

Compression and expansion processes for atmospheric air: teaching thermodynamic response coefficients



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Abstract

In introductory classical thermodynamics courses, the P - V - T systems are frequently employed as examples for presenting the several thermodynamic quantities, which are expressed in terms of measurable macroscopic quantities. The variation of one experimentally measured property as a function of other one, is called a thermodynamic response coefficient. One of the most accessible quantities to analyze is the so-called isothermal compressibility coefficient, $\kappa = -(1/V)(dV/dP)_T$, which contains the P - V relationship under isothermal conditions. For these quantities, the ideal gas model is usually used to illustrate calculations of the thermodynamic quantities. Nevertheless, the idea that any fluid behaves as an ideal gas is frequently taken for granted by students. In this work, two independent experiments considering one the compression and other the expansion of atmospheric air as a study fluid, were performed in order to quantify its $(P$ - $V)_\theta$ behaviour, and clarify the type of PV behavior atmospheric air shows. From these experiments and the corresponding data, the expression for $(dV/dP)_\theta$ was deduced, which resulted in turn volume-dependent. Further analysis yields a linear relationship between the isothermal compressibility coefficient (κ) and $(P_{abs})^{-1}$ values. All the results point to consider the non-ideal behaviour of the gaseous fluid studied when it is involved in two independent processes (a modest isothermal expansion and a modest isothermal compression), primarily due to the air water content.

Keywords: Atmospheric air, PVT behavior, air compressibility factor, thermodynamics teaching.

Resumen

En los cursos de introducción a la termodinámica clásica, los sistemas de PVT se emplean con frecuencia como ejemplos para la presentación de las diversas cantidades termodinámicas, que se expresan en términos de cantidades macroscópicas medibles. La variación de una propiedad medida experimentalmente como una función de la otra, se denomina coeficiente de respuesta termodinámico. Una de las cantidades más accesibles para analizar es el llamado coeficiente de compresibilidad isotérmica $\kappa = -(1/V)(dV/dP)_T$, que contiene la relación P - V en condiciones isotérmicas. Para estas cantidades, el modelo de gas ideal se utiliza generalmente para ilustrar los cálculos de las cantidades termodinámicas. Sin embargo, la idea de que cualquier líquido se comporta como un gas ideal, se da por sentada frecuentemente, entre los estudiantes. En este trabajo se consideraron dos experimentos independientes, tomando ambos al aire atmosférico como fluido de estudio; uno sobre la compresión y otro sobre la expansión. Ambos se llevaron a cabo con el fin de cuantificar el comportamiento $(P$ - $V)_\theta$, y aclarar el tipo de comportamiento PV que muestra el aire atmosférico. A partir de estos experimentos y los datos correspondientes, se dedujo la expresión para $(dV/dP)_\theta$, la cual resulta ser dependiente del volumen. Adicionalmente con otro análisis se obtiene una relación lineal entre los valores del coeficiente de compresibilidad isotérmica (κ) y de $(P_{abs})^{-1}$. Todos los resultados apuntan a considerar el comportamiento no ideal del fluido gaseoso estudiado, cuando está involucrado en dos procesos independientes (una modesta expansión isotérmica y una modesta compresión isotérmica), principalmente debido al aire contenido en el agua.

Palabras clave: Aire atmosférico, comportamiento PVT, factor de compresibilidad del aire, enseñanza de la termodinámica.

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I. INTRODUCTION

The relationship among the relevant extensive and intensive properties for a thermodynamic system is called the equation of state. These relations are a useful tool to understand the physicochemical behavior of

thermodynamic systems, and to also predict the system properties values at different experimental conditions. However, despite their relevance, equations of state tend to receive little attention in traditional physical chemistry courses and conventional textbooks used in the chemistry areas. Furthermore, they are normally defined as the

relation among the P , V and T variables in a system, and are usually limited to the description of gas phases [1, 2, 3, 4]. More specialized chemical engineering textbooks restrict the discussion to fluids in general although in further detail. Few books present the subject in a general fashion [5, 6, 7] and they are usually used in the physics areas. Only more advanced textbooks for graduate students [8] use the postulates formalism, which is general for any kind of thermodynamic system. Moreover, most of the papers on thermodynamics of fluids in science education journals, discuss the PVT fluid behavior by using theoretical models or computational techniques [9, 10, 11, 12, 13, 14, 15, 16, 17], and very few present experimental results on this kind of thermodynamic response [18-21]. Of these, one [18] is devoted to the determination of the thermal expansion coefficient of gases, and the other three, to a very inaccurate and limited determination of the PV relation for air [19, 20, 21].

The old fashion presentation used in undergraduate chemistry courses leads the students to believe that thermodynamics can only be applied to the gas phase, and more drastically, that the only existing equation of state is $PV=nRT$, the limiting $\rho \rightarrow 0$ ideal gas model. Also, they believe that this equation can be applied to any gas at any experimental condition.

Another approach to the study of equations of state [22] is the use of the so-called response coefficients, which in principle, can be experimentally determined.

They are simple partial derivatives involving the thermodynamic states of the system. Moreover, understanding the response coefficients meaning, is of major importance in physical chemistry studies, and it leads to the idea that thermodynamics can be applied to any system for which the relevant variables can be affected by the change of one of the properties (mainly temperature). This discussion is essential in the study, for example, of thermodynamic properties, in the definition of thermometric properties and in the construction of empirical temperature scales and thermometers.

As the measurement of the response of a system to variable conditions has been historically the subject of research in areas like chemistry, physics, the search of new materials, etc., it is very important to learn and teach how to measure the response coefficients of systems showing different characteristics. This communication concerns with experimental methods [23] to measure response coefficients for different thermodynamic systems in a conventional physical chemistry or classical thermodynamics laboratory for undergraduate students; in particular, in here we present the PVT behavior of air under two independent isothermal processes, deduced from experiments that have not been reported in science education journals up to date.

II. THEORY

The thermodynamic equilibrium state of a system is characterized by the specific values of the minimum number of variables (or properties) needed to define the system. This number is determined by the experimental experience. The properties depend on the system nature and on the kind of physical or chemical responses which are intended to obtain. Then, the equation of state is:

$$X_i = X_i(T, X_{j \neq i}, Y_i). \quad (1)$$

Where X_i and Y_i are the relevant extensive and intensive variables, respectively, and T the temperature. For example, for a fixed mass of a fluid or a solid, the relevant properties are V , P and T (volume, pressure and temperature), if the volumetric response is to be studied.

But if we are interested in the magnetic response of the same kind of systems, the relevant variables are M , H and T (magnetization, applied magnetic field and temperature).

Any infinitesimal change in the equilibrium state of the system due to changes in the independent variables, will result in

$$dX_i = \left(\frac{\partial X_i}{\partial T} \right)_{X_{j \neq i}, Y_i} dT + \left(\frac{\partial X_i}{\partial X_j} \right)_{X_{k \neq i, j}, Y_i, T} dX_j + \left(\frac{\partial X_i}{\partial Y_j} \right)_{X_{k \neq i, j}, Y_{m \neq j}, T} dY_j. \quad (2)$$

The partial derivatives involving extensive and intensive properties are the response coefficients. For example, for the volumetric response of a system, the volume is a function of temperature and pressure for a fixed system mass (*i.e.*, $V = V(T, P)$) and an infinitesimal change in the volume can be expressed as:

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP. \quad (3)$$

Here, the response coefficients are defined as:

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P, \quad \kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T. \quad (4)$$

β is known as the isobaric thermal expansion coefficient, and κ is the isothermal compressibility coefficient of the system. Another response coefficients, as

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa}. \quad (5)$$

Can be obtained by simply applying the rules for partial derivatives.

Any response of a system due to a change of its equilibrium state (like magnetic, electric, surface, etc., responses) can be written in terms of the respective response coefficients. By measuring them (for example, β and κ in the above example), the respective differential

equation can be integrated, and the equation of state is obtained for the range of experimental conditions in which the response coefficients were determined.

In here, and as a second proposal [10] concerning the experimental study of response coefficients in thermodynamic systems, the experimental determination of the coefficient $(dV/dP)_\theta$ (being θ the empirical temperature) for a gaseous fluid in a conventional undergraduate physical chemistry or classical thermodynamic laboratory, is presented.

III. EXPERIMENT

As mentioned above, in the study here presented the relationship between pressure and volume for a gaseous fluid mass under isothermal conditions is obtained for: a) a compression process and b) an expansion process. In here, the fluid in study is the atmospheric air in a laboratory. In Figures 1 and 2, details of the instruments and equipment employed in both experiments (the compression and the expansion) are shown. For both processes, the experiment is basically the same, being the differences the pressure instrument employed (Figure 1) and the U-type indicator (with distilled water as manometric fluid; high vacuum oil was added on top of the water meniscus to prevent evaporation and air solubilization) manipulation (the opened tube is moved up for compression, and moved down for expansion).

The atmospheric air (Mexico City) confined (in the right tube in Figure 2) was carefully compressed (or expanded) in several steps. For each one, the corresponding P and V values were stabilized during ca. 30 minutes; in each step, manometric pressure (or relative vacuum) and volume values were collected. Also, the temperature value close to the gaseous fluid in study and equipment (to be constant) was corroborated. As both experiments were performed independently in different days, the gas mass (kept constant throughout each experiment) was not the same for both experiments, and the temperature (maintained constant for each process) differed from 23°C for the compression to 25°C for the expansion.

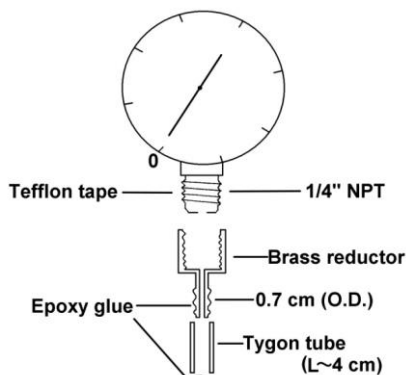


FIGURE 1. a) Compression: An analogic manometer (Marsh) was used for measuring the manometric pressure. Ranges: 0-20 Lat. Am. J. Phys. Educ. Vol. 8, No. 2, June 2014

0-20 in²; 0-90 cm H₂O. Zero-adjust screw is included. b) Expansion: An analogic vacuum gauge (Ashcroft) was used for measuring the relative pressure below the atmospheric (zero) reference. Ranges: 0-7.5 kPa; 0-30 in H₂O. Zero-adjust screw is included.

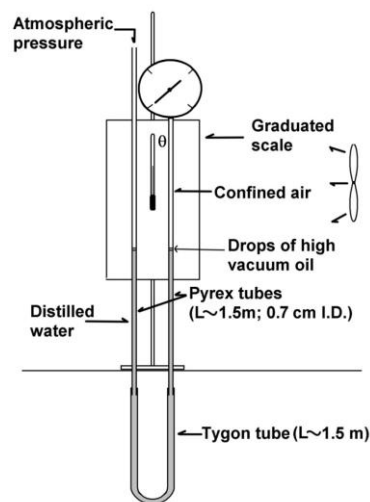


FIGURE 2. Experimental setting for the confined air isothermal a) compression and b) expansion processes.

Manometric pressure (or relative vacuum) values were obtained from both the analogical instrument (units at standard conditions) and the U-type indicator (as level differences, units at local conditions at an altitude of 2218 m at Mexico City). The latter were then converted to standard conditions by employing the local distilled water absolute density and g gravity values. For the compression, $\rho(\text{H}_2\text{O}(l))$ (23°C)=0.993 g/mL, $g=9.78 \text{ m/s}^2$, $P_{\text{atm}}=581.66 \text{ mm Hg(est)}$; for the expansion, $\rho(\text{H}_2\text{O}(l))$ (25°C)=0.992 g/mL, $g=9.78 \text{ m/s}$, $P_{\text{atm}}=581.40 \text{ mm Hg(est)}$. Such homologated values were compared to those of the manometer (or the vacuum gauge) to verify their mutual correspondence. Also, throughout the experiment, values of the atmospheric pressure (with an adjusted electronic barometer and units at standard conditions) were collected. In this way, both manometric pressure (volume and absolute pressure), volume values at 23°C were obtained for the compression process, and relative vacuum-volume and absolute pressure-volume values at 25°C were obtained for the expansion process.

IV. RESULTS AND DISCUSSION

A. Compression

The experimental (PV) data for the compression process is shown in Figure 3. From these, a non-linear relationship between the variables was detected.

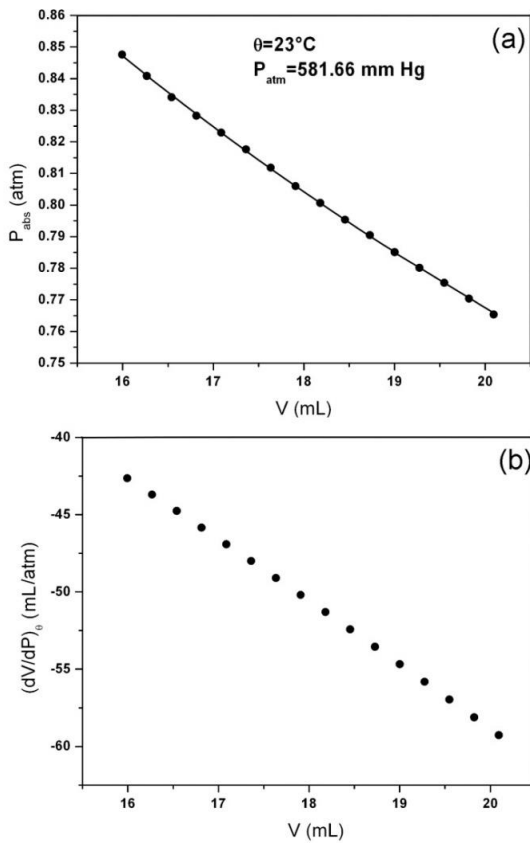


FIGURE 3. (a) Absolute pressure (atm) as a function of volume (mL), and (b) change of volume per unit pressure variation (mL/atm) as a function of volume (mL) for the atmospheric air isothermal compression process.

In order to obtain a quantitative relation between P and V , a fitting process was carefully performed and the resulting equation is

$$P = \frac{2.8909}{V^{0.4427}} \quad \text{or} \quad PV^{0.4427} = 2.8909. \quad (6)$$

Such expression does not correspond to the ideal gas model equation. The first derivative $(dP/dV)_\theta$ is a function of volume. The reciprocal expression for such a first derivative yields $(dV/dP)_\theta = -0.7814V^{1.4427}$, which is shown in Figure 3(b). From this, an illustrative physical behavior arises: at higher volume values, the gaseous fluid becomes comparatively more compressible. On the contrary, at lower volume values, the fluid is less compressible.

In order to further analyze the relationship existing between the $(dV/dP)_\theta$ coefficient and V or P values, its expression (i.e., $(dV/dP)_\theta = -0.7814V^{1.4427}$) was incorporated into the corresponding one for κ (the isothermal compressibility coefficient). The resulting equation for κ was respectively plotted as a function of volume and of the inverse of pressure experimental data.

In both cases, κ shows the same increasing linear behaviour towards ascending V or P^{-1} values. Performing a

linear fit yields: $\kappa = 0.002 + 2.257(1/P)$. A second analysis was made by fixing the zero-condition for the independent term; a satisfactory fitting is obtained (Fig. 4). The equation for the isothermal compressibility coefficient is:

$$\kappa = 2.2589 \left(\frac{1}{P} \right) \quad (7)$$

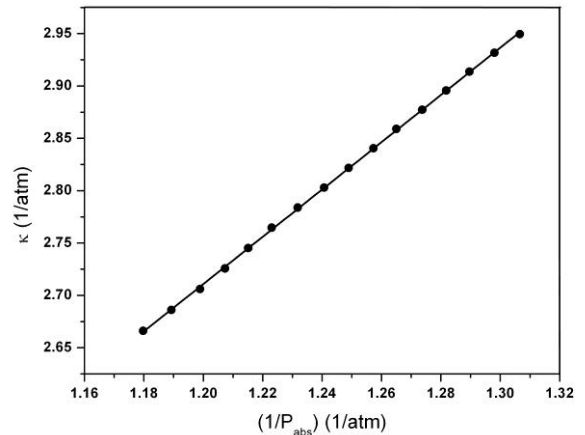


FIGURE 4. Isothermal compressibility coefficient (1/atm) as a function of the inverse of absolute pressure (1/atm) for the atmospheric air isothermal compression process.

In this equation, the slope is in turn $(1/a)$, in accord with $a=0.4427$ in the equation $PV^{0.4427} = 2.8909$. The above results let us quantitatively explore the κ behavior: for the experimental conditions studied, this coefficient ranges from ca. 2.65 atm^{-1} to 2.95 atm^{-1} upon increasing $(1/P)$.

Another pedagogic experience in this analysis is the slope value (ca. 2.26) of the equation commented above.

Being higher than the unit, it is in accordance with the non-ideal PVT character previously discussed for the gaseous fluid here studied.

B. Expansion

As referred in experimental, the lectures of relative vacuum (analogical gauge) – volume and relative vacuum (U-type indicator) – volume were collected. Under standard (homologated) conditions, they are noticeably similar. In the following paragraphs and figures, all they are considered. Figure 5a shows the experimental data.

From this experimental data, a non-linear relationship between the variables is observed. In order to obtain a quantitative relation between absolute pressure and volume, a fitting process was carefully performed. The resulting equation that satisfactorily describes the experimental response of the gaseous fluid in study (Figure 5a) is:

$$P = \frac{1.99869}{V^{0.4144}} \quad \text{or} \quad PV^{0.4144} = 1.99869 \quad (8)$$

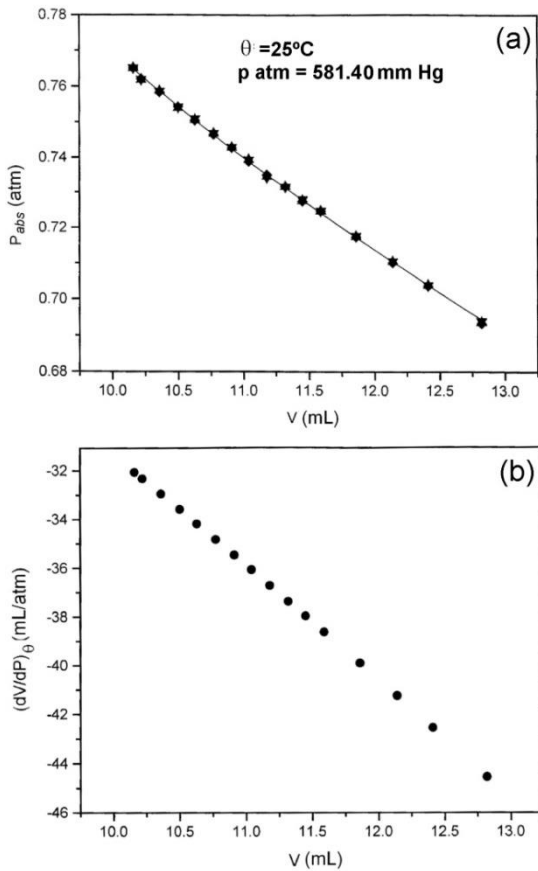


FIGURE 5. (a) Absolute pressure (atm) as a function of volume (ml) and b) volume change per unit pressure variation (ml/atm) as a function of volume (ml) for the atmospheric air isothermal expansion process

As can be seen, such expression ($PV^{0.4144} = \text{constant}$) does not correspond to the ideal gas model $-pVT$ equation. Further on, the first derivative $(dP/dV)_\theta$ of the fitted equation is in turn volume-dependent. The reciprocal expression for this first derivative yields the response coefficient $(dV/dP)_\theta = -1.2077V^{1.4144}$ (Figure 5b). From this, an illustrative physical behavior arises: at higher volume values, the gaseous fluid becomes comparatively more expansible (or also compressible). On the contrary, at lower volume values, such properties are decreased.

In the hope to analyze in a further way the relationship existing between the $(dV/dP)_\theta$ coefficient and V or P values for the expansion process, its expression (*i.e.*, $(dV/dP)_\theta = -1.2077V^{1.4144}$) was incorporated into the corresponding one for κ (the isothermal compressibility coefficient). The resulting equation for κ was respectively plotted vs. volume and $(\text{absolute pressure})^{-1}$ experimental values. In both cases, κ shows the same increasing linear behavior towards ascending V and P^{-1} values. Fitting a linear equation to data yields: $\kappa = 0.009 + 2.14(1/P)$. In a

further step, a second linear fitting process was performed, by establishing the zero-condition for the independent term. A good fitted equation results (Figure 6):

$$\kappa = 2.4139 \left(\frac{1}{P} \right) \quad (9)$$

In this, the slope is in turn $(1/a)$, in agreement with $a=0.4144$ in equation $PV^{0.4144} = 1.9987$. The above results let us quantitatively explore the κ behavior: within the experimental conditions covered, this coefficient ranges from ca. 3.15 atm^{-1} to 3.48 atm^{-1} upon the $(1/P)$ values increase.

Figure 6 shows the above commented results. Another pedagogic experience in this analysis is the slope value of the equation here commented. Being higher than unit, it is in accordance with the non-ideal character previously discussed for the gaseous fluid here studied.

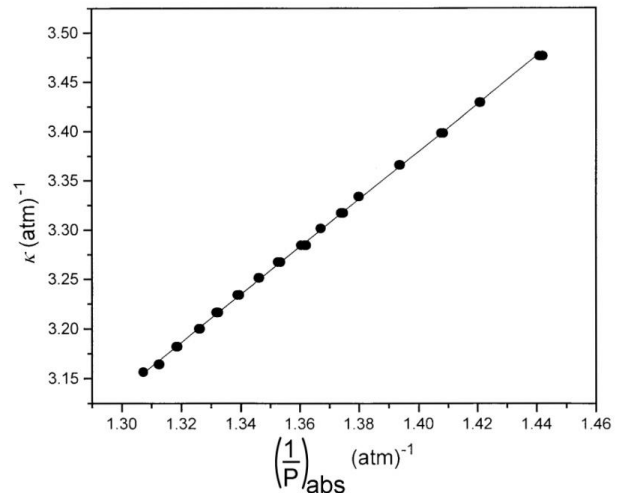


FIGURE 6. Isothermal compressibility coefficient (1/atm) as a function of the inverse of absolute pressure (1/atm) for the atmospheric air isothermal expansion process.

It must be pointed out that when both sets of results for the compression ($\theta = 23^\circ\text{C}$) and expansion ($\theta = 25^\circ\text{C}$) processes are compared, similar expressions for the several facets of the $(p-V)_\theta$ relationship in both processes are deduced.

For example $PV^{0.4427} = 2.8909$, $(dP/dV)_\theta = -1.2798V^{-1.4427}$ and $(dV/dP)_\theta = -0.7814V^{1.4427}$, for the compression process. $PV^{0.4144} = 1.9987$, $(dP/dV)_\theta = -0.828V^{-1.4144}$ and $(dV/dP)_\theta = -1.2077V^{1.4144}$ for the expansion process.

These differences found could be associated with the different conditions (temperature, gas mass and starting volume, for example) at which the respective studies were carried out. Nevertheless the above features, in both cases (moderate isothermal compression and moderate isothermal expansion processes) the atmospheric air shows $(P-V)_\theta$ relationships which are in turn different to those belonging to the idea gas- PVT model.

It must be pointed out that when the κ properties for both processes are compared, some interesting features arise.

When both series of κ - $(1/P)$ values are plotted in a common graph (Figure 7) a clear trend emerges. In such a graph, the lower $(1/P)$ values region belongs to the compression states of the gaseous fluid; for this region, κ also takes comparatively lower values. Upon ascending the $(1/P)$ values, the gaseous fluid is now being expanded, and κ then shows the comparatively higher values. If the small differences between the two linear behaviors are mainly associated with the temperature differences (25 °C for the expansion study; 23°C for the compression process) at which both processes were performed; then a gross linear trend which covers the 1.18 atm⁻¹ – 1.45 atm⁻¹ ($1/P_{abs}$) global range can be proposed. For such a range, κ can be suggested to increase from ca. 2.65 atm⁻¹ to 3.5 atm⁻¹. In this way, two closely related studies on the same type of atmospheric air yields κ estimates for a wider range of $(1/P_{abs})$ values (ca. 0.69 atm – 0.85 atm).

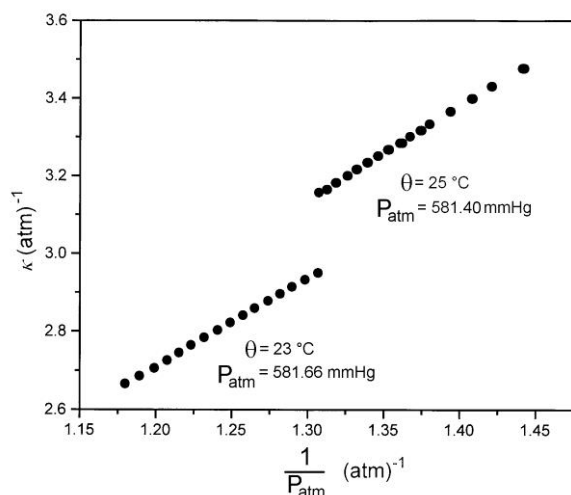


FIGURE 7. Isothermal compressibility coefficient (κ) as a function of P_{abs}^{-1} for the two processes performed on atmospheric air.

V. CONCLUSIONS

From the study here presented, the following conclusions can be drawn:

1. Employing materials and instruments available in an undergraduate laboratory, it is possible to obtain certain responses about the p - V behavior of a gaseous fluid by performing two experiments: a modest compression (at 23°C) and a modest expansion (at 25°C) isothermal processes.
2. The analysis of the experimental data yields expressions for the $(dV/dP)_{\theta}$ response coefficient of the air gas studied and belonging to the corresponding experimental conditions range explored. Both series show the volume dependence of the coefficient, and is similar for the compression and the expansion processes.

3. Further analysis yields a linear relationship between the isothermal compressibility coefficient κ , and $(1/P)$ for both processes. For the compression process, κ ranges from ca. 2.65 atm⁻¹ to 2.95 atm⁻¹. For the expansion process, κ ranges from ca. 3.15 atm⁻¹ to 3.48 atm⁻¹.

4. The several facets of the $(p-V)_{\theta}$ relationship explored, let us consider the non-ideal behaviour of the atmospheric air studied when it is involved in modest isothermal compression and expansion processes. Unfortunately, the experimental data (PV relation at constant T) is not enough to establish a phenomenological equation of state.

5. It is a special valuable experience for undergraduate students, as far as they convince themselves that atmospheric air does not “behave” as an ideal gas, and such equation cannot be used in an indiscriminate way for any gaseous system at any conditions. Deviations from the ideal behavior can be due to the presence of highly non-ideal components: CO₂ and water. Treating atmospheric air as an ideal gas mixture is only a gross approximation for such a complex system, and student should be aware of it.

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