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A simple and sensitive densitometer for critical liquid mixtures

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Résumé. — On décrit un pycnomètre scellé pour l'étude des mélanges de liquides près de leur point critique de miscibilité complète. La cellule utilisée permet d'effectuer aussi des mesures optiques. Quoique la méthode reste très simple, une grande précision peut être atteinte ($d\rho/\rho = 3 \times 10^{-6}$ en relatif et $4 \times 10^{-5}$ en absolu) sur une grande gamme de température.

Abstract. — A sealed volumeter for the study of liquid mixtures near their solution critical point is described. The cell used allows optical investigations to be performed at the same time. Although the method is very simple, high accuracy can be obtained ($d\rho/\rho = 3 \times 10^{-6}$ relative and $4 \times 10^{-5}$ absolute) in a wide temperature range.

For the special purpose of measuring the density of liquid mixtures near their critical solution point a densitometer must exhibit specific features. It must be: i) built in a chemically inert material, ii) sealed to ensure that the concentration remains constant and to avoid external contaminations, iii) easily thermalized with high accuracy. Moreover, in the present case it has to be designed so as to allow simultaneous optical investigations in the liquid mixture.

The choice of a pycnometer (volumeter) rather than a mechanic oscillator [1] or a magnetic suspended buoy [2] was chiefly governed by this last requirement and also because a pycnometer has a high resolution while being much more simple to set up.

A problem with pycnometers is how to reconcile the requirement of a high sensitivity and an extended thermal range (see Ref. [3]). Several stratagems have been used, which all reduce to a change of the liquid volume under study, either by confining the sample with mercury [4] or with a piston [5]. These methods however create some additional problems, so we have developed an alternative method.

1. Description.

In figure 1 is shown the pycnometer. It was built in Pyrex glass which is chemically inert against most substances and it exhibits good optical properties. Moreover the thermal expansion coefficient is very low.

![Fig. 1. — The pycnometer. Symbols are explained in the text.](image_url)

The reservoir (A) which contains the liquid can be designed to allow use as an optical cell as well. Its volume at 0°C is $V_0$. It is connected to a cylinder pipe of inner diameter $a_0$ (at 0°C): the height ($H$) of the meniscus which separates the liquid from the vapour can be detected by optical means. C and D are other reservoirs and E is either a seal or a Teflon screw tab. The rôle of C is to maintain a nearly constant pressure in the cell, and that of D is explained in the following.

2. Filling procedure.

We have adopted the following procedure :
First fill C with a mass $M$ of liquid under atmo-
spheric pressure. Then seal E, then cool A while heating C so as to make the liquid flow from C to A.


The density can be deduced from the height of the liquid through the relation

\[ \rho^{-1} = \frac{1}{M} \left[ V_0(1 + 3 \alpha T) + \left( \frac{\pi a_0^5}{4} \right) (1 + 2 \alpha T) H \right]. \]

(1)

Here \( \rho \) is the density of the liquid and \( \alpha \) is the thermal linear expansion coefficient of Pyrex (\( \alpha = 3.3 \times 10^{-6} \)).

Using the typical values: \( V_0 = 30 \text{ cm}^3, \rho = 1, \ a_0 = 0.1 \text{ cm}, 1/\rho(d\rho/dT) = -1 \times 10^{-3} \text{ K}, \) a maximum useful range \( H_{\text{max}} = 4 \text{ cm} \) corresponds to a temperature range of 1 K.

When \( T \) is such that the meniscus is at the top of B, one further increases the temperature so that some liquid flows from B in the reservoir D. Then by lowering \( T \) it is possible to overlap with the previous measurements and so to finally cover a wide range of temperatures.


The determination of \( V_0 \) and \( a_0 \) has been made by filling the pycnometer with pure water. Equation (1) has been used and the data have been compared to the density reported in reference [6]. In figure 2 are reported the deviations to a fit where \( V_0 \) and \( a_0 \) are free parameters. The scatter of data corresponds to a \( H \)-uncertainty of 0.01 cm or alternatively \( 3 \times 10^{-6} \text{ g. cm}^{-3} \) on \( \rho \). This scatter is mainly due to small inhomogeneities of the diameter \( a_0 \). The relative uncertainty on \( V_0 \) is almost entirely due to that on \( M \) : 

\[ \frac{dV_0}{V_0} = 1.2 \times 10^{-6} \] 

directly from the fit and \( 2 \times 10^{-5} \) when considering a possible weighing error of 0.5 mg (we used a balance with 0.1 mg resolution). The mean diameter \( a_0 \) is determined within 0.1 %, which corresponds to a 1 \( \mu \) uncertainty.

5. Accuracy.

The differentiation of equation (1) gives:

\[ \frac{\delta \rho}{\rho} = \frac{(\delta M/M) + (\delta V_0/V_0) + (\pi a_0^5/4 V_0) \delta H + (\pi a_0 H/2 V_0) \delta a_0}{\rho}. \]

The mass measurements are better than 0.5 mg and the error on \( H \) does not exceed 0.01 cm. Then

\[ \frac{\delta \rho}{\rho} = 4 \times 10^{-5}. \]

As far as relative measurements are concerned only the \( H \)-uncertainty has to be accounted for, and one expects an accuracy of \( \delta \rho/\rho = 3 \times 10^{-6} \), which actually corresponds to the scatter of data in figure 2.

6. Example.

We have reported the data concerning the binary fluid Nitrobenzene-nHexane (N-H), whose critical temperature is \( T_c = 29.022 \text{ °C} \). The slope of \( \rho \) versus the temperature difference \( T - T_c \) is expected to change near \( T_c \). This effect is visible in figure 3.

![Fig. 3. — Volume expansion or density variation in a critical mixture (N-H) near its critical solution point. \( T_c = 29.022 \text{ °C} \) and \( \rho \) is density.](image)

7. Concluding remarks.

Binary fluids whose components exhibit a large density gap may develop non negligible gravity-induced concentration gradients [7]. Although remaining in most cases very small, it is possible to eliminate this effect by setting in (A) a glass-coated magnetic stirrer.

Finally, as noted above, the reservoir A can be used as an optical cell, allowing simultaneous measurements of light scattering, transmission of light, refractive index, etc.
References