

Mechanical Coefficients of Liquids by a Differential Expansion Method

A Physical Chemistry Experiment

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Mechanical coefficients of liquids play an important role in the understanding of the physics of fluids. There are a relatively small number of undergraduate experiments dealing with thermodynamic properties of pure liquids and liquid mixtures. In fact, it is difficult to find experiments other than direct determination of liquid molar volumes or the molar excess volume for binary mixtures, which are usually measured by pycnometry. This paper describes a simple experiment designed to measure the isothermal compressibility, κ_T , and the thermal expansion coefficient, α_p , of liquids. The experiment is based on an expansion principle and can be carried out with a rather simple experimental device. Additional features of the method and advanced experiments are discussed.

Theory

The mechanical coefficients of a given substance are defined by the following thermodynamic relations

$$\kappa_T = -V^{-1}(\partial V/\partial p)_T = \rho^{-1}(\partial \rho/\partial p)_T \quad (1)$$

$$\alpha_p = V^{-1}(\partial V/\partial T)_p = -\rho^{-1}(\partial \rho/\partial T)_p \quad (2)$$

where V is the molar volume, ρ is the molar density, T is the temperature, and p is the pressure. Both quantities give a measure of the relative compression and expansion capabilities of the substance against pressure or temperature changes, respectively.

From the experimental point of view, while α_p of liquids can be determined at atmospheric pressure by pycnometry, the measurement of κ_T requires more sophisticated devices called piezometers. Both quantities are

very sensitive to relative inaccuracies on the determination of the molar volume, so very precise measurements are required to obtain fairly accurate (e.g., 5% or better) results. As we shall show below, the so-called *differential expansion method* provides an alternative choice to determine both quantities in the laboratory in a rather easy way with a good accuracy (about 2–3%).

The *expansion method* (1) has been used in the study of the physics of fluids at high pressures in the last two decades. The basis of this method is to determine the amount of liquid contained in a sample vessel of known volume, V_S , under a given set of conditions of pressure and temperature, by expanding the liquid to the vapor phase into a much greater vessel of known volume, V_{EXP} , which is kept at constant temperature. The measurement of the pressure reached in the *expansion* vessel allows one to calculate the mass contained in the sample vessel with great accuracy using the virial equation for the gas phase. This method has been used to measure the (p, V, T) surface (i.e., the equation of state) of liquids and compressed gases up to several thousands of atmospheres for temperatures above the critical (1). Figure 1 describes a simple scheme that illustrates the expansion method.

Calado et al. (2) introduced a modification in which the *variation* of the amount of liquid contained in the sample vessel was obtained along selected isotherms by performing successive partial expansions of the compressed liquid until the vapor pressure of the liquid at the selected temperature was reached. The volume of the liquid at coexistence was determined in a single expansion step similar to that described for the original expansion method. This modification is already known as the *differential expansion method*.

We recently introduced an additional modification (3), which consisted of measuring a reference isobar (usually that of 1 bar) along which the *variation with temperature* of the amount of substance contained in the sample vessel is also obtained by differential expansions. The final expansion of each isotherm is thus avoided, and a single reference density is required to generate the whole (p, V, T) surface of the liquid.

Since the differential expansion method described above was intended to determine the (p, V, T) behavior of liquids and compressed gases along wide ranges of pressure and temperature, the experimental apparatus was rather sophisticated and expensive. However, the basis for the differential expansion method provides a simple and accurate way to account for the pressure and temperature *variations* of the density of liquids and may be used to determine the mechanical coefficients κ_T and α_p of liquids by using a rather simple device suitable for an undergraduate laboratory course.

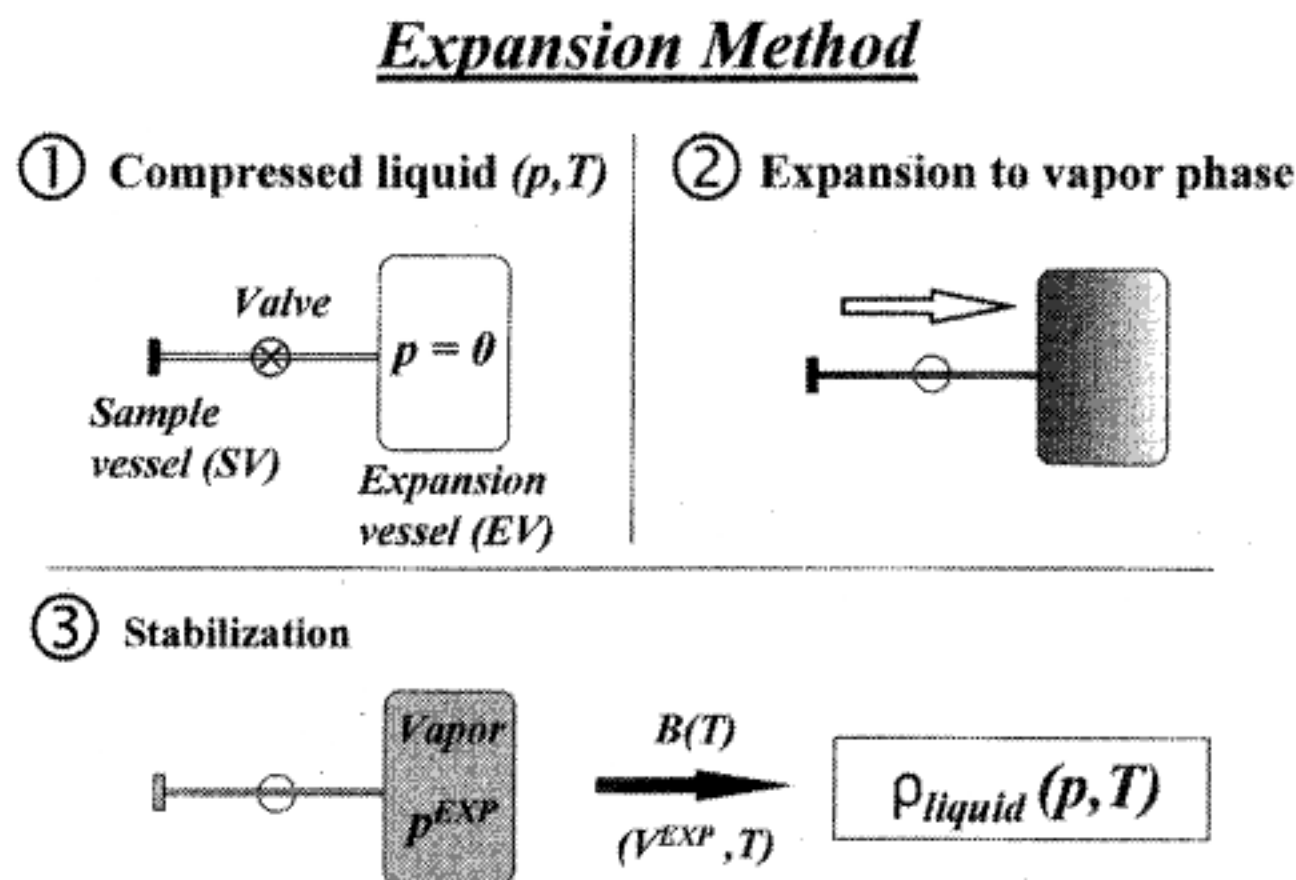


Figure 1. The expansion method.

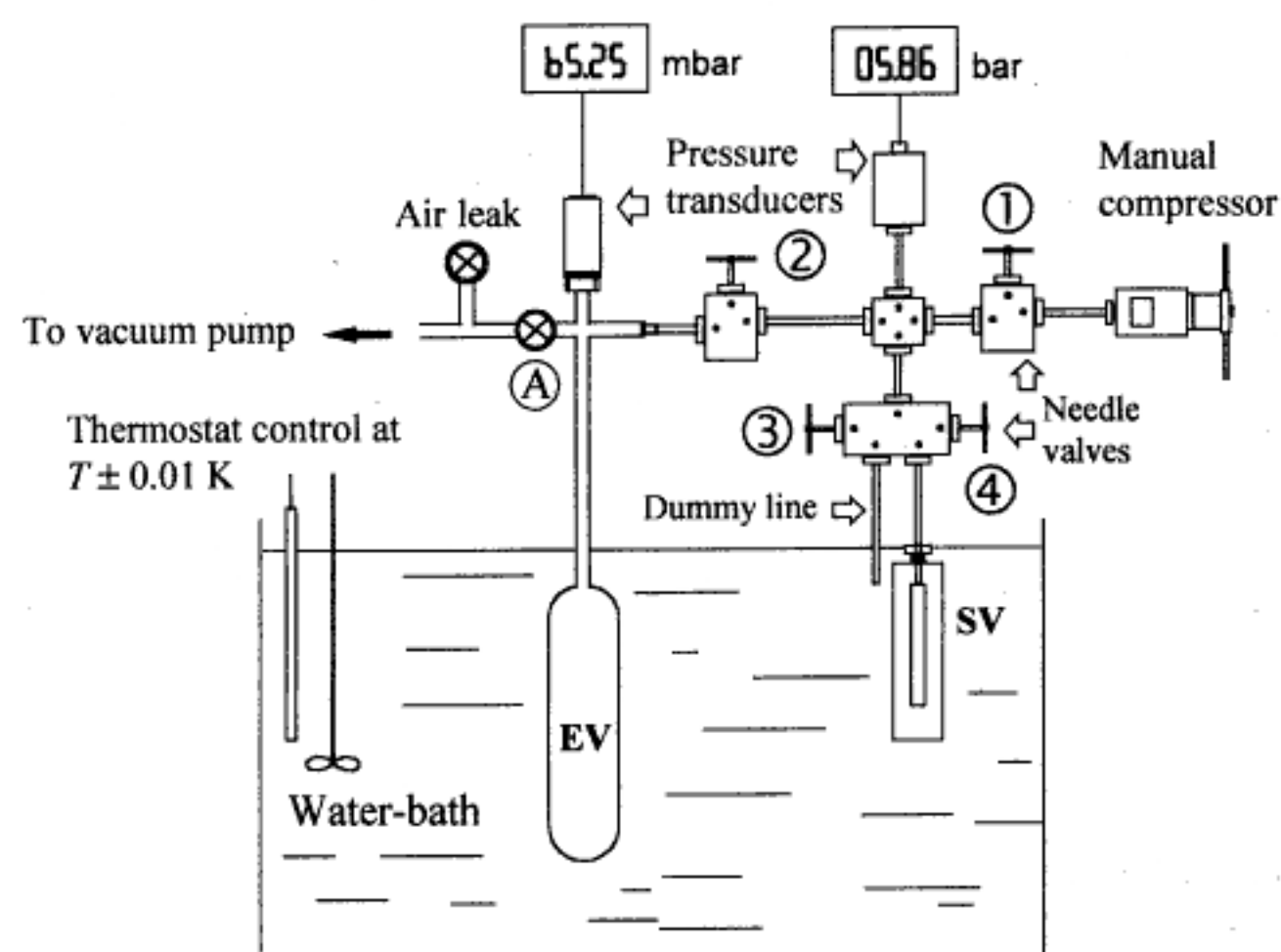


Figure 2. Apparatus for the differential expansion method. SV refers to the sample vessel and EV to the expansion vessel.

Apparatus

A schematic design of the apparatus is shown in Figure 2. The apparatus comprises two parts: (i) the *high-pressure* system, which includes the sample (high-pressure) vessel (SV) and several high-pressure connections and valves (needle valves are most suited), and (ii) the *expansion* system, which includes the expansion vessel (EV) as well as several glass connections and vacuum valves. The pressures in both systems are measured by means of calibrated pressure transducers linked to digital readouts (commonly in bars or atmospheres for the high-pressure transducer and in millibars or torrs for the low-pressure transducer). SV and EV are immersed into a thermostatically controlled water bath. The temperature of the bath should be kept constant within ± 0.01 – 2 K in order to achieve the desired accuracy (about 2–3%) in the calculation of the mechanical coefficients. Finally, it is assumed that the volumes of both vessels, V_S and V_{EXP} , are accurately known. A simple weighing calibration procedure with water and mercury (3) would suffice for this purpose.

Experimental Procedure

Isothermal Compressibility, κ_T

Once the high-pressure system is filled with the liquid under study, set the bath to the desired temperature of operation (usually 298.15 K). The expansion system must then be evacuated. Raise the pressure on the high-pressure system to about 20 bar by using the manual compressor. Once the temperature has been stabilized, check that the high-pressure transducer reading is stable and that the low-pressure transducer reading remains at zero pressure. During the following operations the high-pressure valves 1 and 3 must remain firmly closed, as well as the vacuum valve A. Open high-pressure valve 2 *very slowly*, so that a small amount of liquid will expand to the expansion system. Be careful when opening valve 2 to avoid the sudden introduction of the compressed liquid into the expansion system. Close valve 2 when the pressure in the high-pressure system has diminished between 2 and 5 bar. When both expansion and high pressures stabilize a new expansion can be performed. This procedure is repeated several times until the pressure in the high-

pressure system is slightly higher than the vapor pressure of the liquid (about 1 bar is usually satisfactory).

In fact, following the previous procedure one obtains the variation with pressure of the amount of substance contained in V_S and that contained in what we may call the *high-pressure residual volume* (connections, needle valves, transducer body, etc.). It is then necessary to evaluate the contribution of the liquid contained in the residual volume because only V_S is accurately known. The residual contribution can be evaluated by following a procedure similar to that described in the previous paragraph but closing the high-pressure valve 4 and opening the valve 3. This explains the existence of the so-called *dummy line* described in Figure 2, which is identical to the admission line of the sample vessel but sealed at the bottom end (see Calado et al. (2) for details). Throughout this experiment it is extremely important to open valves 3 and 4 in an identical position to be sure that the residual volume is the same in the two sets of experimental runs.

Thermal Expansion Coefficient, α_p

Set the thermostat control 2 or 3 K below the desired temperature. Once the thermal equilibrium has been reached, set the pressure on the high-pressure system to about 1 bar and check that the reading is stable for a few minutes. Set the thermostat control about 1 K higher and wait for thermal equilibrium (the high-pressure reading must also be stable at a higher value). Expand the amount of substance required to restore the initial pressure in the high-pressure system by opening *very carefully and slowly* the high-pressure valve 2. Repeat this procedure up to 2 or 3 K over the desired temperature at temperature steps of about 1 K. Through this procedure valve 3 should be closed, although the contribution due to the liquid contained in the portion of the dummy line affected by the heating is usually negligible. Throughout this experiment it is necessary to be sure that the height of the water-bath covers SV just up to the inlet, as it is shown in Figure 2.

Data Analysis and Experimental Results

The amount of substance in the expansion system is known by means of the virial equation truncated after the second term,

$$p = nRT/V + n^2RTB/V^2 \quad (3)$$

so only the second virial coefficient B of the substance in the gas phase at the temperature of operation, T , is required. Experimental values of B for most substances as a function of temperature have been compiled by Dymond and Smith (4).

The amount of substance contained in the expansion system is thus obtained from the following expression:

$$n = \{-RTV_T + [(RTV_T)^2 + 4pBRTV_T^2]^{1/2}\} / 2BRT \quad (4)$$

where the total volume V_T is the sum of the expansion vessel volume V_{EXP} and that of the *residual* conductions on the expansion system V_{RES} . Unlike the residual volume of the high-pressure system, which should not necessarily be known, V_{RES} must be evaluated by a calibration procedure.

Figures 3 and 4 show typical results of the variation of the amount of substance contained in the sample vessel obtained in experiments to determine κ_T and α_p , respectively. These results were obtained with a sophisticated apparatus (3) (notice the wide ranges of pressure and temperature covered by the experiments), but allow us to illustrate the general features of the experiment pro-

posed here. The results shown in Figure 3 were obtained with a sample vessel of about 4.2 cm³ (5), the residual volume being about 1.5 cm³. Notice how great the contribution of the residual conductions can be; that is why it is highly recommended that the residual volume be kept to an absolute minimum. Notice also that while the variation with temperature exhibits a quite linear dependence (6), the variation with pressure exhibits a certain curvature. This indicates that different numerical treatments of the rough data of κ_T and α_p are expected when considering wider ranges of pressure and temperature than those described here (see last section).

Results in Figures 3 and 4 should be corrected for the deformation of the vessel due to the severe changes in pressure and temperature occurring during the measurements. These corrections may be evaluated from the elastic constants and the thermal expansion coefficient of the material used to construct the sample vessel (see ref 7 for details). In the present experiment, since the pressure reached in SV is relatively low and the temperature variation of the bath is only about 5 K, it can be assumed that V_S remains constant, so further corrections are *usually* negligible.

In addition, the results in Figures 3 and 4 were obtained with an apparatus in which the expansion vessel is thermostated in an individual bath kept at constant temperature (3, 5, 6). In the present apparatus, since both vessels are thermostated in the same bath, the temperature of EV changes during the α_p experiment, so this change must be considered in the calculations. No further correction need be introduced in the value of the second virial coefficient (which is temperature-dependent only), since it accounts for only a very small correction in the computation of the amount of substance expanded.

Once the volume of the vessel and the variations with pressure, $\Delta n(p)$, and temperature, $\Delta n(T)$, of the amount of substance contained in SV are known, only the molar density of the liquid at the selected temperature is required to compute the mechanical coefficients from eqs 1 and 2. The molar density of the liquid, ρ_{REF} , may be taken from the literature or measured in the laboratory with another technique (see next section).

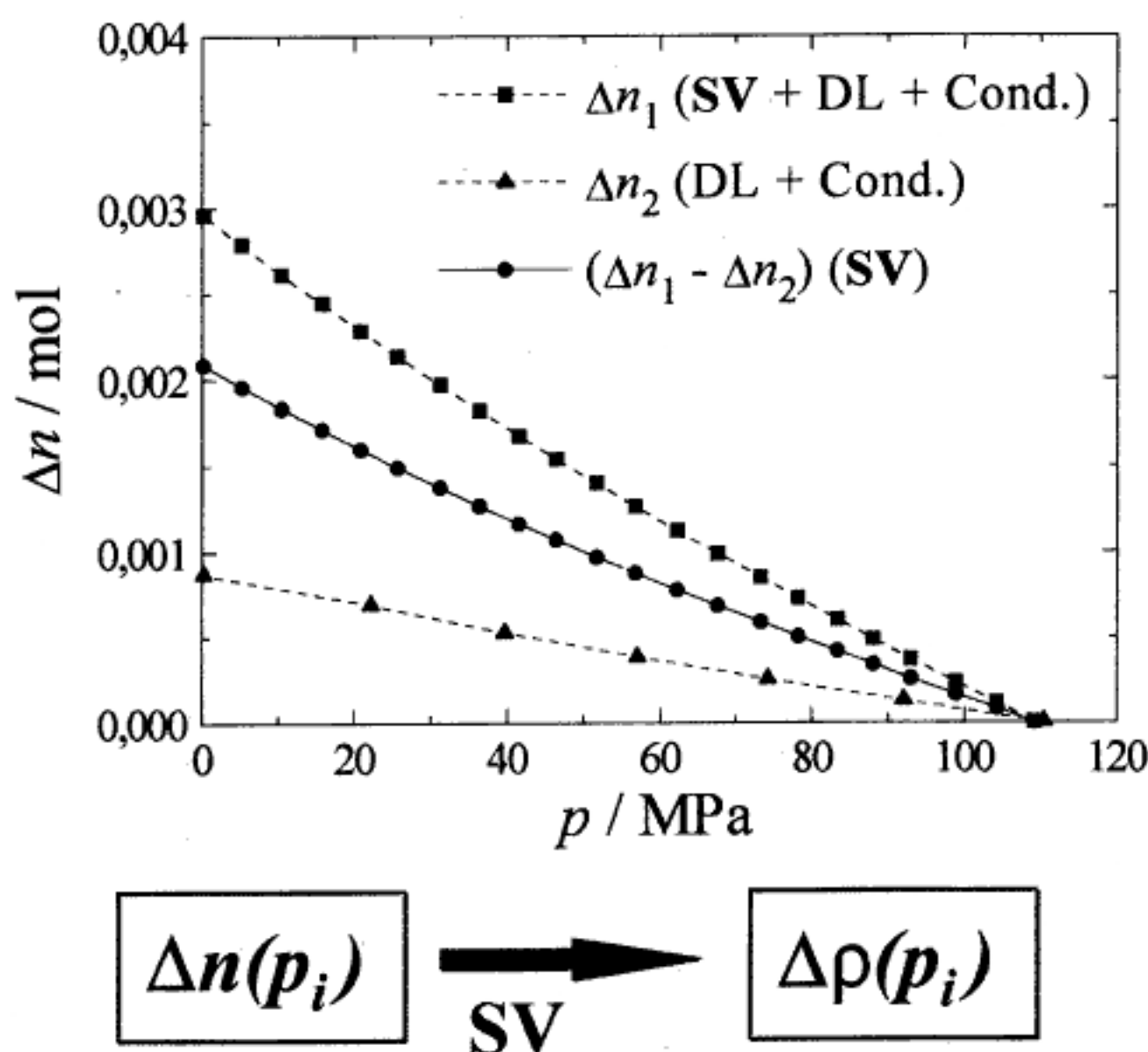


Figure 3. Variation with pressure of the amount of substance into the sample vessel for *m*-xylene at 298.15 K. The volume of the sample vessel was about 4.2 cm³ (5).

Let us finish this section with a few comments on the numerical computation of κ_T and α_p through eqs 1 and 2. Taking into account the relative small ranges of pressure and temperature covered in the present experiments and the relative uncertainties expected in both κ_T and α_p (about 3%), both quantities can be obtained by supposing linear dependencies for $\Delta n(p)$ and for $\Delta n(T)$, which means that κ_T and α_p are supposed to be constant over the pressure and temperature intervals considered here. Notice that the slopes that must be included in eqs 1 and 2 are just the negative values of those obtained from plots analogous to Figures 2 and 3. Thus, the expressions to compute κ_T and α_p are the following:

$$\kappa_T = -(1/\rho_{REF} V_S) [\partial \Delta n(p) / \partial p]_T \quad (5)$$

$$\alpha_p = (1/\rho_{REF} V_S) [\partial \Delta n(T) / \partial T]_p \quad (6)$$

where the slopes referred to above are given by the quantities $[\partial \Delta n(p) / \partial p]_T$ and $[\partial \Delta n(T) / \partial T]_p$. Notice that eqs 5 and 6 are not exactly the same as eqs 1 and 2. The reference molar density used in eqs 5 and 6 is considered as a constant over the small range of the experimental variables covered in this experiment, whereas the molar density in eqs 1 and 2 would be a function of the pressure and the temperature.

General Advice

- The most suitable liquids to carry out the experiments are those having vapor pressures ranging from 100 mbar to about 1 bar at room temperature (hydrocarbons such as *n*-hexane or 2,3-dimethylbutane for instance). With constancy in errors on other variables an accuracy better than 3% in the final results is expected according to the relative accuracy of the low-pressure transducers available on the market.
- The final results of κ_T and α_p are very influenced by the uncertainties in the residual expansion volume, so the calibration of V_{RES} must be done with accurate data from the literature. The calibration procedure can be made by the student and incorporated into the experiment as a whole.

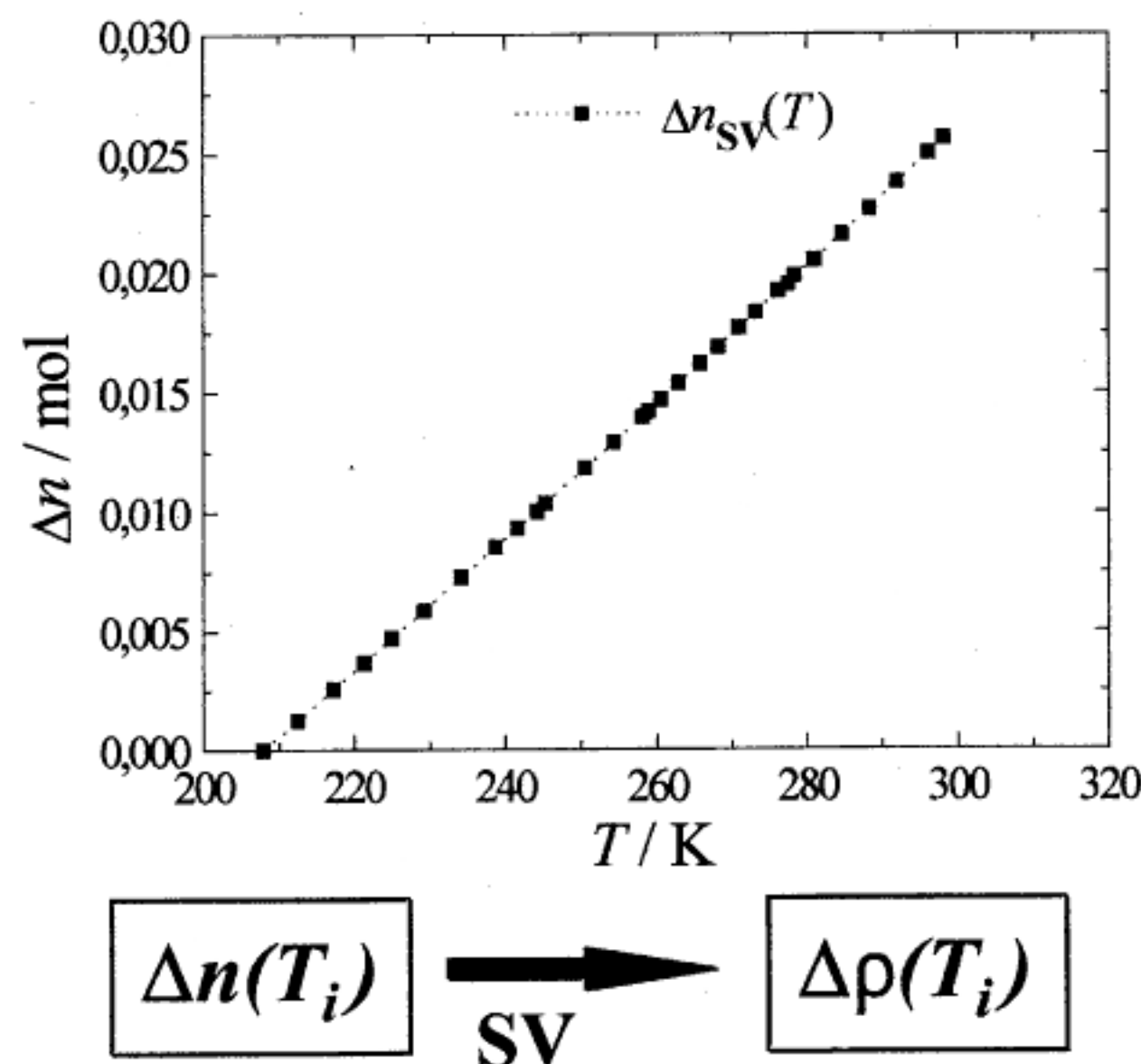


Figure 4. Variation with temperature of the amount of substance into the sample vessel for 2,3-dimethylbutane at 1 bar. The volume of the sample vessel was about 30.6 cm³ (6).

- In both isothermal and isobaric experiments the expansion of the liquid is carried out in several stages such that the pressure in the expansion vessel is never allowed to be above the vapor pressure of the liquid at the selected temperature, so evacuation of the expansion system between the successive expansions is highly recommended.
- Allow a few minutes for both gas and liquid to reach thermal equilibrium in their vessels and for their pressures to stabilize.

Technical Notes

Recommended volumes for the vessels are between 5 and 10 cm³ for SV and between 200 and 300 cm³ for EV. It is recommended that the high-pressure vessel be constructed of stainless steel (7). EV can be constructed with standard laboratory glass. The high-pressure line must be entirely of metal, rated to about 50 bar.

A tentative price for the experimental device would be about \$2500–\$3000. However, this price would be significantly reduced by measuring the expansion pressures with a mercury manometer instead of the low-pressure transducer, as we propose here. In that case, care must be taken when handling mercury. Areas of mercury exposed to the atmosphere should be minimized. In addition, when constructing the manometer, prevent against spills or pressure surge accidents with an appropriate spill basin. Although a limiting factor is the accuracy of the pressure measurement, an accuracy of about 0.5 torr should suffice for our purposes. If a manometer is used, notice that the expansion volume increases as the liquid expands, so an additional correction for V_T is required in eq 4.

Further Experiments

This experiment can be combined or completed with others. The most suitable are those dealing with the two reference quantities required for the present calculations (viz., the second virial coefficient and the molar density). The first quantity can be determined in the laboratory using a modified Burnett method (8)—an expansion

method also! The molar density of the liquid can be measured by standard pycnometry.

The present experiment can be extended to study the high-pressure (about 200 bar) behavior of liquids along a selected isotherm without requiring an expensive apparatus and might be of great interest for the student. In that case, the κ_T experiment should lead to a variation of $\Delta n(p)$ closer to that of Figure 2 (i.e., should exhibit a certain curvature), so the quantity $[\partial \Delta n(p)/\partial p]_T$ in eq 5 must be evaluated at each point by finite differences. In addition, the change in SV with pressure would be not negligible and should be estimated by means of the *theory of elasticity* (7). Notice that the molar density included in eq 5 is a function of pressure also, so the numerical treatment is considerably increased. We strongly recommend avoiding polynomials in the correlation by using instead a universal function for the pressure dependence of κ_T recently described in the literature (9). Advice on both design and numerical computation of the results can be supplied on request. An experiment over a wide range of temperature, although it would be quite interesting, requires too much time, and it is not recommended for an undergraduate laboratory.

Acknowledgment

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A Consistent System for Coding Laboratory Samples

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One of the first tools a beginning research chemist acquires when he enters a laboratory is a research notebook. Experimental details are meticulously documented into this book. At the outset a synthetic chemist realizes a system is needed to code and keep track of compounds. The laboratory bookkeeping strategy that develops is based on prior art by inconspicuously observing the research notebooks of more experienced co-workers and by "word of mouth". The final code system that emerges is a "common sense" approach fortified by repetition and nurtured from years of experience. I present here a formal laboratory coding system that has evolved in our laboratory and has been used successfully for 20 years.

Notebook No.—Identification Initials—Notebook Page No.

Example: 00000-DOE-100

For aliquot samples were removed from the reaction at different times for analysis:

00000-DOE-100-1	Reaction at T_1
00000-DOE-100-2	Reaction at T_2
00000-DOE-100-3	Reaction at T_3

For total crude reaction mixture after workup:

00000-DOE-100-C