



# Measurement of phase equilibria of the systems CO<sub>2</sub> + styrene and CO<sub>2</sub> + vinyl acetate using different experimental methods

Stephanie Peper<sup>a</sup>, Verena Haverkamp<sup>b</sup>, Ralf Dohrn<sup>c,\*</sup>

<sup>a</sup> Helmut-Schmidt-University/University of the Federal Armed Forces Hamburg, Institute of Thermodynamics, D-22043 Hamburg, Germany

<sup>b</sup> Bayer Technology Services GmbH, Process Technology, Conceptual Design, Building E41, D-51368 Leverkusen, Germany

<sup>c</sup> Bayer Technology Services GmbH, Process Technology, Kinetics, Properties & Modeling, Building B310, D-51368 Leverkusen, Germany

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## ABSTRACT

The experimental determination of high-pressure phase equilibria is often the only suitable method to obtain reliable data because high-pressure phase behavior is complex and difficult to predict. This contribution gives a brief classification of applied experimental methods. A new high-pressure apparatus is described, which can be used for phase-equilibrium measurements with different experimental methods, namely the analytical-isothermal method, the synthetic-isothermal method as well as the non-visual-and the visual-synthetic method. The different techniques have been tested for the measurement of the phase behavior of systems containing CO<sub>2</sub> + styrene and CO<sub>2</sub> + vinyl acetate. The measured data were compared with data from literature and discussed in terms of accuracy, advantages and drawbacks of the applied methods.

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## 1. Introduction

Although the experimental measurement of high-pressure phase equilibria is difficult and time consuming it is an almost indispensable method to obtain information of the phase behavior. Many theoretical studies of the thermodynamics of mixtures have shown that the phase behavior is quite sensitive to intermolecular forces. Due to large deviations from ideal behavior at high pressures theoretical models are less accurate than at lower pressures. Usually theoretical models, like equations of state, that are able to calculate the phase behavior with high accuracy need at least some experimental data points so that interaction parameters of the model can be adjusted.

On the other hand predictive calculations with less accurate models can help to reduce the experimental effort that is needed to perform high-pressure phase-equilibrium experiments. The doctoral thesis of Johannes Diderik van der Waals on the continuity of the liquid and the gaseous state in which he derived his famous equation of state, laid the basis for a big family of equations of state that are nowadays used to predict and to correlate high-pressure phase equilibria. We perform predictive calculations, e.g. using the

PSRK model before the start of high-pressure phase-equilibrium experiments to investigate the qualitative phase behavior including the number and type of coexisting phases. Based on these calculations we can determine the appropriate overall composition for experiments when analytical methods are used and the conditions for possible phase changes for synthetic methods. As described in Section 4 of this work, predictive calculations are particularly valuable for the search of critical curves of mixtures. Van der Waals' postulation of intermolecular forces (later called van der Waals forces) and his discovery of the concept of corresponding states are very helpful for the understanding of the phase behavior of pure compounds and of mixtures. So far, the only phase diagram that ever made its way to many envelopes, is a *p*-*T* diagram of a binary system, including critical curves, on the van der Waals' stamp, released in the Netherlands in 1995.

Many different methods are used to measure high-pressure phase equilibria. Which method is suitable in the individual case depends both on the properties of the components and the phenomena to be investigated. As each method has advantages and disadvantages as well as specific error sources a detailed knowledge and understanding of the different methods is necessary for the validation of experimental data. This is true not only for the engineer/researcher planning and performing high-pressure phase equilibrium experiments but also for the user of phase-equilibrium data documented in the literature or in databases. However the

\* Corresponding author. Tel.: +49 214 30 21787; fax: +49 214 30 81554.  
E-mail addresses: [ralf.dohrn@bayer.com](mailto:ralf.dohrn@bayer.com), [ralf.dohrn@web.de](mailto:ralf.dohrn@web.de) (R. Dohrn).

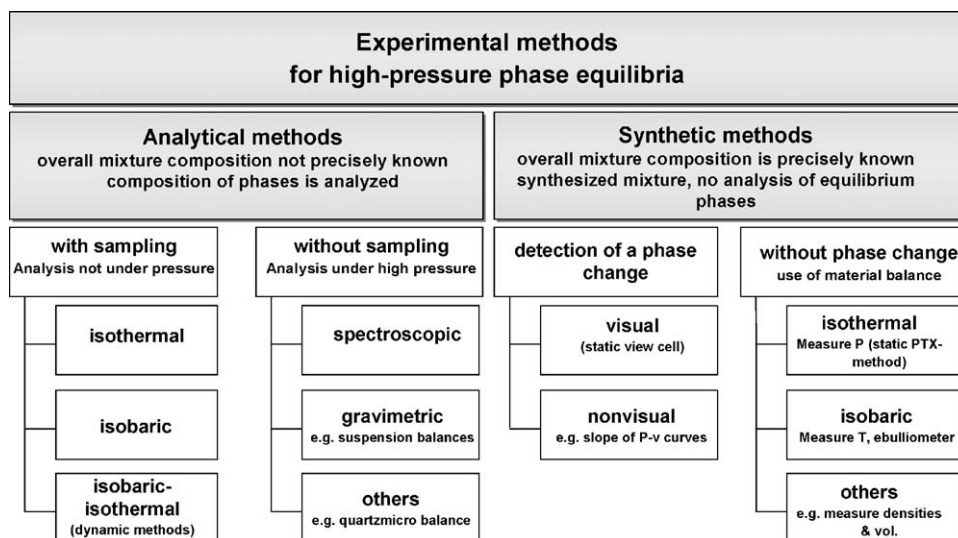


Fig. 1. Classification of experimental methods for high-pressure phase equilibria.

variety of experimental methods described in the literature is often confusing since different authors use different names for the same experimental method. Expressions like 'static' or 'dynamic' are used in connection with many different methods. Therefore in this contribution, a brief classification of experimental techniques is given before a new high-pressure apparatus is described. An overview of review articles about techniques for experimental investigations and of reviews on high-pressure phase-equilibrium data in the literature has been given in Dohrn et al. [1]. From the reviews on experimental methods that appeared after 2004 the articles of Knox [2], Richon [3], Smith and Fang [4] and Fonseca et al. [5] shall be mentioned.

The new apparatus described in this contribution is characterized by its high flexibility. It can be used for phase-equilibrium measurements with the analytical–isothermal method, the non-visual- and the visual-synthetic method, the synthetic-isothermal method as well as for the determination of critical curves in multicomponent mixtures. Results of measured phase equilibria of the binary systems  $\text{CO}_2$  + styrene and  $\text{CO}_2$  + vinyl acetate are presented and compared with data from literature. Thereby the specific error sources and the pros and cons of the different methods are discussed.

## 2. Experimental methods

A schematic classification of experimental methods for the investigation of high-pressure phase equilibria is given in Fig. 1. There are two main classes, depending on how the compositions of the equilibrium phases are determined (analytically or not) and whether the mixture to be investigated has been prepared with precisely known composition or not: analytical methods and synthetic methods. In the following section the experimental methods relevant for this work are briefly described. A more detailed description of all experimental methods mentioned in Fig. 1 is given in our review on high-pressure fluid-phase equilibria [5].

Analytical methods involve the determination of the compositions of the coexisting phases. This can be done by taking samples from each phase and by analyzing them outside of the equilibrium cell at ambient pressure (analytical methods with sampling) or by using physicochemical methods of analysis inside of the equilibrium cell under pressure (analytical methods without sampling). Depending on the attainment of equilibrium, analytical methods with sampling can be classified as isothermal methods, isobaric methods and isothermal–isobaric methods.

When an analytical-isothermal method is used, an equilibrium cell is charged with the substances of interest. After the desired temperature has been reached, the mixture is kept at isothermal conditions. At the beginning of the experiment, the pressure is adjusted above or below the desired equilibrium value, depending on how equilibration will change the pressure. By stirring the mixture or by rocking the autoclave or by recirculating one or more phases, time for equilibration of the phases is reduced. After equilibration, the composition of the phases is analyzed with sampling and analysis under ambient pressure. The pressure can be readjusted, by adding or withdrawing material or by changing the volume of the equilibrium cell. Isothermal methods that use stirring or rocking to ensure a rapid approach to equilibrium are often called analytical–static methods.

The analytical isothermal–isobaric methods are often called dynamic methods. Here one or more fluid streams are pumped continuously into a thermostated equilibrium cell. The pressure is kept constant during the experiment by controlling an effluent stream, usually of the vapor phase. Isothermal–isobaric methods can be divided into semi-flow methods and continuous-flow methods. In *semi-flow methods*, only one phase is flowing while the other phase is fixed in the equilibrium cell. These methods are sometimes called “single-pass flow methods” or “gas-saturation methods”. Most often, only the composition of the vapor phase is analyzed, for example to determine the solubility of a low-boiling substance in a supercritical fluid. In a typical design of a *continuous-flow method*, high-pressure metering pumps feed the preheated components into a mixer, where the desired temperature and phase equilibrium is attained. The feed stream from the mixer is then separated in an equilibrium cell into a vapor and a liquid phase. Effluents from both phases are withdrawn continually, depressurized and analyzed.

The basic principle of synthetic methods is to prepare a mixture of precisely known composition and then to observe the phase behavior in an equilibrium cell and to measure properties in the equilibrium state, like pressure and temperature. As no sampling is necessary, synthetic methods can be applied where analytical methods fail, for example, if the phase separation is difficult due to similar densities of coexisting phases like near or even at critical points and in barotropic systems. However the problem of analyzing fluid mixtures is replaced by the problem of synthesizing them.

Synthetic methods can be applied with or without a phase transition. The observation of the appearance or disappearance of a phase can be detected visually (visual-synthetic methods) or by

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