

An Invariance Property Associated with p - v - T Equations of State

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All p - v - T equations of state that apply uniformly to the liquid, two-phase, and vapor regions, such as the Redlich-Kwong and Peng-Robinson equations and many others, relate to an invariance principle, in which one uses reduced variables but replaces the reduced volume by a new dimensionless volume variable. According to this invariance principle, the relation between reduced vapor pressure and reduced temperature is invariant with changes in the critical compressibility factor, Z_c , for the transformed p - v - T equation. Examples are provided to illustrate the use of the invariance principle to extend the application of equations of state with fixed Z_c to substances with other values of Z_c .

The importance of p - v - T equations and other thermodynamic equations of state is well recognized. In particular, a p - v - T equation, together with an equation for the temperature dependence of the specific heat of the vapor at a low pressure, is completely equivalent to a fundamental (or canonical) equation of state from which all thermodynamic properties can be calculated. The quest for simple and yet accurate equations of state has been pursued by many eminent scientists. We have several simple equations of state, each valid for substances having

a specific value for the critical compressibility, Z_c . More recently, equations valid over a range of Z_c have been advanced by Redlich (1975), Martin (1982), Kumar and Starling (1982), and others; excellent summaries and comparisons are provided by Reid et al. (1987) and Walas (1985). Such general equations are made to encompass several substances by writing the coefficients in terms of molecular parameters such as Z_c , the acentric factor of Pitzer, or the Riedel factor.

In their pioneering report, Lydersen et al. (1955) ad-

vanced Z_c as a good molecular parameter. For instance, they present a plot of $\log(p_{r,\text{sat}})$ against $1/T_r$ obtained from experimental vapor pressure data and show that the resulting curves arrange nicely in the order of Z_c . Others favor the Pitzer acentric factor ω over Z_c , and weak correlations between the different molecular parameters have been suggested. Soave's (1972) modification of the Redlich-Kwong equation has been widely used and is able to reproduce the vapor pressures of pure substances quite accurately. This equation retains the same value of Z_c as the Redlich-Kwong equation, but the coefficients are correlated in terms of the acentric factor.

There is some disagreement about which molecular parameter is the most successful one for treating large classes of substances. No one seems to have recognized an invariance principle that pertains to the question. This principle suggests that Z_c may play a more minor role than is commonly assumed as far as vapor-liquid equilibrium is concerned, and allows an equation with a fixed value of Z_c to be modified to accommodate fluids with different Z_c . We feel that this principle is important to keep in mind in developing new equations of state. It is quite likely that earlier workers used this principle in a subconscious way: many of J. J. Martin's papers employ volume transformations that can be more elegantly stated in terms of the invariance principle, but no explicit statement can be found in the literature.

We cannot give any direct physical argument leading to the invariance principle, but a mathematical derivation of it is simple and straightforward. We shall give this derivation and provide some illustrative examples and applications.

Incidentally, we stumbled upon this principle when we fed wrong Z_c data to a computer program for calculating vapor pressures and found the results to be totally unaffected by the incorrect data.

The Invariance Principle

The invariance principle applies to a reduced and transformed version of the p - v - T equation, and not to the original p - v - T equation. It is best stated and derived using a slightly unconventional reduced volume as an independent variable, to which we are led by two considerations. First, the critical point is a logical origin for volume. Second, we should be able to write the limiting form of the p - v - T equation in the ideal gas region without any critical constants appearing explicitly in it. A variable that satisfies these requirements is

$$r = (v - v_c)/v_c' = (v_r - 1)Z_c = v_r' - Z_c \quad (1)$$

where v_c' is the pseudocritical volume, equal to RT_c/p_c . We could have used the pseudoreduced volume $v_r' = v/v_c'$ in place of r , but r has certain advantages when one wishes to apply the critical conditions, as will be seen shortly. The scaling by Z_c is crucial—the offset is not, and can be chosen to be any constant without affecting most of the equations given below.

Let $F(p_r, r, T_r) = 0$ be any p - v - T equation of state in terms of the new variable r , reduced pressure p_r , and reduced temperature T_r . Let us also assume that this p - v - T equation is uniformly valid for liquid and vapor. Then, the relations and constraints that are used in obtaining the vapor pressure at any given temperature are as follows.

The critical point is $p_r = 1$, $T_r = 1$, $r = 0$. If we require the critical point to be an inflection point for the critical isotherm, the equation $F = 0$ must resemble $r^3 = 0$ at $T_r = 1$ near $r = 0$. (Had v_r' been used instead of r , the equation would have been $(v_r' - Z_c)^3 = 0$.)

To be able to approach the perfect gas limit correctly, we must have

$$\lim_{r \rightarrow \infty} p_r r = T_r \quad (2)$$

We determine the saturation pressure at a given T_r as the value of p_r that satisfies the Gibbs-Maxwell equal-areas condition

$$\int_{r_f}^{r_g} p_r dr = p_{r,\text{sat}}(r_g - r_f) \quad (3)$$

where r_f and r_g are obtained as the smallest and largest roots of

$$F(p_r, r, T_r) = 0 \quad (4)$$

By examining (2)–(4), we notice that nowhere does Z_c appear in them. Thus, we arrive at the invariance principle, which may be stated as follows.

All substances that obey the same p_r - r - T_r equation of state have the same $p_{r,\text{sat}}$ - T_r dependence, even if they have different values of Z_c and obey different p_r - v_r - T_r equations.

Similarly, it is easy to show that many other thermodynamic relations relating the properties of the real gas and the liquid to the ideal gas, when written in terms of p_r , T_r , and r , result in equations that will not contain Z_c . Thus, for example, the equations relating the reduced enthalpy h/RT_c and the reduced entropy s/R to the ideal gas values do not contain Z_c if the variable r is used instead of the reduced volume.

Examples

Transformation of Equations To Alter Z_c . We can make up any number of examples by simply starting with a known p - v - T equation, converting it to its equivalent form in terms of p_r - r - T_r , and converting back to p - v - T using a different Z_c .

Thus, starting with the van der Waals equation (which, incidentally, closely describes mercury [see Shamsundar and Lienhard (1983)])

$$p_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2} \quad (5)$$

and applying the r transformation with $Z_c = 3/8$, we get

$$p_r = \frac{T_r}{r + 1/4} - \frac{27/64}{(r + 3/8)^2} \quad (6)$$

as the r form of the van der Waals equation. Next, we convert back to the v_r form using a different Z_c , say, $1/4$, to get

$$p_r = \frac{4T_r}{v_r} - \frac{27}{(2v_r + 1)^2} \quad (7)$$

The two equations (5) and (7) look quite different—(7) is not much different in form from some of Martin's (1982) equations. The two substances described by these equations have very different values of the critical compressibility Z_c , yet have identical reduced vapor pressures at the same reduced temperature.

Another example, synthesized from the Redlich-Kwong equation, shows us that the two equations of state

$$p_r = \frac{3T_r}{v_r - 0.2599} - \frac{3.8473T_r^{-1/2}}{v_r(v_r + 0.2599)} \quad (8)$$

and

$$p_r = \frac{4.0536T_r}{v_r} - \frac{7.0243T_r^{-1/2}}{(v_r + 0.5268)^2 - 0.0019} \quad (9)$$

have identical reduced vapor pressure versus reduced temperature curves, despite their superficial dissimilarities.

A historical example of a similar type is Berthelot's (1907) equation. Berthelot started with an equation with $Z_c = 3/8$,

$$p_r = \frac{8T_r}{3v_r - 1} - \frac{3}{T_r v_r^2} \quad (10)$$

and empirically modified it into an equation with $Z_c = 9/32$. If we use the procedure just used for the van der Waals and Redlich-Kwong equations, we get

$$p_r = \frac{32T_r}{9(v_r - 1/9)} - \frac{16}{3T_r(v_r + 1/3)^2} \quad (11)$$

Equation 11 has $Z_c = 9/32 \approx 0.28$ and satisfies the critical conditions. Berthelot's empirical modification consists of replacing the $1/9$ in the denominator of the first term on the right by $1/4$, and ignoring the $1/3$ in the denominator of the second term. These replacements will have little effect on the behavior of the equation in the moderate pressure vapor region, which was the region of interest to Berthelot. Unfortunately, the resulting equation no longer satisfies the critical point conditions, although it behaves at moderate pressures as a gas with $Z_c = 9/32$, in the sense that

$$\lim_{v_r \rightarrow \infty} p_r v_r = (32/9)T_r$$

Transformation of Data from Real Fluids. The examples given so far have been synthetic, and more conclusive evidence should be expected from data on real fluids. There are at least three different approaches that come to mind in this regard.

The first and best would be to seek two substances with the same Pitzer factor but different Z_c and compare data for them. This was attempted, based on the observation that, according to the tables in Reid et al. (1987), 1-hexanol and 1-heptanol should have the same Pitzer factor, $\omega = 0.560$. When, however, the Pitzer factor was calculated from the Antoine vapor pressure equations in the same source, the Pitzer factors were found to be 0.647 and 0.557, respectively. This approach was, therefore, abandoned.

The second approach consists of starting with a versatile equation such as the Soave (1972) equation with a variable ω but fixed Z_c and applying the r transformation to it to obtain results that can be compared to data for a real fluid with a different Z_c . Figures 1 and 2 show the results of this calculation for the saturated vapor volumes of water ($\omega = 0.344$, $Z_c = 0.233$) and ammonia ($\omega = 0.252$, $Z_c = 0.246$), respectively, which are the most accurate experimental values from Haar et al. (1984) and Reynolds (1979). The figures show v_{rg} plotted against T_r . The full lines in these figures were obtained from the equations given in Reynolds (1979) and Haar et al. (1984). The dashed lines that are close to the full lines were obtained from the relation

$$(v_{r,\text{Soave,modified}} - 1)Z_c = (v_{r,\text{Soave}} - 1)Z_{c,\text{Soave}} \quad (12)$$

The figure makes it obvious that the Soave equation, which shows large errors when used by itself, can be made to give excellent results by applying the r transformation. This is done without affecting the accuracy of the Soave equation in yielding vapor pressures. Furthermore, we have succeeded in applying the Soave equation to polar substances with substantially different Z_c values without employing any modifications such as those of Graboski and Daubert (1978) or resorting to correlation with experimental data as recommended by Soave (1979).

We were unsuccessful in an attempt made to obtain saturated liquid volumes by the same method.

The third approach for validating the r transformation consists of plotting v_{rg} and r_g against the Pitzer factor ω .

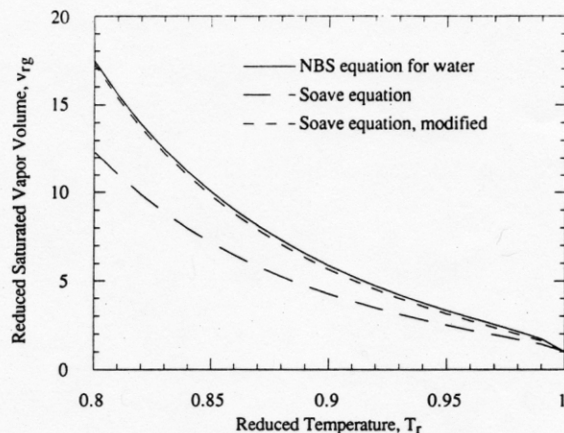


Figure 1. The r transformation applied to the Soave equation resulting in improved saturated vapor volumes for water.

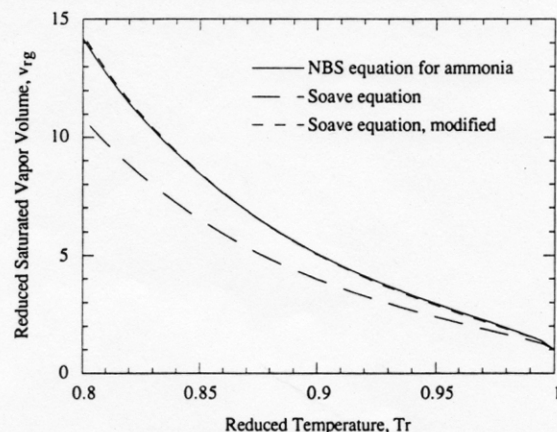


Figure 2. The r transformation applied to the Soave equation resulting in greatly improved saturated vapor volumes for ammonia.

The results of doing so are shown in Figures 3, 4, and 5 for $T_r = 0.7$, 0.8 , and 0.9 . The data were computed by use of the thermodynamics properties library developed by us at the University of Houston. This software is mostly based on the equations compiled in Reynolds (1979), supplemented with some more recent equations from Haar et al. (1984) and Younglove (1982). The values of ω were calculated from the substance-specific p - v - T equations directly and represent the best experimental values available in the literature. The saturation data were found by requiring the Gibbs-Maxwell equal-areas rule to be satisfied by the p - v - T equations.

It is clear from the figures that the r transformation improves the correlation between vapor volumes and ω considerably. At $T_r = 0.7$, the improvement is large. It is also remarkable that the data with negative ω , which are for the liquid metals and hydrogen, fall in nicely after the r transformation has been used. At $T_r = 0.9$, the scatter in the data is reduced but not eliminated. At $T_r = 0.8$ and 0.9 , the p - v - T equations of the liquid metals are not valid and no points can be shown in Figures 4 and 5 for them.

Discussion and Conclusions

We have derived and illustrated the application of the invariance principle. One can easily recognize that the principle may turn out to be quite important in developing new equations of state and correlating thermodynamic data. Yet, we have to leave some questions unanswered.

Above all, we must be careful to note that we do not claim that the $p_{r,\text{sat}}-T_r$ curve is independent of Z_c , although this remains a somewhat remote possibility for specific groups of substances. The weak point of the invariance principle is its unproved, and, possibly incorrect, premise that we can have different substances that obey the same

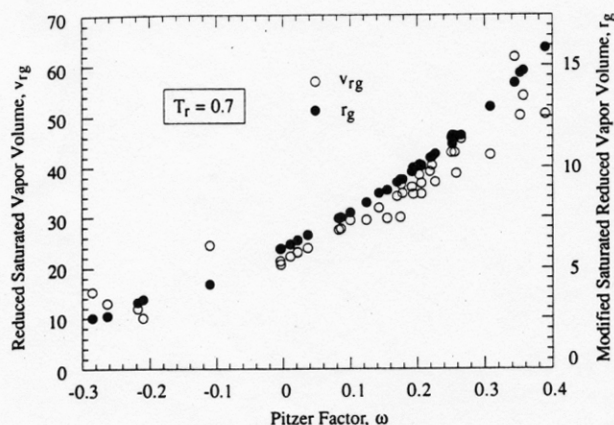


Figure 3. Saturated vapor volume data at $T_r = 0.7$, before and after applying the r transformation.

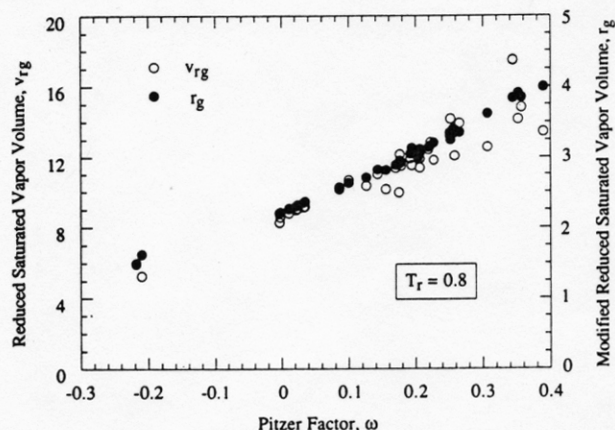


Figure 4. Saturated vapor volume data at $T_r = 0.8$, before and after applying the r transformation.

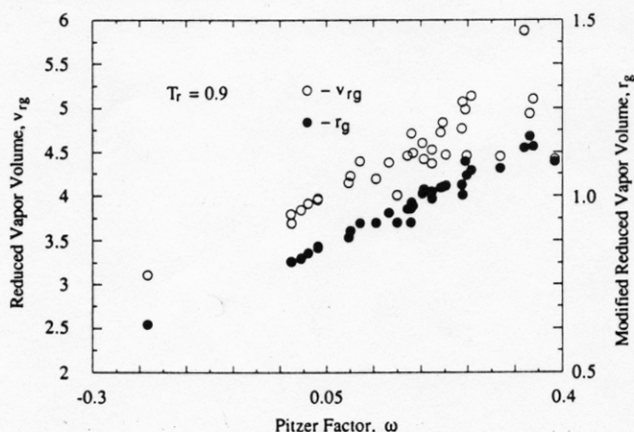


Figure 5. Saturated vapor volume data at $T_r = 0.9$, before and after applying the r transformation.

p_r - r - T_r equation. All that we can conclude at this juncture is that it may be unwise to seek a direct ordering of vapor pressure curves with respect to Z_c , and any observed ordering such as that of Lydersen et al. (1955) may be better explained in terms of other molecular parameters. Perhaps, the invariance principle simply serves to explain why the acentric factor furnishes better correlations of vapor pressure data than does Z_c , as we know well. In this context, we point out that the corresponding pairs of equations (5) and (7) have identical acentric factors and Riedel factors. This is, likewise, true of (8) and (9). Thus, the invariance principle may simply suggest that we should think of the van der Waals equation as representative of substances with Riedel parameter equal to 4, instead of thinking that this equation represents substances with $Z_c = 3/8$.

Another recommendation that emerges from this work is that both Z_c and ω should be used as parameters in developing equations of state, since we found that only by employing values of both were we able to obtain the results of Figures 1 and 2.

Application of the r transformation to improve the correlation of properties other than v_g with ω also appears to hold much promise, and is under investigation.

We have forced r to become zero at the critical point. To some extent, this is arbitrary and has the disadvantage of requiring an accurate value for v_c , which is not always available or, if available, may be less accurate than p_c and T_c . In some applications, it may be more useful to employ pseudoreduced volume v_r' or $(v_r' + \text{a constant})$ in place of r . Either of these choices leaves the invariance principle intact, but equations such as (12) would not be usable near the critical point. Yet another alternative without this drawback is to use instead of the experimental value of v_c a value that gives a best fit with whatever property is desired, and this has often been done.

Acknowledgment

We express our appreciation of the interest and constructive criticism of Dr. J. H. Lienhard. The support of the Electric Power Research Institute through Contract No. RP-8000-27 is also gratefully acknowledged.

Nomenclature

- p = pressure
- r = modified volume variable, see (1)
- R = ideal gas constant
- T = temperature
- v = volume
- Z = compressibility, pv/RT
- ω = Pitzer's acentric factor

Subscripts

- c = critical state
- f, g = saturated liquid and vapor, respectively
- r = reduced property = (property)/(property at critical point)
- sat = vapor-liquid equilibrium state

Superscript

- ' = pseudocritical value

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Received for review March 20, 1990

Revised manuscript received October 17, 1990

Accepted April 22, 1991