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Laboratory Experiment

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A Precise, Simple, and Low-Cost Experiment To Determine the Isobaric Expansion Coefficient for Physical Chemistry Students

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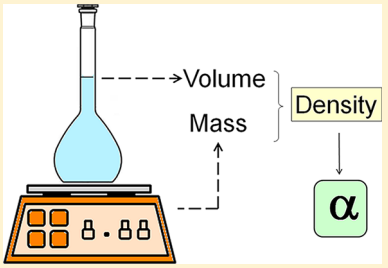
Supporting Information

ABSTRACT: The procedure of a physical chemistry experiment for university students must be designed in a way that the accuracy and precision of the measurements is properly maintained. However, in many cases, that requires costly and sophisticated equipment not readily available in developing countries. A simple, low-cost experiment to determine isobaric expansion coefficient has been designed and successfully implemented. The practice includes measurement of density at controlled temperatures and mathematical and graphical treatment of data. In spite of the simplicity of the experiment, the precision and accuracy of the measurements are not forfeited.



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INTRODUCTION

One of the main concerns of physical chemistry is the determination of the properties of substances. Very often, accurate and precise measurements are required. Measuring devices and procedures must be therefore carefully designed to minimize all systematic and random errors.[1] Understanding this basic principle is essential for the formation of future chemists[2,3] and must be taken into account to design physical chemistry laboratory sessions for second- or third-year students. The proposed experiments should include a rigorous procedure to avoid any kind of experimental errors, and the students should be aware of the reason for this procedure.

Experiments in physical chemistry sometimes require sophisticated apparatus and equipment that it is not always readily available in developing countries such as Ethiopia. Moreover, many universities in developing countries face problems such as unavailability of replacement parts and shortage of trained technical staff that can perform maintenance and repair of instruments.[4] In that case, a clever design of new experiments is needed. These experiments must: (a) allow the student to understand the proposed concept; (b) require simple, low-cost, and easily replaceable equipment; (c) the experimental procedure remains as simple as possible but (d) not forfeiting the accuracy and precision of the experimental data generated. This latter reason is of particular importance for the student to understand the importance of getting quality data to successfully apply the models that describe the observations.

Background and Experimental Overview

The experiment proposed in this work intends to familiarize students with the concept of thermal expansivity through measurement of the isobaric expansion coefficient, α, of a liquid. α is related to the change of the volume of a substance with temperature.[5]

One first approach to determine α is to measure the volume of the substance at different temperatures as it is beautifully demonstrated by Padgett and MacGowen,[6] who built a thermometer-like device and measured change of volume for different changes of temperature, ΔV versus ΔT. α is then determined from the expression: $\alpha = \Delta V/V\Delta T$. This procedure, however, requires the accurate measurement of the volume of the reservoir, V. Moreover, although this laboratory exercise is very suitable for general chemistry of high school students, higher year physical chemistry students are required to use the rigorous definition of α:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{1}$$

At constant pressure, eq 1 can be rearranged and integrated as

$$\ln V = \alpha T + C \tag{2}$$

where C is the integration constant. A well-known alternative approach is to measure densities, ρ, at different temperatures and constant pressure;[7−9] then eq 2 can be written as follows:

$$\ln \rho = -\alpha T + C' \tag{3}$$

and the expansion coefficient is obtained from the slope of the representation $\ln \rho$ versus T.

The most widely followed procedure to determine α is by measuring densities using a vibrant-tube densimeter.[7,8] This piece of equipment is generally not available for undergraduate students and even many universities of Ethiopia do not have one. Furthermore, it does not measure directly the density of a substance but the vibration period of the tube that contains it.

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For that reason, it may not be suitable from a didactic point of view. Simpler and more available instruments are pycnometers, which allow measuring densities of liquids with great accuracy. Interestingly, no reports have been found in the educational literature and very few in the scientific literature on where density is measured by a pycnometer at constant and controlled temperatures.[9] This is probably due to the technical difficulties of keeping the whole bulk at constant temperature while operating the device.

In this paper, an experiment for physical chemistry laboratory to determine the isobaric expansion coefficient for ethanol is designed. It requires simple and low-cost equipment. The experiment is based on the principle of the pycnometer, but this can be replaced by a volumetric flask. The main feature of the procedure is that special care must be taken to keep the sample at constant temperature during the measurement; that means: (a) avoiding heat loss and (b) assuring thermal equilibrium. For that purpose, the recipient that contains the sample is kept immersed in a temperature-controlled bath during almost all the process, and adequate equilibration times are waited to ensure thermal homogeneity.

EXPERIMENTAL PROCEDURE

Isobaric expansion of ethanol is determined by measuring its density at different temperatures. A volumetric flask acting as pycnometer is filled with ethanol up to the mark, and the weight of ethanol filled is determined.

In the first place, a clean and dry 100 mL volumetric flask and stopper are weighed with a precision of ±0.005 g (a two-decimal precision balance can be used). The volumetric flask is immersed into a water bath keeping the mark below the level of water. An Erlenmeyer flask acting as reservoir is filled with about 120 mL of absolute ethanol and immersed in the same bath keeping the level of ethanol below the level of the water of the bath. This latter flask is capped with a cork to avoid ethanol evaporation. A scheme of the experimental arrangement is represented in Figure 1. (Note: it is not indispensable to use absolute ethanol; hydrous ethanol is also acceptable because this procedure is valid either for pure substances or mixtures. Questions are proposed in the manual so that the student can appreciate the difference.)

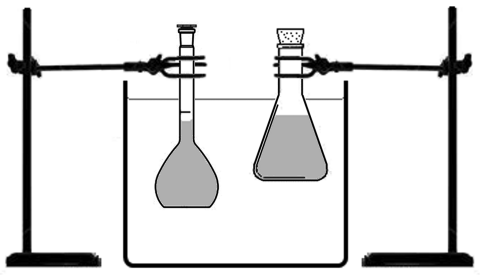

Figure 1. Arrangement of the experiment.

The bath is set to the desired temperature, and once it is stable, 15 min are waited to ensure the temperature of the ethanol in the reservoir is constant. It is convenient to occasionally stir the ethanol to favor the heat transfer. After that, keeping always the volumetric flask immersed in the bath, it is filled with ethanol from the reservoir up to 1 cm below the mark. This procedure must be done as quickly as possible to avoid heat loss. Close the volumetric flask, and place the reservoir back into the bath. Wait 5 min to further stabilize the temperature of ethanol. Measure the temperature accurately in the volumetric flask by a suitable device (with a precision of ±0.05 °C or better). In our laboratory, we used a mercury thermometer with divisions each 0.1 °C, although a slightly less accurate thermometer (divisions each 0.5 °C) can be used if reading is properly taken. Immediately after temperature is recorded, add ethanol from the reservoir to the measuring flask using a dropper until the mark is reached. This process must be done again as quickly as possible while trying to keep the flask immersed in the bath as much as possible (lift the flask only enough to see the mark). Close the flask with the stopper, and remove it from the bath. Dry it thoroughly and weigh it. Set a new temperature (higher). The mass of the ethanol added is the difference from this weight and the weight of the empty flask and stopper.

Alternatively, this experiment can also be done by a subtractive process, that is, add ethanol to a level above the mark and remove liquid down to the mark by using a dropper when the temperature is stabilized. In any case, the level of ethanol must remain below the level of the water of the bath.

Handouts of the experiment (included in Supporting Information) were given to the students at the beginning of the term. They were required to read and understand them before the laboratory session. A prelab session of 15−20 min was done to demonstrate the scientific principles and to explain the details of the experiment and how to read accurately the thermometer. The students were gathered in groups of four. They were required to take four readings. Because of the characteristics of our bath and thermometer, the chosen temperatures were 25, 35, 45, and 50 °C. The total time of the session was about 3 h. After the class, the students were required to fill a report showing the data measured and their mathematical treatment.

HAZARDS

Eye protection should be worn at all times while in the laboratory, and care must be taken when handling laboratory glassware. Ethanol is flammable, but ignition risk is minimal because it is not heated directly but in a water bath.

RESULTS AND DISCUSSION

The students were required to gather the data tabulated in Table 1. Measured mass of ethanol, volume, calculated density, and ln ρ are included for every temperature. Considering an uncertainty in the ethanol weight determination of ±0.01 g and

Table 1. Student-Generated Experimental Data of Density at Different Temperatures

T (set) (°C)	T (measured) (K)	V (corrected) (mL)	m (total) (g)	m (ethanol) (g)	Density (g mL^{-1})
298.15	295.85	100.01	141.96	78.27	0.7826
308.15	307.45	100.04	140.98	77.29	0.7726
318.15	316.75	100.06	140.24	76.55	0.7650
323.15	322.55	100.07	139.75	76.06	0.7601

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an uncertainty in the volume of the flask of ±0.01 mL, the uncertainty in the density measurement was ±0.0002 g mL^{-1}.

To make them understand the importance of accuracy in experimental physical chemistry and of minimizing systematic errors, a correction of the volume of the volumetric flask can also be applied. For the same principle of thermal expansion, glassware volume also depends on temperature. Although in many cases it is negligible, in our case, the magnitude of the correction is slightly larger than the experimental uncertainty, so it must be taken into account. This correction depends on the material of the flask; for soft glass, it is expressed as follows:[10]

$$V_{20} = V(1 + 2.5 \times 10^{-5}(20 - T)) \quad (4)$$

where V_{20} is the volume of the glassware, calibrated at 20 °C (100 mL in our case). V is the volume at a different temperature, T. For example, at 50 °C, the actual volume of the 100 mL flask is 100.08 mL. This difference affects the accuracy of the density calculation in the fourth decimal.

Sample data generated by one group of students are given in Table 1. Representation of ln ρ versus T as well as the trend line is given in Figure 2. α can be obtained from the slope of the

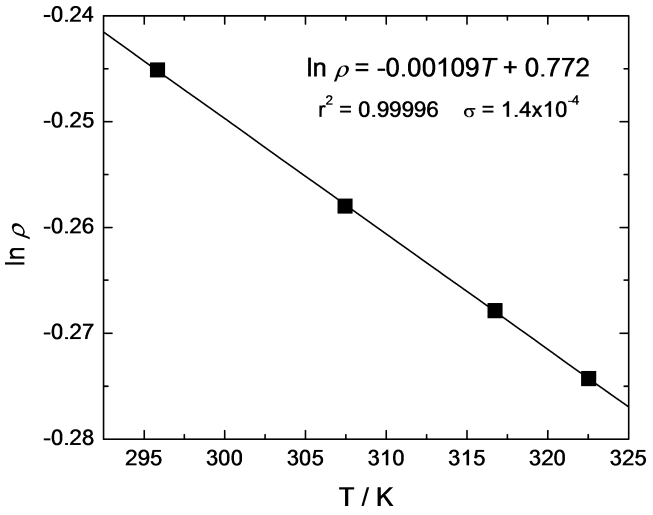

Figure 2. Fitting of data in Table 1 to eq 3.

fitting changed of sign; for the example above, a α value of 0.00109 K^{-1} is obtained with a very good precision. The students were required to treat their data and do the fitting using Microsoft Excel worksheets.

Because of the general lack of access of the students to computing tools, an introductory session to explain the basics of the Excel program was given at the beginning of the term. A total of 17 groups of four students each conducted the experiment. Out of them, eight groups determined α with a very good precision (R^2 > 0.99 for the linear regression), obtaining values for α within the interval of 0.00105−0.00113 K^{-1}. Seven out of the 17 groups measured correctly three of the four data points and one outlier. If this outlier is removed from the fitting, acceptable values of α are obtained. This presents a good opportunity to explain them how to treat data that deviate too much from the regression. In any case, even with the outliers, they obtained values of α within the range of 0.0092−0.00142 K^{-1}. Only two groups obtained an inaccurate value of α, indicating that they must have introduced a systematic error in the procedure. In any case, the didactical goal had been achieved. The students were required to hand in a laboratory report gathering the results and calculations as well as to answer the questions proposed in the handouts. Examination of these reports indicated that they understood the concepts intended. They also carried out a writing test about the different experiments conducted in the lab session, and they scored an average of 68% of the answers related to the current experiment.

CONCLUSIONS

An inexpensive, readily available, and easy to implement experiment to determine isobaric expansion coefficient is proposed. In spite of its simplicity, the determination of α can be done with great accuracy and precision. This experiment can be easily carried out in laboratories with a certain lack of resources such those in developing countries. It was successfully implemented in a real classroom at The University of Addis Ababa (Ethiopia) with satisfactory results. Apart, to help the students understand the concept of thermal expansion, the practice intends to show a rigorous and careful experimental procedure to produce quality data and to make them understand the importance of accurate and precise measurements in physical chemistry.

ASSOCIATED CONTENT

Supporting Information

The handouts given to the students at the beginning of the term, which include a brief theoretical description of the thermodynamic meaning of the isobaric expansion coefficient, detailed description of the experimental procedure and data treatment, and a series of questions proposed to the students to ensure understanding of the concepts. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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