

## Response coefficients in thermodynamic systems (I)

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In the first undergraduate Physical Chemistry or Classical Thermodynamics courses in the Chemistry areas, the study of equations of state is usually included. The differential forms of the equations of state contain the response coefficients, which are the relations among the relevant properties of state of a particular system. The classic solution to the differential equations thus requires that the response coefficients be known, which must be experimentally obtained. A confined gas is one of the systems that can be experimentally studied in a simple manner. The response coefficient  $(\partial P/\partial T)_V$  is important from different points of view. In this communication, the design, the experimental produce and the results for the experimental determination (in an accessible temperature range) of the response coefficient  $(\partial P/\partial T)_V$  for atmospheric air, are presented. The value for this coefficient has been highly reproducible by students throughout the courses, no matter the types of manometers, flasks or thermal baths are used in the experiment.

*Keywords:* Thermodynamics; response coefficients; equations of state.

En los cursos introductorios de Fisicoquímica o de Termodinámica Clásica en las áreas de Química, es requisito la revisión del tema Ecuaciones de Estado. Las expresiones diferenciales de éstas, contienen a los coeficientes de respuesta, los cuales expresan las interrelaciones de las propiedades de estado para el sistema particular. La solución clásica de dichas ecuaciones diferenciales requiere el conocer los coeficientes de respuesta, los cuales se determinan experimentalmente. Uno de los tipos de sistemas más accesibles experimentalmente es un gas confinado. Para éste, el coeficiente de respuesta  $(\partial P/\partial T)_V$  es importante bajo enfoques diferentes. En esta comunicación se presenta el diseño, realización experimental y resultados sobre la evaluación del coeficiente  $(\partial P/\partial T)_V$  para el aire atmosférico, en un rango accesible de temperatura. El valor del coeficiente ha sido notablemente reproducible por estudiantes en semestres consecutivos, sin importar los tipos de manómetros, matraces ó baños térmicos empleados en el experimento.

*Descriptores:* Termodinámica; coeficientes de respuesta; ecuaciones de estado.

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### 1. 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 in understanding the physicochemical behavior of thermodynamic systems, and also in predicting the system properties values under 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 (see for example Refs. 1-4). More specialized chemical engineering textbooks, restrict the discussion to fluids in general in further detail. Few books present the subject in a general fashion (5-7), and they are usually used in the Physics areas. More advanced textbooks for graduate students (8), use the postulate formalism, which is general for any kind of thermodynamic system.

The old fashioned presentation used in 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 equa-

tion can be applied to any gas under any experimental condition.

Another approach to the study of equations of state (9) 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, the understanding of the response coefficient 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, as in the definition of thermometric properties and 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 is the first of a series in which experimental methods are proposed to measure response coefficients for different thermodynamic systems in a conventional Physical Chemistry or Classic Thermodynamics laboratory for undergraduate students.

## 2. 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 experimental experience. The properties depend on the nature of the system and also on the kind of physical or chemical responses which one intends to obtain. Then, the equation of state is

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

where the  $X_i$  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

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

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

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

Here, the response coefficients are defined as

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

$\beta$  is known as the isobaric thermal expansion coefficient, and  $\kappa$  is the isothermal compressibility coefficient of the system. Another response coefficients

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

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

Any response of a system due to a change in its equilibrium state (such as magnetic, electric, surface, etc., responses) can be written in terms of the respective response coefficients. By measuring them (for example,  $\beta$  and  $\kappa$  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.

Here, and as a first proposal for the experimental study of response coefficients in different systems, the experimental determination of the coefficient  $(\partial P/\partial T)_V$  in a conventional undergraduate Physical Chemistry or Classic Thermodynamics laboratory is presented. The results obtained by students are presented and analyzed. The experiment has been highly reproducible by several groups of students, employing different instruments, equipment and gas masses.

## 3. Experimental

The experimental set is shown in Fig. 1. A spherical flask (pyrex glass) is filled with local atmospheric air and is firmly stopped with a rubber cover (which has a hole in the center); the cover is sealed with epoxy glue to the flask. A manometer (various types can be used) is introduced in the hole in the cover, using a copper reductor couple with teflon tape. More epoxy glue is used to seal all the connections. The glue is left to dry for 24 hours to be sure there is no air leak.

The flask is placed in a thermal bath with temperature control and stirring, away from the electric resistance of the bath. The water covers the flask so that the gas is completely in thermal contact with the bath. An auxiliary thermometer is placed close to the flask to register the gas temperature. When the bath temperature is constant, the gas in thermal contact with the bath has reached a thermal equilibrium state, and the pressure in the manometer should be constant; its value is registered together with that corresponding to temperature. The temperature is then raised step by step (by about 2-4°C each step). For each new temperature, the system is left until thermal equilibrium is reached, which is noted by the constancy in temperature and pressure. The temperature and pressure values at each thermal equilibrium state are registered.

Thermal bath with T control and stirring

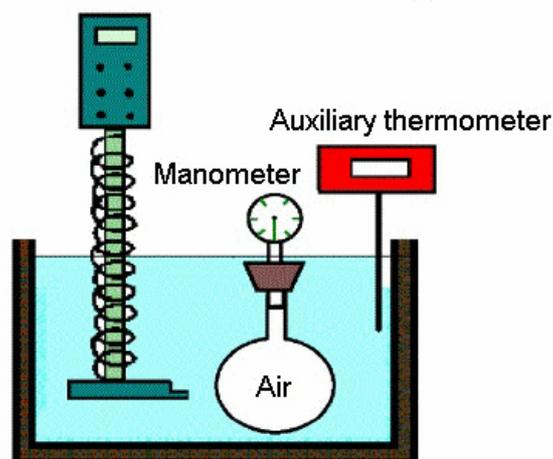


FIGURE 1. Experimental set for the response coefficient  $(\partial P/\partial T)_V$  determination.

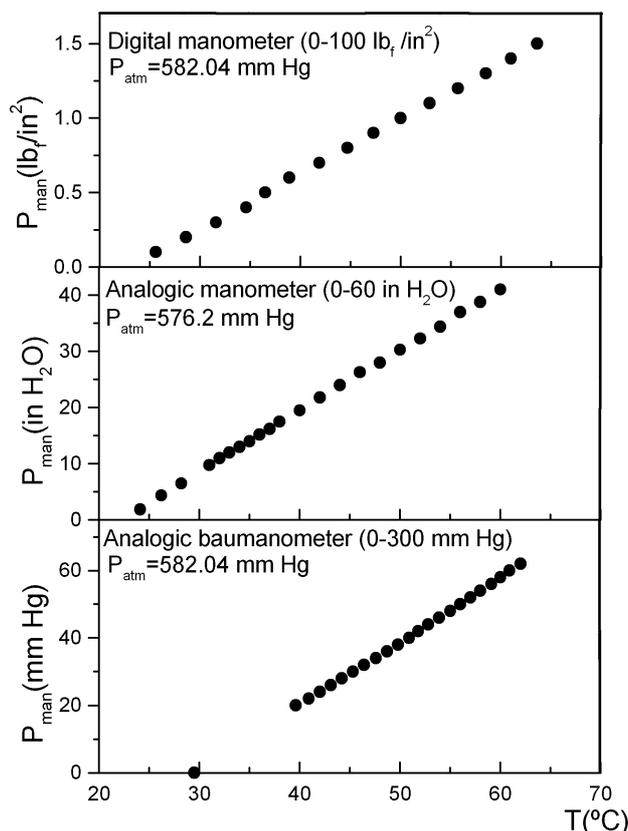


FIGURE 2. Experimental data  $P(T)$ , using three different kinds of manometers at different values of local atmospheric pressure.

If possible, the temperature is raised to a maximum of about  $60^{\circ}\text{C}$ . The experimental values are used to construct a graph of  $P_{man}$  (standard pressure units given by the manometer)- $T(\text{K})$ . The manometric pressure (converted to atm at standard conditions) is added to the atmospheric local pressure (also expressed in atm at standard conditions) to yield the gas absolute pressure (in atm), which is graphed as a function of  $T(\text{K})$ . The results are analyzed to obtain  $(\partial P/\partial T)_V$  for the air (g) studied under experimental conditions set (volume range of flasks employed: *ca.* 200-250 ml).

#### 4. Results and discussion

Figure 2 shows the graphs of the experimental data  $P_{man}$  (pressure standard units) vs.  $T(^{\circ}\text{C})$  for three of the different types of manometers used and under different atmospheric conditions, obtained by undergraduate students. A high correlation is obtained for the three sets of data. The last graph shows a gap between the first and second experimental points, because the baumanometer scale starts at 20 mm Hg.

Figure 3 shows a representative set of experimental data as absolute pressure (atm) vs. temperature (K) (dots), and the numerical fit of a linear equation of the type  $P=a_0+a_1T$  (continuous line). The values of the fitted parameters are:  $a_0=0.01978 \pm 0.0049$  and  $a_1=0.00252 \pm 0.0002$ , with  $R=0.99976$ . As can be deduced from

the fitted equation, the value for the response coefficient  $(\partial P/\partial T)_V = \beta/\kappa \cong 0.0025 \text{ atm/K}$  for air under experimental conditions. Also, the gas total pressure as a function of temperature at a constant volume, can be expressed as  $P=0.01978+0.00252 T$ . Here, a measure of a pressure value can yield the system temperature value. If two fixed points are further used to define a scale, then a gas thermometer has also been constructed. We must point out that this experiment has been performed by undergraduate students at least 80 times, and the results of the linear fit ( $a_0$  and  $a_1$ ) are reproducible no matter what type of manometer, gas container or bath is used.

More information can be obtained from the results. First, the air gas does not seem to behave like an ideal gas, because the numerical fit to a linear response shows that, although the total pressure is a linear function of temperature,  $P$  is not zero for  $T=0 \text{ K}$  (which would represent the ideal model behavior  $P/T = nRV = \text{constant}$ ); for  $T=0 \text{ K}$ ,  $P$  is *ca.* 0.02 atm, which is a significant value in the measured pressure range.

This aspect is important, because students could believe that the  $P$ - $T$  behavior of a gas mass should always correspond to the ideal gas model. Here, the experimental conditions imposed on the gas being studied (which in turn lead to the fact that  $\rho$  of air does not tend to zero) yield results that point to the suggestion that there can be another equation of state for the PVT behavior of the gas fluid studied here. Nevertheless, more experimental information is needed to establish the complete equation of state.

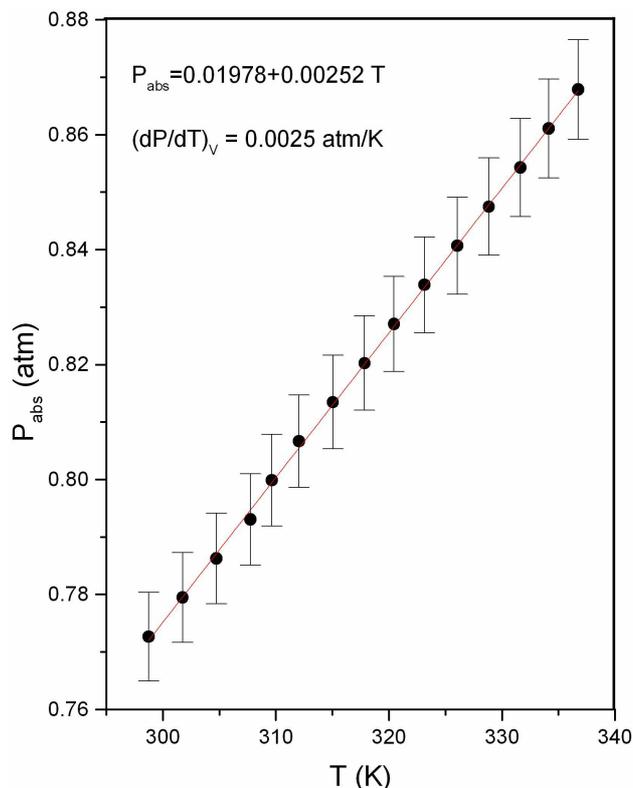


FIGURE 3. Experimental absolute pressure (atm) as a function of temperature (K) for the digital manometer readings. The linear fit to the experimental data is also presented.

The response coefficients  $\beta$  and  $\kappa$  are usually functions of the state variables. If the experimental  $\beta(T,P)$  and  $\kappa(T,P)$  are obtained within a range of T and P conditions, then the equation  $dV = \beta(T,P)VdT - \kappa(T,P)VdP$  can be integrated, provided that they satisfy the thermodynamic consistency condition

$$\left(\frac{\partial(\beta V)}{\partial P}\right)_T = -\left(\frac{\partial(\kappa V)}{\partial T}\right)_P$$

and the equation of state for the system under experimental conditions can be obtained.

## 5. Conclusions

The experiment presented here allows us to obtain the response coefficient  $(\partial P/\partial T)_V$  for air within the absolute pressure (0.76-0.88 atm) and temperature (290-340 K)

ranges, using undergraduate laboratory conditions. This coefficient is related to the isobaric thermal expansion coefficient, and the isothermal compressibility coefficient of the system. The relation between the response coefficients  $\beta$  and  $\kappa$  obtained is:

$$\beta(T, P) = (0.0025 \text{ atm/K})\kappa(T, P).$$

This represents a first step toward the analysis of the determination of a gas equation of state for a first undergraduate Thermodynamics course.

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