

## Experimental techniques for the determination of thermophysical properties to enhance chemical processes\*

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*Abstract:* It is of utmost importance to have accurate experimental data available in order to develop accurate modeling for scientific and engineering purposes as it is emphasized through several herein-reported discussions with reknown scientists and engineers. Many methods are used to determine phase equilibria. Classification of the methods is not straightforward as several basic principles can be mixed in several different ways. In this paper, we have selected some techniques, developed in our laboratory, to illustrate one type of classification. Several apparatuses are described. The techniques where all phases are analyzed are very often preferred to those relying on partial determinations requiring data treatment through models. The internal analyses by means of spectroscopic or other in situ analysis techniques are not applicable every time. Then, sampling devices are necessary. Sampling devices must be reliable and lead to extract sample amounts small enough not to disturb the equilibrium under study. The ROLSI™ sampler developed at MINES ParisTech is a very powerful device allowing one to work up to 100 MPa, 850 K, with corrosive components and with samples from 1 µg to some mg. Applications of this sampler are described for fundamental research (phase equilibrium measurements) and industrial purposes (process control and monitoring).

*Keywords:* dynamic methods; experimental methods; high pressure; phase sampler; PVT; recommendations; ROLSI™; static methods; VLE.

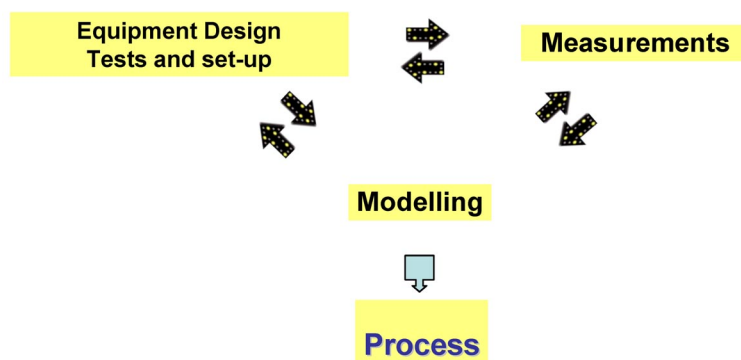
### INTRODUCTION

Scientists and engineers agree that modeling and simulation cannot stand alone and provide response about thermodynamic behaviors and phase diagrams without the help of good experimental data. In fact, many industrial applications require accurate data at relatively high pressures. Unfortunately, bibliographic studies show a scarcity of data above 20 MPa. Furthermore, published results are often not accurate enough. In such a situation, representations or prediction ability through thermodynamic models of thermodynamic properties cannot be extensively tested. One priority is then obtaining accurate data for both “vapor–liquid equilibria” (VLE) and “volumetric properties”. Depending on several factors, such as the chemical nature and physical properties of compounds to be studied, equilibrium pressures and temperatures, and type of equilibrium data to be measured, the right apparatus has to be carefully selected and, if not available, it has to be designed and constructed. Our laboratory has

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been confronted with various studies in relation to industrial problems: energy saving, process optimization, supercritical fluid extraction, acid gas absorption, hydroliquefaction of coal, tertiary oil recovery, safety and environment problems, and so on. It is the reason why the laboratory has been involved in the design, construction, and use of much equipment. Furthermore, the strategy of our laboratory is to rely on several techniques for comparison of obtained data and also on modeling (see Fig. 1) to check for any systematic error that could occur. In fact, nobody can be sure of never having any hidden technical problems.



**Fig. 1** Strategy.

It is important to note that excellent metrology is the preliminary condition to get accurate and reliable data. The choice of the measuring devices for temperatures, pressures, volumes, compositions, and so on is very important at the initial step of experimental work. These devices must be selected to provide consistent accuracy along all chain of measurements and thus must have consistent propagation of errors. Convenient calibration of these devices is also essential. At any step of his work the experimenter must be very careful and must be aware of possible errors when working with computers (bad copy and paste, incomplete sorting, bad cell references in spreadsheets...).

“Thermopack” and “TepThermoSoft” softwares have been developed at MINES ParisTech. They are extensively used for data modeling. A demonstration version of “TepThermoSoft” software is available for free at <[http://www.fcep.ensmp.fr/ThermoSoft/TEP\\_ThermoSoft\\_eng.htm](http://www.fcep.ensmp.fr/ThermoSoft/TEP_ThermoSoft_eng.htm)>.

Some people think experimental work, compared to modeling and simulation, is more tedious, more expensive, and less appreciated in our community. However, numerous e-mail exchanges have confirmed my feeling that good thermodynamic data are absolutely necessary (from databases or experimental laboratories), because process design relies on accurate modeling and modeling relies on reliable experimental data. Simulation also requires data for potential fittings.

Consequently, young researchers have to be convinced to consider such an important field: “experimental thermodynamic research”. In the annex, I have reported for them some sentences extracted from concerned e-mail exchanges.

## CLASSIFICATION OF EQUIPMENT

There are several reviews available (see, e.g., refs. [1–3]). In this paper, we shall focus on analytical methods with accurate and reliable samplings.

## Open-circuit methods

### Flash at given pressure and temperature with sampling of both flowing phases

Knowledge of the thermodynamic properties of highly corrosive components (e.g., acids) at high temperatures is useful in the design of plants for several industrial processes, for example, the pyrolysis reaction of sulfuric acid contained in water-sulfuric acid mixtures as involved in some cycles for production of hydrogen from water. To determine  $P$ ,  $T$ ,  $x$ ,  $y$  data up to 823 K, only a dynamic method allowing the design of a glass or quartz apparatus may be considered [4]. The equilibrium is reached in a coil placed inside a thermostat (liquid or fluidized alumina bath for temperatures higher than 473 K), the equilibrium phases are separated inside the thermostat and sampled after cooling. The flow rates of the phases leaving the separator are adjusted through needle valves, which makes it possible to control the interface level inside the separator. The samples of vapor and liquid phases collected in the sampling systems are analyzed through acid–base titrations.

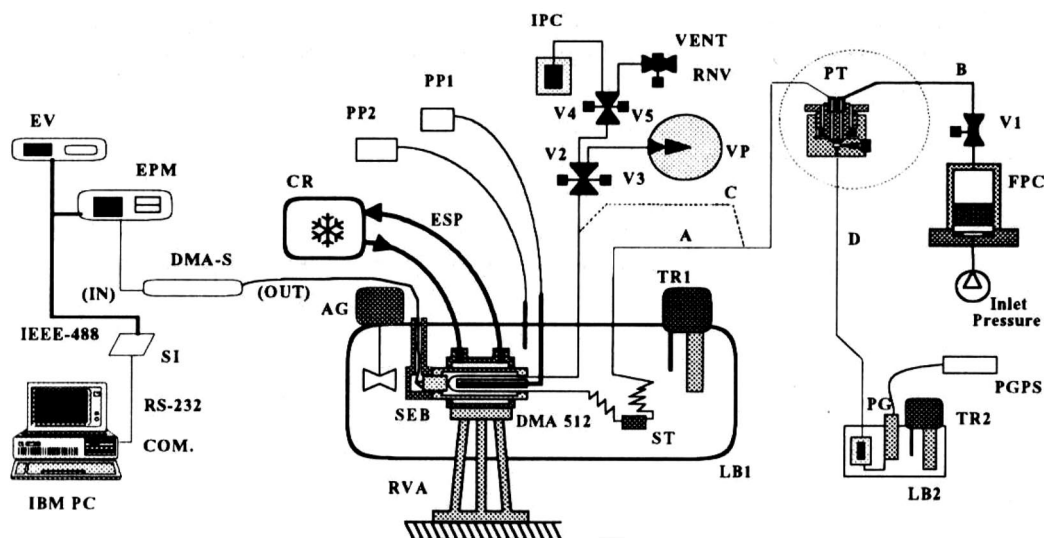
Reliability and reproducibility tests have been performed with the water-acetic acid system [5]. Very good agreement has been found with the data of Othmer et al. [6].

### Stripping of a solute from a solution [7]

An equilibrium cell contains nonvolatile solvent and infinitely diluted solutes. Solutes are continuously carried away in a stripping gas flow. The decrease of concentration of solute in stripping gas is recorded from chromatographic analysis. From writing mass balance and equilibrium equations, we can determine the solutes partition coefficients at infinite dilution with an accuracy better than 2 % in a temperature range of 298–473 K and a pressure range of 1–20 MPa.

### Dynamic synthetic method

The apparatus [8,9] (see Fig. 2) takes advantages of several methods (synthetic, dynamic...). A commercially available external vibrating-tube densimeter has been used—the DMA 512 (ANTON PAAR)

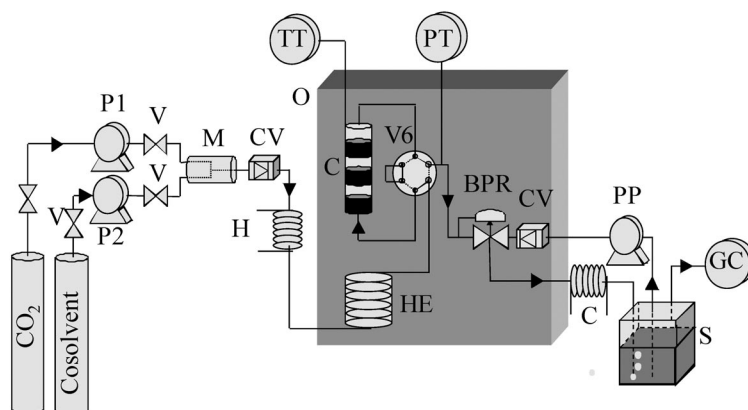


**Fig. 2** Flow diagram of the apparatus. AG: agitator; COM: serial communication port; CR: cryostatic regulator; DMA 512: external vibrating densimeter cell (Anton Paar); DMA-S: DMA power supply and control; EPM: electronic period-meter; ESP: external soft pipe; EV: electronic volt-meter; FPC: feeding and pressurizing cell; IPC: initial purge capacity; LB(i): liquid bath; PG: pressure gauge; PGP: pressure gauge power supply; PP(i): platinum probe; PT: pressure transmitter; RNV: regulating needle valve; RVA: rigid vibration absorber; SEB: sealed electric box; SI: serial interface; ST: security trap; TR(i): thermal regulator; V(i): shut-off valve; VP: vacuum pump.

K.G.). It includes a stainless steel U-shaped hollow tube, electrically excited in an undamped harmonic mode. The vibration period of the U-tube can be measured through an accurate frequency-meter. The mass of the studied fluid located within the U-tube influences its vibration period. Calibration information is available in [10]. Much data has been obtained using this equipment, for example, see [11–13].

#### *Solid entrainments by a supercritical fluid*

The pharmaceutical industry needs accurate solubility data of various compounds in supercritical fluids to perform efficient extractions and design processes to produce very fine powders for drug development. For these studies, a new apparatus was designed [14–17]. Its flow diagram is shown in Fig. 3. The main parts of this apparatus are: high-pressure pumps, a mixer, a heater, a heat exchanger, an equilibrium cell, a back-pressure regulator (BPR), and a separator.



**Fig. 3** Flow diagram of the apparatus. V: two-way valves; P1,P2: high-pressure pumps; M: mixer; CV: check valve; H: heater; O: thermoregulated oven; HE: heat exchanger; V6: six-way, two-position valve; EC: equilibrium cell; TT: temperature transducer; PT: pressure transducer; BPR: back-pressure regulator; C: cooler; S: separator; PP: peristaltic pump; GC: gas volumeter.

Liquid carbon dioxide is compressed at ambient temperature by means of a syringe pump P1 (Isco, model 260D) at the desired pressure. The Isco pump can be operated in either constant flow or constant pressure mode, for flow rates ranging from 0.1  $\mu\text{l}/\text{min}$  to 90 ml/min and pressure up to 50 MPa. The eventual cosolvent is introduced by means of another syringe pump P2, in a parallel flow, at a flow rate depending on the desired composition. To achieve a homogeneous mixing of the two liquid solvents, they circulate through a mixer, M. The mixer is a special device built up for this equipment. The high-pressure fluid then passes through a heater, H, which consists of a brass body, containing a heating resistance, around which is coiled the solvent circuit (stainless steel tubing). The heater, H, is used to heat rapidly the solvent to temperatures over its critical temperature. The supercritical fluid then enters an oven (Spame), where the solubility cell is thermoregulated. The oven can be used up to 400 K, with a temperature regulation within 0.1 K. Due to thermal inertia of the equilibrium cell, its internal temperature is found to be stable within 0.05 K. A heat exchanger, HE, contained in the oven, is used to set the temperature of the solvent at the desired temperature (temperature of the required solubility measurement) before it enters the solubility cell. The HE consists of a brass cylinder around which is wound the stainless steel solvent circuit. The cylinder and tubing are covered with a brass radiator.

Downstream the heat exchanger, a six-way, two-position, high-pressure Valco valve is found in the circuit to either direct the supercritical fluid to the cell or bypass it. This provides a means for re-

moving eventual solid deposits from the line. Cylindrical in shape, the cell EC contains three compartments placed one above the other and fitted at their bottom with stainless steel fritted disks and O-rings. This is equivalent to three different cells connected in series. The solid powder, for which solubility measurements are required, is put inside the three compartments, which have a total volume of about 5 cm<sup>3</sup>. The fritted disks prevent stripping of the solid during the experiment and allow a small pressure drop, advantageous to attain the saturation, while a good dispersion of the supercritical solvent is achieved. EC withstands pressures up to 50 MPa at temperatures up to 400 K. The cap of the cell is sealed in the bottom part using a silicone O-ring. The two parts (cap and bottom) are pressed against each other with a fast connecting mechanical device. The pressure of the supercritical phase is monitored upstream and released downstream through the BPR (Tescom, model 26-1722), which can be either heated or not, to have it at temperatures higher or lower than the extraction temperatures. The BPR allows pressure constancy to within 0.5 % in the lowering line. It can be used up to 473 K and 70 MPa. At the outlet of the BPR, the mixture pressure is reduced to about the atmospheric pressure, then a recovering liquid solvent (a good solvent at atmospheric pressure) stream is used to get the solute in liquid state for collection. Without the solvent to recover the solute, this latter would precipitate during the pressure drop and lead to potential clogging. A separator, S, is used to vent off the gas and collect the solvent phase. At the end of each experimental run, the liquid solvent line is washed with fresh solvent to recover all the solute. The total volume of used gaseous solvent (extraction solvent), is measured by means of a volumeter check valve (CV) and the concentration of solid in the solute recovering liquid phase by a gas or liquid chromatography. From these two data and knowing the total volume of the solute recovering liquid solvent, the solubility of the solid in supercritical fluid can be calculated. It is also possible to consider, instead of the just described recovering method, a direct sampling method, using, for example, the ROLSI™ samplers [18] (see <www.rolsi.com>).

## Closed-circuit methods

### *Static methods with sampling of both phases*

The equilibrium cell is kept at constant temperature in an air thermostat. It is filled by given amounts of components. Pressure and composition of both phases at equilibrium are measured, respectively, by a pressure transducer and chromatographic analyses of small samples taken from the cell. Several apparatus are based on these principles, they differ by their sampling systems and their ranges of operation:

- The apparatus with microexpansion sampling system [19] has been used up to 40 MPa and 623 K for studying mixtures containing hydrogen with hydrocarbons [20,21] and white oil [22]. Samples are directly injected in the carrier gas flow of a gas chromatograph (GC) by a very short time opening of microvalves.
- The apparatus with microcell sampling system [23] allows one to work up to 100 MPa and 473 K at equilibrium temperatures lower than boiling temperature of the heaviest component of studied mixtures [24]. Samples are taken from equilibrium cell into microcells. Each microcell is taken off and transferred to a special chromatographic injection port.
- An apparatus using a capillary-microvalve sampling system [25] had been designed to work especially on the water-ammonia system [26] up to 7.5 MPa and 558 K. It has been used afterwards to perform some measurements on CO<sub>2</sub> propane mixtures [27].
- Another apparatus [28] uses a new capillary sampling system. The principles are very similar to those of the apparatus with microexpansion sampling system, but the chromatographic injection port being situated at one end of the capillaries allows one to work at equilibrium temperatures below boiling temperature of the heaviest component as the injection temperature can be chosen independently of the equilibrium temperature. This kind of apparatus [29] has been used in conditions up to 673 K and 40 MPa for measurements of phase equilibria involving products ob-

tained through direct coal liquefaction. A sapphire equilibrium cell with a movable ROLSI sampler to study fluid multiphases is displayed in Fig. 4, and an electromagnetic ROLSI sampler in Fig. 5.



**Fig. 4** Equilibrium cell with a movable ROLSI sampler.



**Fig. 5** Electromagnetic ROLSI sampler.

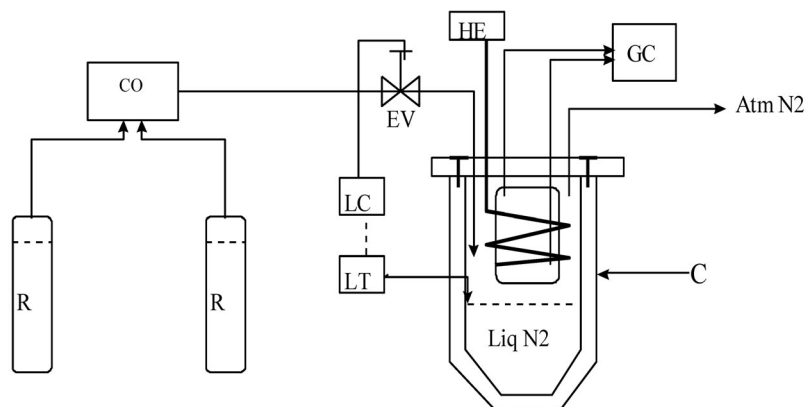
Sampling is really the important point in most of the studies where analyses are necessary. Great care has been taken to develop reliable tools.

In the industrial field, Fraser [30] talks about liquid fractionation towers (columns) which can be controlled by optimizing the inlet feed flow rate, reflux flow rate, reflux temperature, and column pressure. He explains that on-line chromatographs can provide both compositions: of liquids in column bottoms inlets and of vapors in column overheads for process control. The GC should be located as close

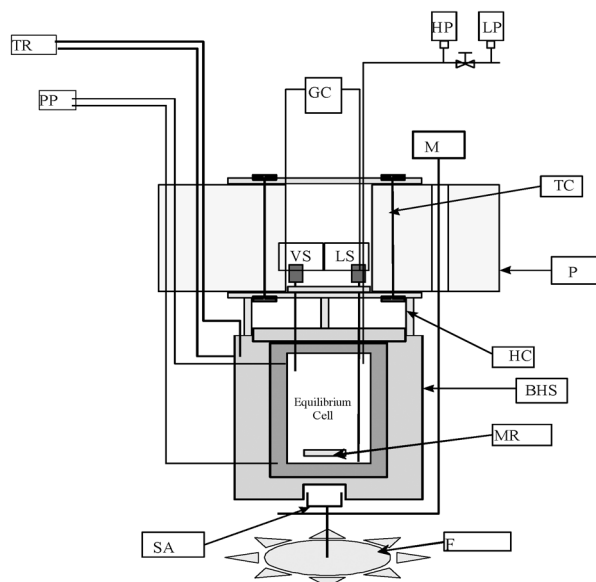
as possible to the sample point, and the samplers must allow fast vaporization of liquid samples and reliable withdrawing. This is not satisfactorily obtained using rotating sampling valves that could be advantageously replaced by the ROLSI samplers [18]. Furthermore, there is no need to transport the fluid (with the possibility of modification of its composition if strict thermodynamic conditions are not fulfilled) to be sampled to the sampling system as the ROLSI™ samplers can be fixed directly on the process lines.

Much data has been already obtained with this apparatus [31–46]: mixtures of olefins, CO<sub>2</sub> with propane, CO<sub>2</sub> with propane and methanol, methane with several heavy compounds differing by their chemical nature, etc. Apparati with microexpansion, microcell, and capillary sampling systems have been extensively used to develop a database related to gas processing for the Gas Processors Association.

Based on the static-analytic method, a new apparatus [47] was designed to work on cryogenic systems for VLE and solid solubility measurements. This equipment has been selected to highlight special features of the technique and present an application related to safety problems in industry. Its flow diagram is given in Figs. 6 and 7. Accurate VLE data for the Ar–O–N system were obtained to improve efficiency of distillations toward production of very pure compounds. Solid–liquid phase equilibrium (SLE) data play an important role in cryogenics, for instance, in the equipment design or in the transport of liquefied gases where the formation of solids plugs can cause important safety problems. Solubility data of nitrous oxide and carbon dioxide have been measured as independent solutes [48] and as mixtures [49] in liquid oxygen at several temperatures between 90 and 110 K.



**Fig. 6** Overview of the apparatus. HE: heat exchanger; LT: level transducer; LC: level control; EV: electrovalve; GC: gas chromatograph; C: cryostat; R: liquid nitrogen vessels; CO: commutator.



**Fig. 7** Schematic view of the cell. F: fan; M: variable-speed motor; PP: platinum probe; MR: magnetic rod; P: plug of the cryostat; BHS: brass heating sleeve with rounded heating resistance; GC: gas chromatograph; HC: holding column; HP, LP: high- and low-pressure transducers; VS, LS: vapor and liquid samplers; TR: PID temperature regulator; TC: Teflon thermal shield columns; SA: stirring assembly.

For measuring the cosolubility of solids in cryogenics systems, the original apparatus was modified. The main target of the modifications was to be able to inject, into the studied solvent, homogeneous distributions of solid particles corresponding to their loading mole fractions. For these purposes, a new device was designed, constructed, and tested, namely, the injector-atomizer. This new device leads to a significant improvement of the technique over the previous traditional apparatuses used to measure solubility data of mixed solids.

#### *Static methods with variable volume cell*

No sampling is needed. The components of the mixture are introduced separately and weighed in the equilibrium cell. Then, the cell is brought to the equilibrium temperature inside a thermostat. The  $P$  vs.  $V$  curve is recorded, and the break point displayed in the curve gives the equilibrium pressure and the saturated molar volume of the liquid mixture.

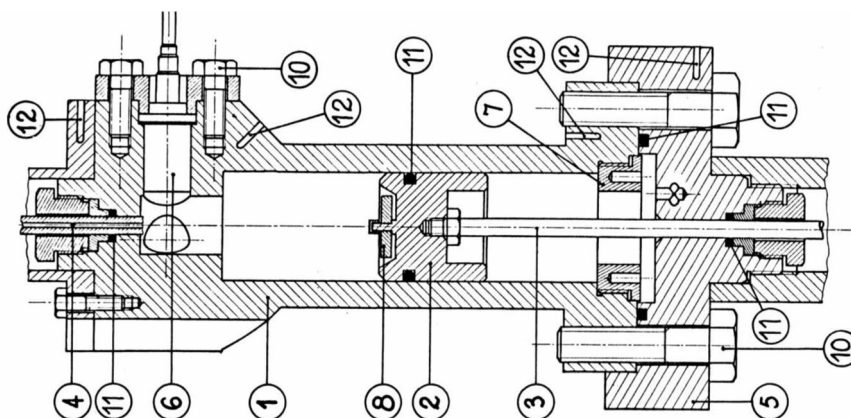
#### *Variable-volume cell, weighing*

In the moderate-temperature apparatus [50], the volume is changed by moving a piston through a hydraulic fluid. This apparatus has been used to study mixtures of chlorofluorohydrocarbons up to 373 K and 5 MPa, and then obtain bubble pressures and saturated liquid molar volumes. For the high-temperature apparatus, the piston was replaced by a bellows [51,52] to extend the temperature range to 573 K for pressures up to 60 MPa. Mixtures of ethylene with polyethylene have been investigated with this apparatus [53,54].

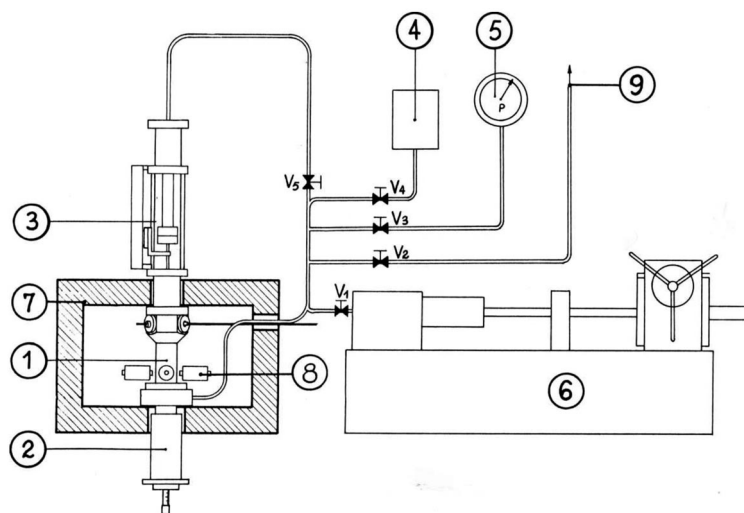
#### *Variable-volume cell, weighing and interface level measurement [55]*

The equilibrium cell and the flow diagram are given in Figs. 8 and 9.





**Fig. 8** Equilibrium cell. (1) cell body; (2) piston; (3) probe for piston level measurements; (4) thermistor probe for vapor–liquid interface level measurements; (5) pressurizing assembly; (6) membrane pressure transducer; (7) stop screw; (8) magnetic rod; (10) bolts; (11) viton O-ring; (12): thermocouple well. Reprinted with permission from F. Fontalba, D. Richon, H. Renon. *Rev. Sci. Instrum.* **55**, 944 (1984). Copyright © 1984, American Institute of Physics.



**Fig. 9** Flow diagram of the apparatus. (1) equilibrium cell; (2) assembly for piston-level measurements; (3) assembly for interface-level measurements; (4) pressurizing liquid reservoir; (5) manometer; (6) high-pressure pump; (7) air thermostat; (8) solenoids to create a rotating magnetic field; (9) fitting to vacuum pump; ( $v_i$ ) shut-off valves. Reprinted with permission from F. Fontalba, D. Richon, H. Renon. *Rev. Sci. Instrum.* **55**, 944 (1984). Copyright © 1984, American Institute of Physics.

By writing mass balance equations such as

$$n_i = x_i \frac{V^L}{v_{i,LS}^L} + y_i \frac{V^V}{v_{i,VS}^V}$$

we note that for a binary mixture we have four unknowns: compositions  $x$  and  $y$ , and saturated molar volumes  $v_{i,LS}^L$  and  $v_{i,VS}^V$ .  $n_i$  are obtained from weighing and  $V^L$  and  $V^V$  from interface level measurements.

Then, at given temperature and pressure, two loadings of different total compositions are needed to write four equations and calculate the four unknowns.

A good procedure consists of recording  $P$  vs.  $V$  curves and solving mass balance equations in the common diphasic range (see Fig. 10) to get the corresponding parts of bubble and dew curves; in addition, two bubble pressures and two saturated liquid molar volumes are obtained graphically from the two  $P$  vs.  $V$  curves.

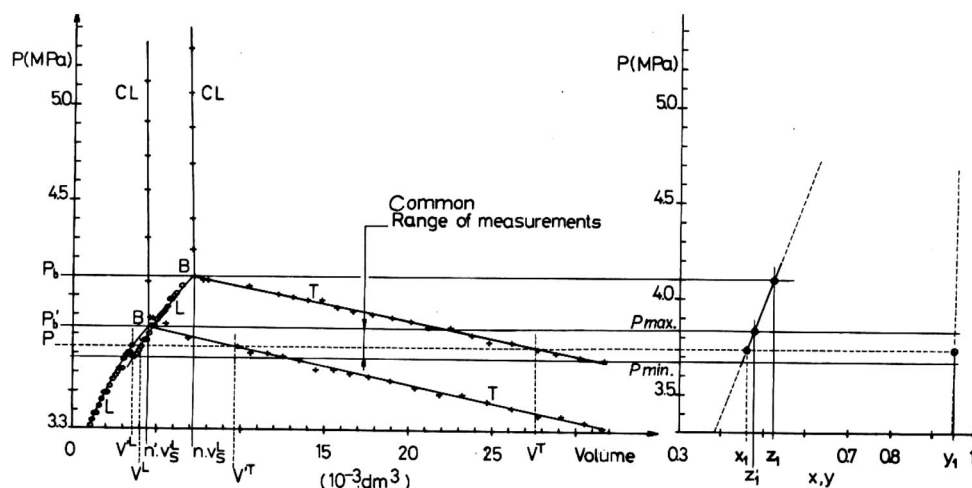


Fig. 10 Pressure as a function of liquid volume  $V^L$  and total volume  $V^T$  for mixtures of two different global compositions  $z$  and  $z'$ .

This apparatus was especially designed to work with  $\text{CO}_2$  and hydrocarbons in relation to tertiary oil recovery up to 45 MPa and 433 K. It has been used for many measurements on refrigerants (see, e.g., [56]).

Based on the variable-volume cell, an equipment for  $PVT$  and gas–oil ratio measurements has been designed for production assistance to petroleum industry [57]. Its temperature and pressure limitations are, respectively, 473 K and 70 MPa. For triphasic measurements, another piece of equipment [58] was designed (cell consisting of a sapphire tube) with a piston and a mobile sampler allowing us to treat the vapor phase independently if required (e.g., due to low values of total pressures leading to small vapor densities and finally bad solutions of mass balance equations).

## CONCLUSIONS

Efficient, clean, and cheap processes are expected to satisfy modern requirements. Consequently, more and more new accurate data will be required, in the future, for model developments (predictive or representation tools). Then, experimental thermodynamics are essential. The choice of the techniques to be used for determining the required physical property depends strongly on experimental conditions and on the types of applications. Although much equipment is available to satisfy most needs, particular applications can still require either adapting equipment or new equipment designs.

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## ANNEX: GOOD REASONS TO PERFORM EXPERIMENTAL MEASUREMENTS

- “Not only are experimental results of direct use in industrial design but, in addition, they provide the essential information needed to determine the force fields that are required for simulation.”
- “Models come and go, but data are forever!”
- “The principal reason experimental work is to be highly prized, is that experiments are the only way to recognize the physical world. Modeling is only as good as the molecular (or atomic) potential, and all molecular potentials are inexact, so that those errors multiply in going from the molecular scale to the macroscopic scale.”
- “We still cannot do everything with theory—far from it. Experiment is crucial as input to theory and essential for validating theory. We theorists need academic experimental laboratories to continue to provide experimental data that challenges us to improve our theories.”
- “As everyone knows, a prerequisite for the synthesis, design and optimization of the different processes both in chemical, pharmaceutical, gas processing, petrochemical, food industry and pollution control with the help of process simulators, is the reliable knowledge of thermophysical properties of pure compounds as function of temperature and pressure and mixture data as function of temperature, pressure and composition.”
- “I should start by saying that I feel that experimental thermodynamics is an essential core discipline that we cannot do without. I do not believe that theory and simulation can stand on its own without the availability of high quality experimental. The vast majority of theoretical techniques are not completely predictive and require some experimental input for the refinement of the intermolecular parameters (e.g., equation of state modeling, group contribution methods, classical molecular simulation). The predictive ab initio techniques are not yet good enough to provide a good description of bulk fluids and materials (e.g., quantum simulation techniques overestimate the vapor pressure of water by almost 100 %).”
- “The situation in all science is that an excellent, well-done experimental measurement is the ‘gold standard’ to which all theories and models have to be compared. There are many examples in science in which a well-done experiment showed the problems and errors in theory, and theory had to be redone.”
- “Our problem today is that we don’t have enough experimentalists and have too many modelers. We need experimental data on complex systems that are outside of our existing database.”
- “I believe that experimental measurements are the bedrock on which modeling and simulations are based.”
- “When we do research whether experimental or theoretical, it is the quality and novelty which matters. We need to do both novel laboratory work, and modeling and simulation.”
- “Obviously people differ on what is ‘honorific’; my feelings are to highly respect careful measurement and believe not enough is being done.”
- “Some will say that computation will provide all the answers for us. But even if that will be true ultimately (I am skeptical about this), that situation will take many years to achieve. And along the way, the only reliable validation of the methods will be via comparison with data. Without data, the computational results may only be “photons from a screen” and have little to do with reality.”
- “We need new property data in order to solve complex problems of removal of carbon dioxide from combustion streams, understand opportunities with methane gas hydrates, transport natural

gas at both high pressure and as a liquid at low temperature and the utilization of more complex heavy oils and their conversion to gasoline and diesel fuel high quality experimental facilities are essential.”

- “The key to cost effective data is close coordination between data taking and modeling. Many times these are considered separate activities. If they can be done at the same time under common leadership then both the data collection and modeling benefit. Many times fewer data points can be collected if the proposed model shows that a good correlation has been found which describes the data. Too many times we develop a large data matrix without carefully considering the model development need.”
- “Wider range (temperature, pressure), very wider targets (polymer solution, inorganic materials, and so on) will be more required, I think. New experimental data will strengthen databases and prediction methods more and more.”
- “Data are essential to understanding thermodynamic systems. Without those data, we cannot properly build and tune our models.”
- “From my perspective in the Dow Chemical Company, I can almost always find someone with the particular modeling skills a particular project may require. If not, these skills can usually be cultivated in an experienced modeler quite quickly. On the other hand, finding someone with good experimental skills is considerably more difficult. The supply of good experimental labs is low and the cost/time to cultivate new skills is long.”
- “While new modeling developments can make it easier to extrapolate from existing data, there will always be a need to generate data for validation and for systems beyond the scope of existing models. Personally I am more worried about the decrease in good experimental capabilities in academia, research institutes and contract labs than I am about the need for more modelers. Within the oil & gas industry there is increasing emphasis on developing (a) hydrocarbon resources at extremes in T & P (e.g., arctic regions, deep water), (b) gases contaminated with high levels of H<sub>2</sub>S and/or CO<sub>2</sub>, (c) very ‘heavy’ oils, and (d) unconventional resources such as tar sands and oil shales. Many of the new technologies being developed for these resources require conditions and/or introduce components that are beyond usual operations. Moreover, there are increasing pressures to minimize CO<sub>2</sub> emissions and lower levels of, for example, sulfur compounds in fuel.”
- “Measurements are needed as well as people who have experience in measuring thermophysical property data.”
- “In my experience, there are quite a number of very good researchers working in the field of modeling thermodynamic systems. There are now only a very few who focus on measuring high quality data and even fewer who can develop new methods and equipment.”

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