a_i = \frac{\hat{f}_i(T, P, x)}{f_i^0(T, P, x^0)} \quad (2.10)$$

In the ideal solution:

$$a_i^{id} \equiv x_i \quad (2.11)$$

The activity coefficient of component i , γ_i , measures the deviation from ideal solution behaviour:

$$\gamma_i = \frac{a_i}{a_i^{id}} \quad (2.12)$$

so the fugacity of a solid or liquid solution can be written as

$$\hat{f}_i = x_i \gamma_i f_i^0 \quad (2.13)$$

The activity coefficient γ_i can be calculated from the molar excess Gibbs energy g^E :

$$RT \ln \gamma_i = \left(\frac{\partial \left(\sum_i n_i g^E \right)}{\partial n_i} \right)_{P, T, n_{j \neq i}} \quad (2.14)$$

The standard-state fugacity of the liquid or solid component f_i^0 is usually the fugacity of the pure solid or liquid component at the same

temperature and pressure and is related to the sublimation pressure P_i^{sub} or vapour pressure P_i^{sat} , respectively.

On the sublimation curve of a pure component, we have

$$f_i^S(P_i^{sub}, T) = f_i^V(P_i^{sub}, T) = \phi_i^V(P_i^{sub}, T)P_i^{sub} \quad (2.15)$$

where superscripts *s* and *V* indicate a solid or vapour phase, respectively.

$$f_i^S(P, T) = f_i^S(P_i^{sub}, T) \exp\left(\int_{P_i^{sub}}^P \frac{d\mu_i^S}{RT}\right) = f_i^S(P_i^{sub}, T) \exp\left(\int_{P_i^{sub}}^P \frac{v_i^S}{RT} dP\right) \quad (2.16)$$

where v_i^S is the molar volume of pure solid *i*.

Combining Equations (2.15) and (2.16), we get

$$f_i^S(P, T) = \phi_i^V(P_i^{sub}, T)P_i^{sub} \exp\left(\int_{P_i^{sub}}^P \frac{v_i^S}{RT} dP\right) \quad (2.17)$$

A similar derivation is possible for a liquid:

$$f_i^L(P, T) = \phi_i^V(P_i^{sat}, T)P_i^{sat} \exp\left(\int_{P_i^{sat}}^P \frac{v_i^L}{RT} dP\right) \quad (2.18)$$

At low pressure the fugacity coefficients and the exponential terms are close to 1, so

$$f_i^S \approx P_i^{sub} \quad \text{and} \quad f_i^L \approx P_i^{sat} \quad (2.19)$$

From this assumption for the standard state fugacity, it follows that the activity coefficient of component *i* is equal to unity when the composition $x_i = 1$ (i.e. for the pure component *i*).

This assumption is convenient if the component, at the temperature and pressure conditions of the mixture, exists in the same physical state. This is neither realistic nor practical when considering liquid mixtures if one of the components is supercritical. In this case the more convenient reference state is not that of pure component but that of the component infinitely diluted. The fugacity of the component *i* in an ideal mixture when $x_i \rightarrow 0$ is expressed by

$$\hat{f}_i^L(T, P, x_i) = x_i H_i(T, P) \quad (2.20)$$

where H_i is the Henry constant and is a function of temperature, pressure and the solvent–solute pair in the system. At high concentration there is no linear proportionality between $f_i^L(T, P, x_i)$ and the molar fraction x_i . Equation (2.20) can also be used for high concentrations considering a new activity coefficient γ_i^* :

$$\hat{f}_i^L(T, P, x_i) = x_i H_i(T, P) \gamma_i^*(T, P, x_i) \quad (2.21)$$

This new coefficient is different from γ_i : when $x_i \rightarrow 0$, $\gamma_i^* \rightarrow 1$ while when $x_i \rightarrow 1$, $\gamma_i \rightarrow 1$. It is possible to write

$$\hat{f}_i^L(T, P, x_i) = x_i H_i(T, P) \gamma_i^*(T, P, x_i) = x_i \gamma_i(T, P, x_i) f_i^0(T, P) \quad (2.22)$$

If the fugacities of the phases at equilibrium are calculated using the equation of state approach through Equation (2.8) for one phase and the activity coefficient approach (Equation (2.22) for the other phase, the method is named the γ - ϕ or activity-fugacity coefficient approach.

2.2.1 Calculation of γ

In typical mixtures, the ideal (or Raoult law) approximation provides no more than a rough approximation and it is valid only when the components are similar. The activity coefficient, therefore, plays a key role in the calculation of vapour-liquid equilibria.

Classical thermodynamics gives information on the effect on the activity coefficients of pressure (related to the partial molar volume) and of temperature (related to the partial molar enthalpy).

The Gibbs-Duhem equation, however, is a useful tool for correlating and extending limited experimental data due to the fact that, in a mixture, the activity coefficients of the individual components are not independent of one another but are related by a differential equation. For a binary mixture, the equation is

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P} \quad (2.23)$$

This equation means that in a binary mixture, activity coefficient data for one component can be used to predict the activity coefficient of the other component. Alternatively, with extensive experimental data for both activity coefficients as a function of composition, it is possible to test the data for thermodynamic consistency by determining whether or not the data obey Equation (2.23). In the case of limited data, the integral form of the Gibbs-Duhem equation provides an equation to extend the information. To do so, it is necessary to assume a mathematical expression of the excess energy as a function of composition. The numerical values of the constants are calculated from the fitting of the limited data. Normally these constants, independent from composition, depend on temperature. Once the values of the constants are known, the activity coefficients can be calculated by differentiation.

Different expressions are proposed for the evaluation of the excess energy (Prausnitz *et al.* 1999): usually for moderately non-ideal systems, all equations containing two or more parameters give good results.

The older expressions are those proposed by Van Laar and by Margules (see the list following in this section). These expressions are mathematically easier to handle than the modern and new models (the Wilson, Nonrandom

Two Liquids (NRTL) and Universal Quasi-Chemical (UNIQUAC) equations), but their use is often limited to the correlation of data for binary mixtures alone (for this reason, in the list for these models, the equations are reported for binary systems).

The Wilson equation, with two parameters, gives good results for strongly non-ideal binary mixtures and it is often used for vapour-liquid calculations: it is simpler than the UNIQUAC equation and contains only two parameters per binary mixtures, whereas the NRTL equation requires the knowledge of three parameters. Also the dilute region is represented with reasonable accuracy. The main deficiency of the Wilson equation is the impossibility to represent mixtures which exhibit a miscibility gap. For the systems that have incomplete miscibility and as a consequence are very non-ideal, the NRTL and UNIQUAC equations are very useful. The NRTL equation contains three parameters but very often the numerical value of the nonrandomness parameter α_{ji} is fixed (at the value 0.2 or 0.3). The UNIQUAC equation has the advantage that it uses only two parameters (with often a lesser dependence on temperature) and since the primary concentration variable is a surface fraction (rather than mole fraction), it is applicable to solutions containing small or large molecules.

Sometimes there is a total absence of experimental data to fit for the evaluation of the parameters used in the models for the activity coefficients. Then, a completely predictive model must be used. These models are based on the groups' contributions concept. Each molecule in the mixture is considered as formed by functional groups. The behaviour of the mixture can be predicted by knowing the interaction between the functional groups in the mixture. The interaction between functional groups, called a_{mn} , is evaluated by studying the experimental data of known mixtures and it is assumed to be the same in every mixture in which the functional groups are considered. This allows predicting the equilibrium for systems with no experimental data. The UNIFAC (Fredenslund *et al.* 1977) and ASOG (Kojima and Tochigi 1979) are the most important models based on the functional groups method for mixtures. The most used is the UNIFAC model because it can be applied to a great number of compounds. The UNIFAC is the version based on the contribution of the functional groups of the UNIQUAC model, while the ASOG uses the Wilson model. To use the UNIFAC model it is necessary to identify the functional groups of the molecules in the system and evaluate the values of the parameters from its tables. The equations describing this model are very similar to that one of the UNIQUAC model:

Van Laar equation

$$\frac{g^E}{RT} = \frac{A_{12}A_{21}}{A_{12}x_1 + A_{21}x_2} x_1x_2 \quad (2.24a)$$

$$\ln \gamma_1 = A_{12} \left(\frac{A_{12}x_1}{A_{12}x_1 + A_{21}x_2} \right)^2 \quad (2.24b)$$

Margules equation

$$\frac{g^E}{RT} = [A_{12} + (A_{21} - A_{12})x_1]x_1x_2 \quad (2.25a)$$

$$\ln \gamma_1 = [A_{12} + 2(A_{21} - A_{12})x_1]x_2^2 \quad (2.25b)$$

Wilson equation

$$\frac{g^E}{RT} = -\sum_i x_i \ln \left(\sum_j x_j \Lambda_{ij} \right) \quad (2.26a)$$

$$\ln \gamma_i = 1 - \ln \sum_j x_j \Lambda_{ij} - \sum_j \frac{x_j \Lambda_{ji}}{\sum_k x_k \Lambda_{jk}} \quad (2.26b)$$

Parameters

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp \left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \quad (2.26c)$$

NRTL equation

$$\frac{g^E}{RT} = \sum_i x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} \quad (2.27a)$$

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left[\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_m G_{mj} x_m} \right] \quad (2.27b)$$

Parameters

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \quad (2.27c)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (2.27d)$$

UNIQUAC equation

$$\frac{g^E}{RT} = \sum_i x_i \ln \frac{\varphi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\vartheta_i}{\varphi_i} - \sum_i q_i x_i \ln \left[\sum_j \vartheta_j \tau_{ji} \right] \quad (2.28)$$

$$\ln \gamma_i = 1 - \frac{\varphi_1}{x_i} + \ln \frac{\varphi_i}{x_i} + \frac{z}{2} q_i \left(1 - \frac{\vartheta_i}{\varphi_i} + \ln \frac{\vartheta_i}{\varphi_i} \right) + \quad (2.29a)$$

$$q_i \left[1 - \ln \left(\sum_j \vartheta_j \tau_{ji} \right) \right] - \sum_j \vartheta_j \frac{\tau_{ij}}{\sum_k \vartheta_k \tau_{kj}}$$