

EXPERIMENTAL METHODS FOR STUDY HIGH-PRESSURE PHASE BEHAVIOUR. PART I. STATIC METHODS.

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abstract: The paper presents a review of the experimental methods used in the investigation of high-pressure phase equilibria. The main categories of methods and installations are described. For each case, the aspects concerning the type of experimental data, experimental conditions and experimental procedures are discussed.

Introduction

Information about high-pressure phase equilibrium is of importance for many separation processes, which are conducted at high-pressure especially supercritical fluid extraction. Applications of this technology cover the food, pharmaceuticals, chemical, coal and oil processing and production industry.

There are many experimental routs to obtain data about the phase behaviour of the fluid mixtures. Among these, the direct measurements remain an important source, though it is difficult and expensive to take accurate experimental data. But, it is also expensive for a company to use average data or to estimate data with a thermodynamic model if the literature does not offer (enough) experimental data. Thus, the understanding of the complex phenomena, which occur at high pressure in the critical region, is mainly conditioned by the quality of the experimental information, [1].

Classification of the experimental methods

In order to classify the experimental methods and installation it is necessary to specify the two criteria that must be taken into account. Thus:

A) Depending on how the composition of the two coexisting phases is determined the methods are divided in:

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- *analytical methods* (direct sampling methods) – involve the determination of the compositions of the coexisting phase by sampling each of them and then by analysing these samples inside (spectroscopy) or outside (refractometry, chromatography or pressure drop) of equilibrium cell, [1,2].
- *synthetic methods* (indirect methods) – no sampling is necessary. The overall composition of the mixture is known and the temperature or the pressure is adjusted until a homogeneous phase is obtained. The observation can be done visual or non-visual. Each experiment yields one point on the P-T-x phase envelope (where x represents the composition of the liquid phase). These methods are applied when the analytical path fail, i.e when the phase separation is difficult due to the similar densities of the two phases or in barotropic systems, where at certain conditions the densities of the two coexisting phase have the same value, [3].

B) *Considering the working regime* (criterion used in this paper) the experimental methods can be divided in:

- static methods – during the experiment, the phases does not leave the equilibrium cell;
- dynamic methods – continuous separation of the coexisting phases in a stationary regime, [3].

Based on the last criterion, this paper is a review of the static installations and techniques and gives a brief overview of different methods for the study of high-pressure phase behaviour.

Static methods

The static methods allow the obtaining of complete equilibrium data - P-T-x-y (**y** - the vapor composition) and the methods are called static analytical methods, or partial data P-T-x, when y is calculated – the case of the static synthetic (indirect) methods.

There are two reasons why it recommended calculating y:

- the density of the vapour phase is much lower than the density of the liquid phase, thus it is very difficult to extract samples from this phase without any perturbation of the equilibrium state;
- can be easily calculate by using with equations of state (EoS).

The composition of the liquid phase can be determined at atmospheric pressure, outside of the equilibrium cell (i.e. titration, refractometry) or directly inside of the cell (by spectroscopy), in the modern installations.

The main parts of a static installation are presented in Fig.1. Basically, the apparatus consist of a degassing system (2) – to eliminate the air dissolved in the pure compounds or mixtures, an equilibrium cell immersed in a liquid thermostated bath (7), a system for measuring the pressure (5).

In order to avoid the condensation, the pressure gauge and the tubings are placed in an air thermostated bath, at higher temperature than the temperature of the equilibrium cell.

The sample is introduced in the equilibrium cell (preliminary vacuumated) at fixed temperature and stirred until the equilibrium is reached. At this moment the pressure and composition are determined. The accuracy of the experimental data is limited by the measurement devices.

The equilibrium cell can be visual (with high pressure resistant windows e.g. sapphire), allowing the visual observation of phase behaviour or nonvisual, usually built up from stainless steel.

Moreover if the volume of the cell is constant or can be modified, static installations are divided in *constant volume cell apparatus* (methods)-CVC methods or *variable volume cell apparatus* -VVC methods.

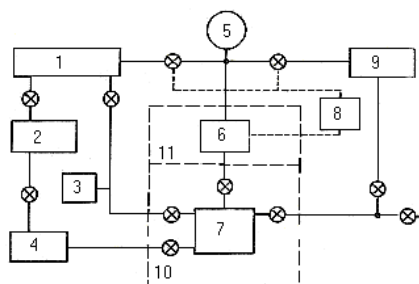


Fig 1. Schematic representation of a static apparatus: (1, 3) –vacuum devices; (2) – degassing system; (4) - transfer chamber; (5) – pressure gauge; (6) –differential null for pressure; (7) –equilibrium cell; (8) – compressor; (9) – feed for inert gas; (10, 11) – thermostated baths.

The general description of the static installation is valid for both synthetic and analytical measurements and some particular cases are presented in this paper.

There are two main aspects to take into account for the measurements with a static apparatus:

- the problem of degassing the sample
- the problem of taking sample from the coexisting phases and their accurate analysis.

A) Static installations with constant volume cell – CVC methods.

The *degassing problem* is discussed especially for volatile compounds or mixture with significant volatility. Researches were developed and different solutions and apparatus were proposed:

a) In the apparatus of Van Ness and Abott [4] the degassing process is insured by the continuous flow of the liquid under vacuum condition. The authors consider 24 hours sufficient for the degassing procedure.

b) Using an installation based on the procedure of alternating freezing – melting cycles under vacuum conditions, Vilcu *at. all* [5] obtain VLE data for different pure compounds and mixtures. The measurements follow the general procedure of static installations: when

the equilibrium is reached, the pressure and temperature are measured with a mercury manometer (± 20 Pa), respectively with Beckmann thermometers (± 0.02 K). The composition of liquid phase is determined by refractometry, with previously calibration (± 0.0002). If the total pressure [4, 5] is measured the method is also called *total pressure method*.

This procedure of freezing – melting cycles is a successful alternative for the degassing problem in the VLE static installations. Literature [5-10] presents many static types of equipment based on the degassing method previously described.

If the pressure of the sample is measured using the pressure of reference fluid, the method is called *differential pressure method*. The equipment consists of two equilibrium cells, one charged with sample, the other with reference fluid, with known vapor pressure. Some examples are the installations presented by Morgan and Kobayashi [6], Giuliani, Polonara and Di Nicola [7,8], Stryjek [9] or Mokbel *et al.* [10].

The equipment of Morgan and Kobayashi [6] is presented in Fig. 2:

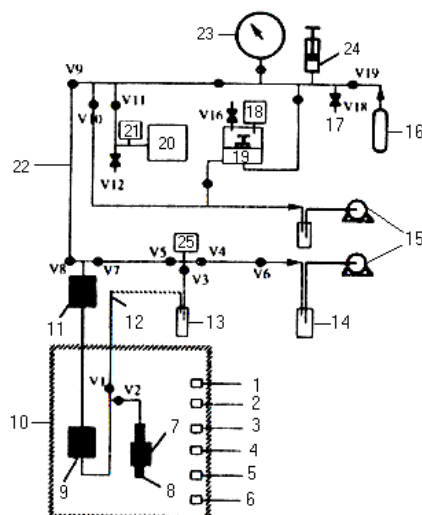


Fig. 2. Schematic representation of the differential pressure apparatus [5] (1) – stirrer; (2, 3) – heating elements; (4) – platinum resistance thermometer; (5) – nitrogen purge; (6) – thermocouple for Over-Temperature Limit Control; (7) – magnetic slusher; (8) – equilibrium cell; (9,11) – null-type differential pressure indicator; (10) – thermostat; (12) – heated line; (13, 14) – cold traps; (15) – vacuum pumps; (16) – nitrogen supply; (17) – vent; (18, 21, 25) – thermovac vacuum gauge; (19) – air Dead Weight Gauge (1- 4136 kPa); (20) – Digital quartz Pressure Gauge (0-138 kPa); (22) – Pressure Supply and Measurements System; (23) – Heise Gauge (0-3446 kPa); (24) – Hand Pump; V1...V19 – valves.

The equilibrium stainless steel cell (8), previously vacuumated is directly connected with the diaphragm of a differential pressure transducer and differential pressure indicators (9,11). The position of the metal diaphragm in the DPI, which separated the sample from the reference pressure, is measured when an equal reference pressure is applied on both side of the diaphragm. The pressure of the reference gas can be automatically controlled, [6]. Then, with the sample exerting its pressure on one side of the diaphragm and the reference

gas on the other side, the reference pressure is adjusted until the initial zero position of the diaphragm is reproduced. This pressure is measured with the air dead weight gauge (19). The apparatus allow measurements for pressure less than 1.3 MPa (± 0.01 KPa), temperatures less than 588 K (± 0.02 – 0.09 K). The mostly used method for analysis of sample composition in the case of mixture is chromatography [11,12], but also gravimetry [5] and densimetry (*eg.* with a vibrating tube densitometer) [11, 12] are used.

The uncertainty in composition evaluation is situated in the range (± 0.002 ... ± 0.008). The use of a chromatograph allows more accurate data and makes the analysis easier and more rapid than in the other cases.

It is also important to discuss the problem *of sampling* the coexisting phases because withdrawing a large sample volume from an autoclave causes a considerable pressure drop, which disturb the phase equilibrium significantly. This pressure drop can be avoided by:

- using variable volume cells or a buffer autoclave in combination with a syringe pump;
- blocking off a large sampling volume before the pressure reduction;
- withdrawing small quantities of sample comparing with the cell volume using capillaries, special valves (HPLC - valves or fast acting pneumatic valves) syringe pumps, [1,2].

Examples of apparatus with special devices for taking very small quantity of sample are presented in literature by many authors. Wahlström and Wamling, [12] or Wagner and Vichterle, [13] installations use mobile pneumatic capillary samplers; Luna and Rodriguez [14] describe the work with capillary samplers injectors; Tochigi *et. all*, [15] apparatus contain six direction valves that introduce the sample into the gas chromatograph while Kao and Lin, [16] presents an equipment that use a micrometer syringe to withdrawn the sample at equilibrium from the coexisting phases. By reducing the quantity of extracted sample, the perturbation of the equilibrium state is avoided and the time of the experiment is reduced. The uncertainty for the composition determination depends on the accuracy of the analysis method. Literature [12-16] gives for the above-mentioned apparatus, uncertainty less than 1%.

In Romania there exist a few installations equipped with a constant volume cell, working in a static regime. It can be mentioned an apparatus for solubility data at atmospheric pressure (Laboratory of Physical Chemistry – University of Bucharest), [17], but also two other installations for high pressure (Laboratory of Physical Chemistry, University of Bucharest and respectively Laboratory of Applied Physical Chemistry and Electrochemistry, “Politehnica”, University Bucharest), [18, 19].

The schematic representation of the installations Vilcu and Gainar is given Fig. 3 [18]:

The equilibrium is reached under stirring condition within a few hours. The sampling system is evacuated and valve (7') is carefully opened. A sample of about 1 mL of solvent containing gas dissolved is collected in the ampoule (8'). The gas absorbed is then desorbed and the pressure produce in this way is read using a cathetometer (attached to the mercury manometer).

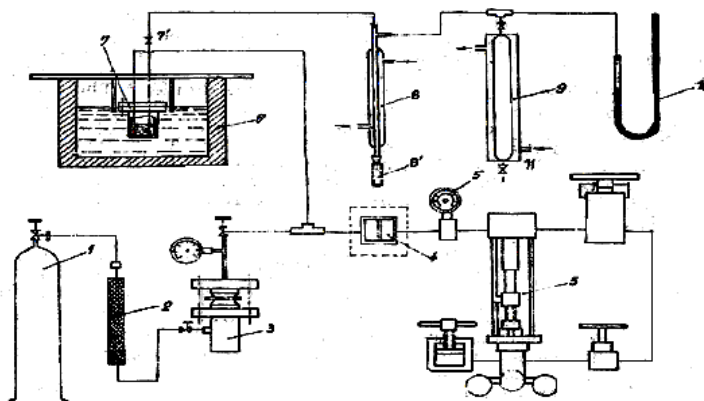


Fig. 3. Schematic representation of apparatus for solubility data of Vilcu and Gainar [18] (1) – compressed gas bottle; (2) – steel cylinder with molecular sieves for eliminating water traces; (3) – autoclave as manostat and fine handling of gas supplying the equilibrium cell; (4) – differential monometer; (5) – pressure gauge with rotative piston and weights; (6) – thermostated bath; (7) – equilibrium cell; (7', 11) – valves; (8) – refrigerant; (8') – ampoule for sample; (9) – thermostated reservoir; (10) – mercury manometer.

The volume, pressure, temperature and mole number of desorbed gas can be correlated using a EoS. After the pressure is read, the valve (11) is opened atmospheric pressure air is introduced. The ampoule (8') is detached and weighed. The volume of solvent is estimated based on the solvent density and the mass of the ampoule. The apparatus work at pressure up to 5 MPa and at room temperature, [18].

Another example is the isochoric apparatus for VLE data, [19]. The elements contained are presented in Fig. 4.

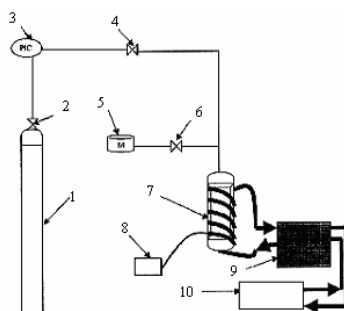


Fig. 4. Schematic representation of the isochoric apparatus of Geană [19]. (1) – gas reservoir; (3) – pressure regulator; (2, 4, 6) – valves; (5) – manometer; (7) – constant volume cell; (8) – thermocouple; (9) – thermostat; (10) – cryostat.

The apparatus can work at pressure up to 25 MPa ($\pm 0.5\%$) and temperature in the range of 283... 350 K (± 0.1 K).

B) Variable volume cell installations - VVC installations.

The use of a variable volume cell for studying high-pressure phase behaviour offers higher flexibility of the measurements. There are different possibilities to change the volume of the cell, moving up and down a piston [20] or injecting small quantity of an immiscible

fluid into the system [21]. Simultaneously, the pressure drop due to the sampling is compensated.

If the P-T-x-y complete data are obtained with VVC apparatus, the method is called *analytical VVC methods* and if the phase transition is observed at constant pressure and temperature than the method belongs to the *synthetic (indirect) VVC methods*.

Similar to the CVC methods, majority of cells are visual (with high pressure resistant windows or entire cell is built from glass) but also non-visual cell from stainless steel are used.

According to analytical VVC methods the experiments follow the same procedure described in the previous section.

In the static regime the phases are separated inside the equilibrium cell. For a given temperature and pressure, an adequate volume of each phase is collected and analysed using physico-chemical analysis method.

The perturbation of the equilibrium state caused by the sampling procedure is avoided by one of the method discussed above. Often, one [23, 24] or two pistons [20] achieve the change in volume cell.

The volume of the cell can be evaluated by measuring the position of the piston by means of a cathetometer [1, 2] or directly if a scale is attached to the cell [23].

A constructive type of this category of installations is given in Fig. 5, [21]

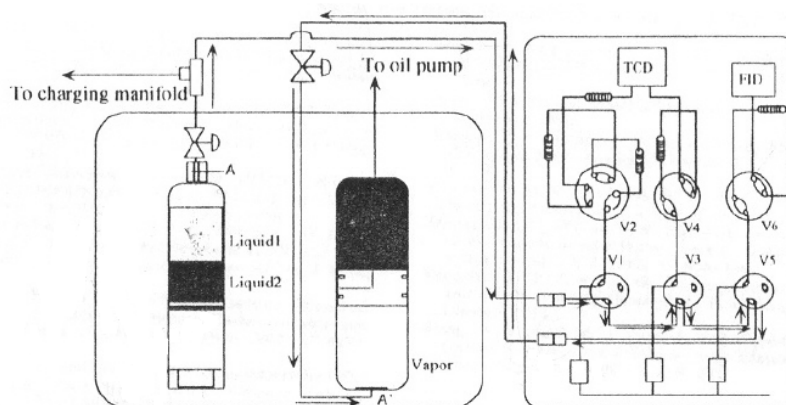


Fig.5. Schematic representation of a VVC apparatus

Barrufet and Rahman [20] use two PVT variable volume cells each of them equipped with a movable piston. A computer controlling stepping motor can separately change the volume of the cells and the mobility of the sample within the system can be achieved at constant temperature and pressure. The cell is connected with a gas chromatograph using specially on-line sampling system with digitally operated valves. These valves are connected to a switching valve for back – flushing to eliminate column contamination and separate columns for various phase analyses, (Fig. 5). Thus the mass of the withdrawn sample is reduced and the equilibrium is not disturbed. The uncertainty in composition determination

is less than 1% in the experimental conditions - pressures up to 27 MPa (± 0.005 MPa) and temperatures up to 500 K (± 0.2 K).

In Romania a similar apparatus with variable volume cell working at pressure up to 30MPa is reported by Geana *et al.* The main part of the equipment is the visual cell with two sapphire windows, one of the window acting as piston. A hand pump actions the piston, so the volume can be change between 25 and 60 cm³. When the equilibrium is obtained samples are collected by depressurisation and expansion into glass trap (with calibrated volume) using manually operated valves. The uncertainty in mole fraction is less than 0.003.

It can be conclude that both static analytical techniques (CVC and VVC) are simple and allow obtaining complete P-T-x-y for large pressure and temperature limits, but these methods cannot be applied in the regions where the phase separation in not sharp. The quality of data is conditioned only by the accuracy of the measuring devices.

Synthetic VVC methods.

These methods are used when the experimental condition (high pressure, system characteristic) yields a lot of difficulties withdrawing and in the composition analysis of the coexisting phases (barotropic inversion points, critical region). Basically, an experiment consists of the visual observation of the Dew and/or Bubble Point pressure at various temperatures, for pure components or mixture of known composition. No sampling is necessary.

The main parts of a synthetic installation are presented in Fig. 6 [25]:

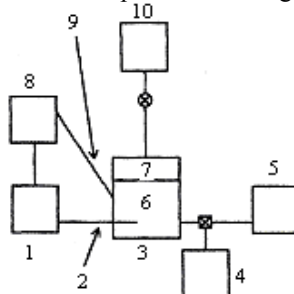


Fig. 6. The main parts of a synthetic VVC device [34] (1)– temperature controller; (2)– thermocouple; (3)– equilibrium cell; (4)–sample inlet; (5)–pressure transducer; (6)–sample; (7)– pneumatics; (8)– powerstat; (9)– band heaters, (10) - syringe pump.

Using one or more pistons or a pressure transmitting fluid, the pressure is modified until a homogeneous phase results. So, two and three phase equilibrium can be visual observed, but better results are obtained by using different devices - magnifiers, microscopes or video cameras, [26].

In order to improve the accuracy for the volume cell evaluation different modifications in the piston geometry have been proposed. Thus, the movement of the piston can be insured using of a fluid pumped behind the piston, [27]. If a rod is attached to the movable piston, the position will be fixed by reading the displacement of the rod, with a Vernier microscope. The volume of the cell and the rod position should be first calibrated with pure liquid [28]. In the equipment presented by Kihran and Pohler [29] the piston is attached to a steel rod with feromagnetic metal pieces, acting as sensing element. The position of the

piston is registered using a piston locator screw, correlated with volume of the cell. The accuracy in volume determination is $\pm 0.0025 \text{ cm}^3$. In Fig.7 is schematically presented Cailletet apparatus that respect the procedure of the synthetic variable volume cell installations.

The main part of the apparatus is a thick-walled Pyrex glass tube (Cailletet tube), about 50 cm long and with an inner diameter of 4 mm and an outer diameter of 12 mm. This tube acting as equilibrium cell and is equipped with a window, a movable piston, a pressure generator and video monitors can be also attached.

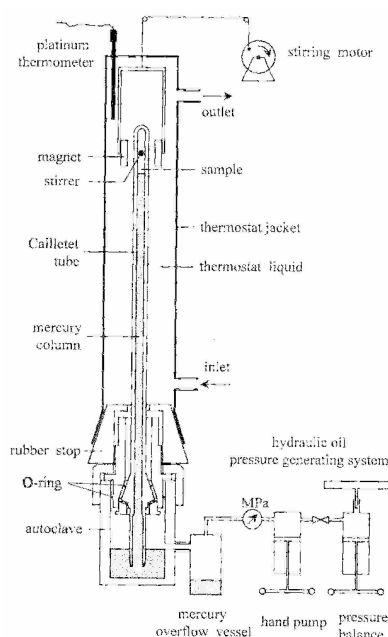


Fig.7. Schematic representation of Cailletet apparatus

An amount of liquid is dosed in the in the top end of the high-pressure tube by a micrometer syringe. The exact mass is determined by weighting. The liquid is degassed by alternating freezing and melting under vacuum condition (using liquid nitrogen as cooling agent). A high vacuum oil diffusion pump or a high vacuum turbo pump creates the vacuum, and the quality is controlled with an ionisation vacuum gauge.

The tube is evacuated and the other component (gaseous at room temperature) is added by displacement with mercury in a gas rack construction. Knowing the volume, pressure and temperature of the gaseous component the exact quantity of it is determine by calculation from an equation of state.

The sample is frozen in the sealed end of the Cailletet tube and the rest of the tube is filled with mercury. Under this condition the tube is transferred from the gas rack to the Cailletet apparatus. Then, the system is pressurized and after that warmed up to the room temperature using the same liquid as the thermostat liquid.

The mixture can be agitated by a stirrer (a stainless steel ball with a diameter slightly less than the bore of the glass tube), which is moved up and down by two button magnets driven by a rotating disk of a stirring motor.

The open end of the tube is placed in an autoclave filled with mercury. The autoclave is connected to a hydraulic oil system, generating the pressure by means of screw type hand pump.

The pressure is measured by means of a dead-weight pressure gauge with an accuracy of 0.005 MPa. The mercury serves as a pressure transmitting fluid between the hydraulic oil pressurizing system and the sample and provides the sealing for the sample. A Viton O-ring, placed at about 2/3 of the tube length, achieves the sealing of the connection between the tube and the autoclave.

The temperature is adjusted by a thermostat bath with circulating ethanol, water or silicon oil depending on the temperature range of interest. The temperature of the thermostat liquid is kept at the desired value with accuracy better than 0.02 K at temperatures up to 370 K.

A platinum resistance thermometer (Pt 100) records the temperature of thermostat liquid near the sample with accuracy within 0.01 K.

The Cailletet apparatus above described is suitable to perform measurement at pressure up to 15 MPa and temperature ranging from 250 K to 450 K.

According to the synthetic methods, the experiment consists on varying the pressure and temperature in order to observe the phase boundaries.

In conclusion, the synthetic methods have the advantages that allow obtaining equilibrium data near the critical region and even in the critical point or in the points of barotropic inversion, because no sampling is necessary.

Similar with the first categories of methods, the accuracy of the obtained data is conditioned by the quality of the degassing procedure and the precision of the measuring instrument.

Consequently the development of new gauge instruments designed for high-pressure conditions will insure a high quality of the equilibrium data.

Conclusions

Experimental methods and installations for investigation of high-pressure phase behaviour are presented, analysed and each category is briefly characterized.

The experimental procedure, the description of the equipment and the improvements are presented for each type of installation. For increasing the accuracy of the experimental data obtained with static techniques different solutions presented in literature are discussed and compared.

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