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# AN EQUATION OF STATE FOR GASES AND LIQUIDS

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## ABSTRACT

We present an equation of state that can represent within experimental error most individual sets of published *PVT* data for most fluids, whether in the range of vapor at moderate pressures, or compressed liquids, or gases at very high temperatures and densities, any region in fact except the vicinity of the critical point. In terms of pressure the equation is

$$P = DRT\left[1 + (D/T)\,(c_1T + c_2D - 1)/\left(c_3 + c_4T^{1/2} + c_5D + c_6D^2\right)\right]$$

where $D = 1/V$, the density in mole $l^{-1}$. The coefficients are readily determined by a least squares fit of the data. An additional term is sometimes needed if the $D$ range is very wide, say several times $D_c$. Different fluids can be simultaneously represented over a limited range, such as the compressed liquid region, by a single reduced form of the equation in which all but three of the constants are the same for all, and these three (a reducing $T$, $1/c_1$, a reducing $D$, $1/c_2$, and a dimensionless parameter) are characteristic of each individual fluid. The equation can also simultaneously represent many data sets for a single fluid from many labs and covering various $T$ and $D$ ranges. From this, a consistent representation of its thermodynamic properties can be derived.

An equation of state is presented for use in all temperature, pressure, and density regions of gases and liquids except the critical region. The equation has the form

$$D(c_1T + c_2D - 1) = (Z - 1)TW \tag{1}$$

where $Z = P/(DRT)$, $P$ is pressure, $T$ is temperature, $D$ is density, and

$$W = c_3 + c_4T^{1/2} + c_5D + c_6D^2 \tag{2}$$

Equation (1) is linear in the six coefficients, and to determine them from experimental data by simple least squares, any one of the variables, e.g. $T$, or $D$, or $DT$, etc., could be taken as the dependent variable. In practice it has been convenient to take the constant unity as the dependent quantity

$$1 = c_1T + c_2D - (Z - 1)(T/D)W \tag{3}$$

Once the coefficients are determined, the equation can be used to calculate $P$ explicitly

$$P = DRT[1 + D(c_1T + c_2D - 1)/(TW)] \tag{4}$$

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To find $D$ from $P$ and $T$, or $T$ from $P$ and $D$, the simplest procedure is iteration.

The quantity $W$ appears to vary with the 1/2 power of $T$ over wide temperature ranges, but if the range is narrow, then any power between 1/2 and 1 will do. If the density range is very wide, e.g., two or three times $D_c$, then another density term, $c_7D^3$, is sometimes needed in $W$. The equation has been applied successfully to literature data over most of the accessible experimental region, ranging in pressure from 0 to 22 kbar, in temperature from the triple point to ten times critical, and in density from zero to over four times critical.

In this report we will:

(1) demonstrate its suitability for representing individual experimental *PVT* data sets within experimental error in various regions of the variables;

(2) show how it can represent simultaneously several sets of data for a given substance as measured by different investigators in different *PVT* regions;

(3) show how it can be used in reduced form in a limited region, e.g., the compressed liquid region, to represent data for many different substances by the same equation with only three characteristic parameters needed to distinguish each substance;

(4) indicate how it can be used to determine virial coefficients, to evaluate the parameters of any three-constant intermolecular potential, and to correlate various thermodynamic properties in reduced form.

## INDIVIDUAL DATA SETS

### *Region I: supercritical gases (*T *above* $T_c$*, low to moderate* D*)*

As an example of data in this region we take the measurements by Michels et al. [1] for carbon monoxide. These range in temperature from 0°C to 150°C, which is about 2 $T_c$ to 3 $T_c$ on isotherms at 25° intervals. The pressure is from 0 to 3000 atm, and the density is from 0 to about 27 mole $l^{-1}$, which is over two and a half times $D_c$. With the $D^3$ term included, eqn. (1) fits these data with an average absolute deviation in density of two parts in 10000. This accuracy is a measure of the quality both of the data and the equation. The original authors represented their data by isothermal virial expansions to the seventh power in $D$, thus requiring 49 constants to represent the seven isotherms, which are good of course only at these seven temperatures and not in between. Many other examples of data in this range have been tested, with the goodness of fit usually agreeing with the reported experimental error.

The measurements of Michels et al. [2] for neon are especially well represented by eqn. (1) with just six constants even though the density range extends from 0 to about 2.3 $D_c$. The $T$ range is from about six to 10 times $T_c$. The average density deviation is only seven parts per 100000.

The equation holds just as well for mixtures as it does for pure gases. Examples include the $CH_4$–$CF_4$ mixtures investigated by Douslin et al. [3].

Unfortunately, as the experimental temperature approaches $T_c$, even to below about 1.3 $T_c$, the fit worsens. The rapid change of density with pressure is less and less accurately represented. Therefore near $T_c$, the density region between about 0.5 $D_c$ and 2 $D_c$ must be excluded.

### *Region II: compressed liquids (*T *below* $T_c$, D *above* 2 $D_c$*)*

In this region, the power of $T$ in $W$ is not crucial, as noted above, and the term $c_7D^3$ is not needed. Liquid data often have an error of one or two parts per 1000 in density, although frequently the self-consistency of any one data set is much better than this. Any experimental density points below about 2 $D_c$ will be for $T$ near $T_c$ and should be excluded. Otherwise the equation usually matches the consistency of the data.

A good example of data in this region is provided by Streett and Staveley for liquid krypton [4]. The temperature range is from 120 to 220 K, roughly from $T_c/2$ to $T_c$. The pressure ranges from the vapor pressure to over 3500 atm. Excluding a few points below 2 $D_c$, the density ranges from 2 $D_c$ to 3 $D_c$, which is up to about 33 mole $l^{-1}$. The original authors represented the data with an average density deviation of three parts in 10000 using the 16-constant Strobridge equation. Equation (1) fits with the same accuracy.

Many other liquids can also be fitted within the experimental error. These include other noble gas liquids, nitrogen, oxygen, and ammonia. The data of Benson and Winnick [5] for liquid octane fit with an average density deviation of 3.5 in 10000. The temperatures ranges from −15 to 85°C, and the pressure goes up to near freezing at each $T$, to over 7000 atm at 85°C.

*PVT* data for molten KCl as a typical example of an ionic melt are presented by Goldmann and Todheide [6]. They represent the data, which ranges in $T$ from 770 to 1050°C and in $P$ up to 6 kbar, by a Tait equation with $T$-dependent parameters and obtain a standard deviation of 0.04% in density. Equation (1) fits their reported values (smoothed by the Tait equation) with an average density deviation of less than 0.02%.

Other relatively incompressible liquids also fit extremely well. Glycerol, for example [7], in the $T$ range from −50 to 80°C, and for pressures up to 2800 kg $cm^{-2}$ exhibits an average deviation of 1.6 in $10^4$. The most notable example so far encountered is mercury. In this case the unrounded experimental values of Davis and Gordon [8], given by MacDonald [9], are reproduced with an average deviation of only a few parts per million.

### *Region III: high density, high temperature (*T *above* Tc, D *above about 2* $D_c$*)*

Robertson and Babb [10] have reported results in this region for a number of fluids. Their measurements of nitrogen, for example, range in temperature from 35 to 400°C, which is about 2.5 $T_c$ to 5.5 $T_c$, in pressure from 1.5 to 10 kbar and in density from about 2 $D_c$ to 3.5 $D_c$. With six coefficients (a seventh does not help) the average density deviation is 4.7 parts per 10000, well within the reported uncertainty of the measurements.

The highest pressures and densities encountered thus far are for measurements on nitrogen by Mills et al. [11] which extend from 3 to 22 kbar, and from about 2.5 $D_c$ to 4.2 $D_c$, reaching the freezing line even though the temperatures are above 2 $T_c$. The fit of eqn. (1) to their smoothed molar volumes shows an average deviation of less than two parts per 10000.

Although this data region is fairly extensive, still the coefficients of eqn. (1) are not determined uniquely by data in this region alone. For example, variations in $c_1$ and $c_2$ of several percent can still produce good agreement. This will be discussed further later.

We also note that in this region, and in the others as well, eqn. (1) can apparently adapt itself to small systematic errors. In this sense it is perhaps too pliable and accomodating, especially for data of limited extent.

We should also point out that the discussion of data in these three arbitrary regions is not intended to exclude its application to data which do not fit exactly into one of them or to low density vapors.

## TWO OR MORE REGIONS COMBINED

In this section we discuss the simultaneous fitting of *PVT* data for a single fluid from several sources and covering more than one of the above regions. When we do this we must be prepared in most cases to accept somewhat greater average deviations than before. This is because apparently good data sets from different investigators, even in the same data region, sometimes disagree by a few tenths of a percent. And eqn. (1) usually cannot follow small systematic errors in two data sets simultaneously.

Even so, fits having average density deviations of less than one part per 1000 are obtained in some cases. A good example is the combination of data from Regions I and III, that is, data covering all densities at supercritical temperatures. The Region I data for argon by Michels et al. [12] and the Region III data for argon by Robertson et al. [13] fit together with an average density deviation of seven in 10000. The same is true of nitrogen data by these same investigators. Data from Regions II and III also combine well. This includes all temperatures, and all densities above about 2 $D_c$. The Region II (liquid) data of Streett and Staveley [14] for argon fit simultaneously with Robertson et al.'s [13] higher $T$ data for argon with an average deviation of seven in 10000. The same is true for the nitrogen data of these investigators.

When we attempt a combined fit of data from all three regions or just from Regions I and II, the average deviation goes up to several parts per 1000. While this is within the claimed accuracy of some of the data, and good enough for some purposes, still the deviations are grossly systematic and indicative of a fundamental problem.

To understand the problem and its solution, we need to take a moment to examine one of the features of eqn. (1), namely the unit compressibility line (UCL). The compressibility factor, $Z$, equals unity when $D$ is zero, and also whenever $c_1T + c_2D - 1 = 0$. Thus, in the latter case, $T$ and $D$ are linearly related for those states of the fluid for which the ideal gas condition, $P = DRT$, holds [15–18]. Defining a temperature $T_0$ as $1/c_1$, and a density $D_0$ as $1/c_2$, we have that

$$T/T_0 + D/D_0 = 1 \qquad (5)$$

for $Z = 1$, and we see that $T_0$ is the zero density intercept, and $D_0$ the zero temperature intercept, of the $T$ vs. $D$ UCL. Most sets of data for compressed liquids (Region II) include a section of the UCl, and with a few exceptions like $H_2$ and $H_2O$, the line is remarkably straight, well within experimental error. Many data sets in Region I also include a section of the UCl, and again in most cases it is amazingly straight, within the experimental error. The constants $c_1$ and $c_2$ (and thus $T_0$ and $D_0$) are then of course determined without very much leeway. Region III at high temperatures and densities does not include the UCL at all, and it is for this reason that the coefficients are determined with less precision here.

Now we note an unfortunate fact, which is the source of our difficulty. The values of $T_0$ and $D_0$ determined in the gaseous region (high $T$, low $D$) for a given fluid usually disagree by a few percent with those found in the liquid region (low $T$, high $D$). The lines seem perfectly straight in both regions, but they are slightly different straight lines. For example, $T_0$ values as found for liquid and gas are about 416 and 408 K for argon, and about 338 and 326 K for nitrogen. As was mentioned, Region III data allow some tolerance in $T_0$ and $D_0$, and so this region can be fitted simultaneously with either Region I or Region II. But Regions I and II, for high accuracy fits, demand their own values.

If we assume that the differences between the coefficients for these two regions, and the consequent relatively poor combined fit to eqn. (1), are due to real differences and not simply to experimental discrepancies, then we are assuming that the UCL is not exactly straight over its entire course from high $T$, low $D$ gas to low $T$, high $D$ liquid. This assumption is reinforced by the obvious experimental curvature of the UCL for some fluids such as $H_2$ and $H_2O$. This in turn then requires a modification of eqn. (1), whose UCL is straight. The simplest modification is an added term in the parentheses on the left of eqn. (1), allowing a small curvature in the UCL. When this is included, the overall combined fit of the three regions is improved. The best form for the added term is still being investigated, but for nitrogen a $D^{1.5}$ term permits the Region I data of Michels et al., the liquid data of Streett and Staveley, and the Region III data of Robertson and Babb, to be fitted simultaneously with an average deviation of nine in 10000. Similar results are obtained for argon.

## EQUATION (1) IN REDUCED FORM

If we return to data sets covering only a limited region, such as one of the three (I, II or III), then we can return to the unmodified form of eqn. (1) and to a straight UCL. Then we can discuss the simultaneous fitting of data for many different fluids in a given region to a single reduced form of eqn. (1). For this purpose we take $T_0$ as a reducing temperature and $D_0$ as a reducing density, and define

$$\theta = T/T_0 \textit{ and } \delta = D/D_0 \tag{6}$$

as the reduced temperature and the reduced density. If we define a third (dimensionless) reducing parameter, $K_0$, as

$$K_0 = c_1/c_2\left(c_3 + c_4/c_1^{1/2}\right) = D_0/T_0\left(c_3 + c_4 T_0^{1/2}\right) \tag{7}$$

we can write eqn. (1) as

$$K_0\,\delta(\theta + \delta - 1) = (Z - 1)\theta\left(a_1 + a_2\theta^{1/2} + a_3\delta + a_4\delta^2\right) \tag{8}$$

in which $a_1 + a_2 = 1$. From previous work [19], it is to be expected that many liquids can be fitted to the same reduced equation, that is, eqn. (8) with the same $a_i$ coefficients, requiring only the three characteristic parameters ($T_0$, $D_0$, $K_0$) to distinguish one from another. Provisional results confirm this expectation. For example, with $a_1 = 0.84$, $a_3 = -1.572$, and $a_4 = 0.765$, eqn. (8) represents the liquid (Region II) data for mercury [8,9], ammonia [21], and xenon [22] with the respective average density deviations of 1.2, 8, and 4 parts per 10000.

Earlier work with another equation [20] for gases up to $D \simeq D_c$ demonstrated that a large number of substances can be represented in this region also by a single reduced equation, requiring only the same three parameters, but now evaluated at low densities (Region I).

## VIRIAL COEFFICIENTS, INTERMOLECULAR POTENTIALS, AND REDUCED THERMODYNAMIC PROPERTIES

The equation of state in the virial form may be written as

$$Z = 1 + BD + CD^2 + \ldots \tag{9}$$

in which $B$ and $C$ are the second and third virial coefficients. Equation (1), fitted to data in the region of low to moderate densities, serves to determine these early virial coefficients as functions of temperature. Thus, from $B = Z_0'$ and $C = Z_0''/2$, where $Z_0'$ and $Z_0''$ are the first and second partial derivatives of $Z$ with respect to $D$ at constant $T$ and zero $D$, we find that

$$B = (c_1T - 1)/TW_0, \text{ and } C = (c_2 - c_5TB)/TW_0 \tag{10}$$

where $W_0 = c_3 + c_4T^{1/2}$.

We also find that the three parameters, $T_0$, $D_0$, and $K_0$, when evaluated from Region I data, have the following physical identities: $T_0$ is the Boyle temperature, $T_B$, at which $B$ is zero; $K_0/D_0$ is the Boyle volume, $V_B$, defined as $TdB/dT$ at $T_B$; and $K_0/D_0^2 = V_B/D_0$ is $C_B$, the value of $C$ at $T_B$.

It has also been shown previously [23] that these three parameters ($T_0$, $D_0$, $K_0$) uniquely specify any given three parameter intermolecular potential. Such potentials are described by a potential energy well depth, $\epsilon$, which can be evaluated from $T_B$, a molecular volume, which can be evaluated from $D_0$ or $V_B$ and a third, dimensionless, parameter, which can be evaluated from $K_0$.

To correlate thermodynamic properties in reduced form, we define corresponding fluids as those that obey eqn. (8) with the same values of the $a_i$ coefficients in a given region such as the compressed liquid region. And we define a corresponding reduced property as one that has the same value for all corresponding fluids at any given $\theta$ and $\delta$ [24]. It can be seen from the relation $Z = 1 + K_0Y$, where $Y$ is a function of $\theta$ and $\delta$, that $Z$ is not a corresponding property, but has different values for different fluids at a given $\theta$ and $\delta$, depending on $K_0$. Reduced pressure, defined as $\pi = P/(D_0RT_0)$, also does not correspond because it equals $Z\theta\delta$. But of course, $(Z - 1)/K_0 = Y(\theta, \delta)$ is a corresponding property for corresponding fluids. And so are the so-called residual properties, such as residual energy, enthalpy, and entropy, when properly reduced [25]. Some properties, such as the zero density reduced Joule–Thompson coefficient, are functions of $\theta$ only. This is also true of the reduced virial coefficients, $\beta = B/V_B$ and $\gamma = C/C_B$. Thus

$$\beta = (\theta - 1)/\theta w_0, \text{ and } \gamma = (1 - a_3\theta\beta)/\theta w_0 \tag{11}$$

where $w_0 = a_1 + a_2\theta^{1/2}$ with $a_1 + a_2 = 1$.

If a corresponding property is set at a constant value, this yields a universal $\theta$ vs. $\delta$ curve. For example, a family of such curves results from setting $(Z - 1)/K_0$ at a series of constant values. If the value is set at the ideal gas value, the resulting curve is called an ideal curve [17]. Such ideal curves are produced by setting any of the following equal to zero: $(Z - 1)$; the Joule–Thompson coefficient; the slope of $Z$ on an isochore (giving $Z$ maximum); the slope of $Z$ on an isotherm (giving $Z$ minimum); $(\partial^2\pi/\partial\delta^2)_\theta$, giving the locus of inflection points on isotherms of $\pi$, and the $\theta$ vs. $\delta$ curve on which the critical point must lie; and $(\partial^2\pi/\partial\theta^2)\delta$ giving the universal $\theta$ vs. $\delta$ locus of $C_V$ maxima.

And finally, once the $a_i$ are known, then evaluation of the three parameters, $T_0$, $D_0$, and $K_0$, for any corresponding fluid in the region allows the calculation of all the properties of the fluid that can be derived from the equation of state.

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