Reclaiming the Central Role of Equations of State in Thermodynamics

Vicente Talanquer
Department of Chemistry, University of Arizona, Tucson, AZ 85721; vicente@u.arizona.edu

Equations of state are key elements in the study of the thermodynamic behavior of physical systems. They describe the relationships that exist between relevant extensive and intensive parameters for any given system and thus are useful tools for prediction. Moreover, all the thermodynamic information of a system can be derived from the knowledge of a limited number of equations of state, which interrelate the system's state variables. However, despite their predictive efficacy and thermodynamic relevance, equations of state tend to receive little attention in traditional physical chemistry courses. In fact, most conventional textbooks in chemistry courses approach the subject in a more general fashion. Although chemical engineering textbooks and courses may discuss equations of state in further detail, their main emphasis is limited to the case of gases or liquids. Fewer authors approach the subject in a more general fashion. Although chemical engineering textbooks and courses may discuss equations of state in further detail, their main emphasis is on the behavior of fluids. Moreover, a review of many of the articles published in this journal on the topic of equations of state illustrates the pervasiveness of this narrow definition.

This approach to the study of equations of state in thermodynamics is problematic not only for being limited in scope but also because it may mislead students. The traditional association between the topics of equations of state and properties of gases leads students to believe either that only the behavior of gases can be described by these types of relationships or that equations such as $PV = nRT$ can be applied to any type of system. Additionally, students are not given the opportunity to develop an understanding of how equations of state for systems as varied as a rubber band or a paramagnetic solid may be systematically derived from experimental measurements of their thermodynamic properties.

The central goal of this article is to present an alternative approach to the derivation, analysis, and discussion of equations of state in our physical chemistry courses. This strategy relies on the use of "response coefficients" that can be measured experimentally and on the systematic manipulation of simple thermodynamic relationships. These response coefficients are simple partial derivatives involving the thermodynamic state variables of the system. The use of response coefficients such as the compressibility of a fluid, $\kappa$, or the magnetic susceptibility of a paramagnetic solid, $\chi$, to derive an equation of state highlights the importance of experimental work geared towards the measurement of these types of physical properties. It illustrates how equations of state in classical thermodynamics are derived from experimental results and not from theoretical models. This methodology also makes explicit the intrinsic similarities among the thermodynamic behavior of diverse systems. In the following section we describe the proposed strategy and illustrate how it can be used to derive basic equations of state for a variety of systems.

General Formalism

Physical systems tend to reach, when isolated or unperturbed, a state in which no further change is perceivable. This state is characterized by the specific values of a small number of quantities, identified as the state variables of the system. The number of independent variables needed to describe this state is not known a priori; thus, one must rely on experience to answer this question. What parameters are selected to accomplish the task depends on the nature of the system and how readily measurable the parameters are.

Through experience summarized in the zeroth law of thermodynamics, we know that for thermodynamic systems it is possible to measure the absolute temperature, $T$. From additional experiments for different systems we find that one can express the absolute temperature as a function of selected independent variables,

$$T = T(X_1, X_2, \ldots; Y_1, Y_2, \ldots)$$ (1)

where $X_i$ and $Y_j$ represent, respectively, the relevant extensive and intensive thermodynamic variables of the system.

For a simple fluid, for example, eq 1 can be expressed as $T = T(V, P)$ for a fixed amount of substance, and equilibrium states may be specified by any two of the three variables $P$, $V$, and $T$. In a fluid mixture, the equation of state will also include a functional dependence on the concentration of the various components. For other types of systems such as an elastic band, the equation of state may define the functional relationship between the band’s temperature, length, $L$, and applied tension, $\tau$ [$T = T(L, \tau)$]. For a dielectric solid, the equation of state interrelates the solid’s temperature, polarization, $P_d$, and applied electric field, $E$ [$T = T(P_d, E)$].

The structure of the equation of state for a given system may be derived from experimental measurements. For example, one can measure the volume of a certain amount of gas at several temperatures and pressures and analyze the data to find the function $V = V(T, P)$ that best represents the experimental behavior. This procedure can be systematized for different types of systems by using the experimental information to derive what we will call the system’s response coefficients. These quantities contain information about the system’s response to changes in the state variables.

The proposed systematic determination of a system’s equation of state is best accomplished by rewriting eq 1, selecting the extensive parameter $X_1$ as the dependent variable:

$$X_1 = X_1(T; X_2, \ldots X_n; Y_1, \ldots Y_m)$$ (2)
Any infinitesimal perturbation in the state of the system due to changes in the independent variables will result in the change,

\[
dX_1 = \left( \frac{\partial X_i}{\partial T} \right)_{V_i; j=2 \ldots n} dT + \sum_{i=2}^{n} \left( \frac{\partial X_i}{\partial X_j} \right)_{V_i; k=1 \ldots m} dX_j + \sum_{i=1}^{m} \left( \frac{\partial X_i}{\partial P} \right)_{V_i; j=2 \ldots n, k \neq i} dP_i \tag{3}
\]

where the partial derivatives involving both extensive and intensive variables in this differential, \( \partial X_i/\partial T \) and \( \partial X_i/\partial Y_k \), define the system's response coefficients. Knowledge of these parameters may then be used to integrate eq 3 and derive the corresponding equation of state. Let us illustrate the procedure for a variety of mono-component systems. In all of the following examples we assume that the amount of substance in the system \( n \) is fixed and known, and thus \( n \) is not considered an independent variable.

**Condensed Systems: \( V = V(T, P) \)**

For a simple fluid or solid, variations in the system's volume with temperature and pressure are determined by the relationship, where we have used the standard definitions of the intensive variables in this differential,

\[
dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP \tag{4}
\]

\[
= \alpha V dT - \kappa V dP
\]

where we have used the standard definitions of the associated response coefficients:

\[
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \text{isobaric thermal expansion} \tag{5}
\]

\[
\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad \text{isothermal compressibility} \tag{6}
\]

Equation 4 can also be expressed as \( dV/V = \alpha dT - \kappa dP \), and, if we assume that for many condensed systems \( \alpha \) and \( \kappa \) are practically constant in a limited range of temperatures and pressures (13–14), the terms on the right-hand side of this differential form may be independently integrated from a reference state at \( T_0, P_0 \) and, volume \( V_0 \) to an arbitrary state at \( T, P \), and \( V \):

\[
\ln \left( \frac{V}{V_0} \right) = \alpha (T - T_0) - \kappa (P - P_0) \tag{7}
\]

\[
\Rightarrow V = V_0 \exp \left[ \alpha (T - T_0) - \kappa (P - P_0) \right]
\]

For most condensed systems, the thermal expansion and compressibility coefficients are very small and thus this equation of state can be approximated by keeping only the linear portion of the Taylor series for the exponential term:

\[
V = V_0 \left[ 1 + \alpha (T - T_0) - \kappa (P - P_0) \right] \tag{8}
\]

Given the experimental values of \( \alpha \) and \( \kappa \) for a specific liquid or solid, this relationship is a useful tool to predict changes in the system's volume with temperature and pressure.

**Gases at High Temperatures and Low Pressures: \( V = V(T, P) \)**

According to experimental data, the behavior of many gaseous systems at high temperatures and low pressures is characterized by the following simple inverse relationships between the characteristic response coefficients of the system and the associated intensive properties (13–14):

\[
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{T}; \quad \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{1}{P} \tag{9}
\]

Thus, eq 4 reduces to the simple differential \( dV/V = dT/T - dP/P \), which can be integrated term by term to generate the familiar equation of state for an ideal gas,

\[
\ln(V) = \ln(T) - \ln(P) + \ln(c)
\]

\[
\Rightarrow V = \frac{c T}{P} \tag{10}
\]

where \( c \) is an integration constant that depends only on the amount of substance \( n \) in the system. For most systems \( c \) is a linear function of \( n \) and is normally expressed as \( nR \), where \( R \) is the gas constant. In contrast with the equation of state for condensed phases, eq 7, the behavior of gases at high temperatures and low pressures does not seem to depend on the chemical nature of the system. This equation of state, however, fails to describe the behavior of most systems under a wider set of conditions. The properties of various gases, such as hydrogen at moderate pressures (15), are better described by the following response coefficients,

\[
\alpha = \frac{1 - b}{T}; \quad \kappa = \frac{1 - b}{P} \tag{11}
\]

where \( b \) is a constant characteristic of each gas. These relationships, in conjunction with eq 4, can be used to easily derive a better equation of state for these systems: \( V = b + cT/P \).

**Elastic Fiber: \( L = L(T, \tau) \)**

For a thin elastic fiber, small changes in temperature \( T \) and tension \( \tau \) result in variations to the system's length \( L \) given by,

\[
dL = \left( \frac{\partial L}{\partial T} \right)_\tau dT + \left( \frac{\partial L}{\partial \tau} \right)_T d\tau \tag{12}
\]

\[
= \alpha_L L dT + \frac{L}{A_Y} d\tau
\]
where \( \alpha_T = (1/L)(\partial L/\partial T) \) is the linear thermal expansion, \( Y = (L/A)(\partial T/\partial L)_T \) is Young’s modulus, and \( A \) is the cross-sectional area of the fiber. For small deformations, the coefficients \( \alpha_L \) and \( Y \) for an elastic fiber can be approximated by (16),

\[
\alpha_L = -\left(1 - \frac{\lambda}{T}\right); \quad Y = bT\lambda^2 \tag{13}
\]

where \( \lambda = L/L_0 \), with \( L_0 \) as the length of the fiber at zero tension, and \( b \) is a constant characteristic of the elastic material. Substituting these relationships into eq 12 and solving for \( d\tau \) we obtain:

\[
d\tau = \frac{AbT}{L_0} dL + \frac{Ab(L - L_0)}{L_0} dT \tag{14}
\]

The corresponding equation of state can be derived by integrating any of the terms in this exact differential form along any well-defined path from a state at \( L_0, T_0 \) to a state at \( L, T \). For example, the integration along a rectilinear path from \( L_0 \) to \( L \) at constant \( T = T_0 \) followed by a \( T_0 \) to \( T \) step at constant \( L \) yields

\[
\tau = \frac{AbT_0 (L - L_0)}{L_0} + \frac{Ab(L - L_0)(T - T_0)}{L_0} \tag{15}
\]

The final result in this equation can be expressed as

\[
\tau = AbT(\lambda - 1) \Rightarrow \sigma = bT\epsilon \tag{16}
\]

where \( \sigma = \tau/A \) is the stress on the fiber and \( \epsilon = \lambda - 1 = (L - L_0)/L_0 \) is the corresponding strain. Thus, the equation of state for small deformations corresponds to Hooke’s law for an elastic system.

There is a striking resemblance between eq 10 for an ideal gas, and eq 16 for an elastic fiber. The similarity is due in part to the fact that both relationships describe the behavior of the associated systems in a well-defined limit: high temperatures and low pressures in the case of gases and moderate temperatures and small strains for the elastic systems. Under these conditions, there is a simple relationship between the values of the constraining intensive fields (pressure or stress) and the coupled extensive variables (volume or elongation). There are, however, interesting differences in the nature of the system’s responses to changes in temperature and mechanical action (pressure or stress). While the gas volume increases with increasing temperature and decreasing pressure, the fiber shrinks when the temperature is increased or the applied tension is reduced.

As it is the case for gaseous systems, one can derive equations of state for elastic fibers that describe the behavior of the system in a wider range of conditions. For example, the response of polymeric fibers to changes in temperature (\( \alpha_T \)) and applied tension (\( \tau \)) is better described by the following functions:

\[
\alpha_L = -\frac{1}{T}\left(\lambda^3 - 1\right); \quad Y = b\lambda(1 + 2\lambda^2) \tag{17}
\]

where \( b \) is a constant characteristic of the elastic material. Integration of eq 12 using these response coefficients leads to the so-called Guth–James equation of state for ideal elastic materials: \( \tau = b\lambda T(\lambda - \lambda^2) \) (17–18).

**Paramagnetic Materials: \( M = MT, H \)**

The thermodynamic state of simple paramagnetic systems can be described by any two of the three variables temperature, \( T \), magnetic field, \( H \), and magnetization, \( M \). Experimentally, the following response coefficients are often measured:

\[
\alpha_H = \frac{\partial M}{\partial T} \tag{18}
\]

\[
\chi_T = \frac{\partial M}{\partial H} \tag{19}
\]

Thus, it is convenient to use the following differential form to derive the corresponding equation of state for the system:

\[
dM = \left(\frac{\partial M}{\partial T}\right)_H dT + \left(\frac{\partial M}{\partial H}\right)_T dH \tag{20}
\]

In the limit of low magnetizations, the response coefficients, \( \alpha_H \) and \( \chi_T \), for long and thin samples of many paramagnetic materials exhibit the following simple behavior (5, 16),

\[
\alpha_H = -\frac{CH}{T^2}; \quad \chi_T = \frac{C}{T} \tag{21}
\]

where \( C \) is a constant that depends on the type of material. Substitution of these equations into eq 20 results in the exact differential form \( dM = -CHdT/T^2 + CdH/T \). Following a similar procedure to that described in the case of an elastic fiber, we can integrate this differential equation holding one of the variables constant. The value of the associated integration constant can be derived from the fact that \( M = 0 \) for \( H = 0 \) in a paramagnetic material. The corresponding equation of state, also known as Curie’s law, can finally be expressed as

\[
M = \frac{CH}{T} \tag{22}
\]

Once more, one can readily notice the similarities between this relationship and the equations of state for the ideal gas and elastic fiber.

Ferromagnetic substances become paramagnetic above a characteristic temperature known as the Curie temperature \( T_C \). For temperatures higher than \( T_C \), the system’s response to variations in temperature and magnetic field can also be approximated by simple functions (7, 16), in particular, \( \alpha_H \).


\[ \frac{cT}{A - b} + \frac{2a}{A^3} \]

with \( a \) and \( b \) as characteristic constants for each type of substance. These response coefficients lead to an equation of state analogous to the van der Waals equation of state for fluid systems: \( \Pi = \frac{cT}{(A - b)} - a/A^2 \). In particular, the equation of state predicts the existence of a phase transition from a gas-like monolayer to a dense, liquid-like film as the surface area is reduced at any constant temperature lower than a critical value \( T_c \).

**Final Remarks**

A summary of the basic relationships that characterize the thermodynamic behavior of the various systems just described is found in Table 1. We have included some additional examples that can be used to further illustrate the general applicability and efficacy of the proposed approach to derive equations of state for a diversity of systems.

The equations of state in Table 1 express the characteristic relationship between state variables for particular thermodynamic systems. From the perspective of classical thermodynamics, equations such as these can only be de-
terminated by experimental means, and they are only as accurate as the experiments that led to their formulation. In that sense, equations of state are only valid within the restricted range of values in which the relevant properties were measured. The different examples discussed in this article illustrate a systematic method to derive equations of state from measurable response coefficients for the systems of interest.

Some of the equations of state included in Table 1 were originally derived using methods of statistical mechanics for particular molecular models. We have not made a distinction between phenomenological and theoretical equations of state because we want to keep our discussion within the realm of classical thermodynamics. From this perspective, one of the central points that we want students to understand is that equations of state are not theoretically deduced using the formalism of thermodynamics, but inductively built from experimental information. The fact that we do not need to rely on a molecular model to describe and predict the thermodynamic behavior of a system is not always clear to students who tend to not distinguish macroscopic from microscopic models (20).

The analysis and discussion of the concept of “equation of state” using the proposed approach has several advantages over the more traditional method centered on properties of gases. First, it clearly illustrates the power of thermodynamics as a tool to derive useful information for a variety of systems and stresses the central role that the measurement of thermodynamic properties has in experimental physical chemistry. Moreover, it opens the door to the critical analysis of the similarities and difference in the physical behavior of a wide variety of systems. Additionally, with a little extra effort and information, the same methodology can be used to derive the equation of state for the energy, \( U \), of the various systems as a function of the corresponding state variables. In order to do so, the only thing required is information about the properties of the associated heat capacities. For example, for an ideal gas the associated equation of state for the energy function \( U \) results in \( U = C_v T \), where \( C_v \) is the isochoric heat capacity (1). With this knowledge in hand, one can essentially derive all the thermodynamic properties of the system. To illustrate the point, let us take a gas whose behavior is described by the equations of state \( PV = nRT \) and \( U = (3/2)nRT \). For this system, a differential change in the entropy \( S \) at fixed \( n \) can be expressed as \( dS = dU/T + PdV/T \), or

\[
dS = \frac{3}{2} \frac{nR}{U} dU + \frac{nR}{V} dV
\]

Direct integration of this relationship yields the fundamental equation for an ideal gas

\[
S = S_0 + \frac{3}{2} nR \ln \left( \frac{U}{U_0} \right) + nR \ln \left( \frac{V}{V_0} \right)
\]

This relationship can then be used to derive a variety of thermodynamic properties for the system. This inductive approach to the derivation of fundamental thermodynamic equations can help students build a more comprehensive understanding of the scope and limitations of classical thermodynamics.

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**Literature Cited**