

Critical Appraisal of the Volume-Entropy-Energy Equation for Liquids

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Synopsis

The author's six articles on VSE equation of state for liquids are summarized in tabular form, and certain conclusions, applicable to the direction of research on plastics, are drawn.

INTRODUCTION

This article summarizes the author's research, extending over many years, on the thermodynamic properties of simple liquids.

Equilibrium thermodynamics gives equations, which must be exactly obeyed, relating certain of these properties, but it does not give the magnitudes of properties, such as the energy, volume, or entropy, characteristic of any particular substance at any temperature or pressure. Empirical "equations-of-state," with parameters deduced from experimental data, have often been used to represent the dependence of the volume on the temperature and pressure. Alternatively, one can relate the volume to the entropy and the energy. The author has shown that this relationship can be expressed by relatively simple equations, giving good agreement with experiment over large ranges of temperature—in some cases over the whole liquid range. Our volume-entropy-energy (VSE) equation can then be used to calculate all the other usual thermodynamic properties with high accuracy.

It was observed that all of the liquids examined have two modes of behavior, which we have termed the "regular" and "irregular" regions. Our VSE equation of state applies without correction to the regular region only. The characteristic dividing the two regions is the average separation of the molecules. In an homologous series, such as the *n*-alkanes, this distance has the same value for all members of the series.

The present article gives the general equations used, their theoretical and experimental justification, references to the article in which the calculated and experimental magnitudes of the properties of certain liquids have been published, and a summary of the standard percentage differences between the calculated and experimental properties.

THEORETICAL

According to Gibbs,¹ there are five quantities that determine the thermodynamic state of any system: temperature, pressure, volume per unit of mass, entropy per unit, and energy per unit. Any combination of three of these five state functions is called an equation of state. Thus, there are ten possible equations of state, but only one of these can be fundamental.² This is the one

combination involving the three attributes volume, entropy, and energy. Callen² states that only the fundamental equation (the VSE equation of state) can give "all conceivable thermodynamic quantities" by calculation.

The present study was undertaken for the purpose of gaining a better understanding of the nature and behavior of liquids and it seemed quite obvious that the VSE equation of state should be identified with this goal.

The equation that we have proposed and evaluated by comparison with measured thermodynamic quantities from the literature is

$$\epsilon = f_1 s^{f_2} + f_3 \quad (1)$$

where ϵ is the specific energy (J/g), s is the specific entropy (J/g deg), and f_1 , f_2 , and f_3 are volume-dependent functions to be defined later.

Equation (1) may be derived as follows:

First, consider that in a liquid, heat and energy are substantially interchangeable because the expansion volume Δv is so slight that the work of expansion $P\Delta v$ is practically negligible.

Second, it is known that in every liquid there is a region, to be defined later, over which heat capacity at constant volume is directly proportional to entropy. That is,

$$c_v = (\text{slope}) s \quad (2)$$

Therefore, one may write what we call the "fundamental differential equation of the liquid state" as follows:

$$\frac{ds}{s} \propto \frac{dT}{T} \quad (3)$$

By definition

$$c_v = \left(\frac{\partial \epsilon}{\partial T} \right)_v \quad (4)$$

and

$$(\partial \epsilon)_v = c_v (\partial T)_v \quad (4a)$$

However, in the regular region of a liquid, from eq. (2), one may substitute (slope) s for c_v , when

$$d\epsilon = (\text{slope}) s dT \quad (5)$$

Also,

$$d\epsilon = T ds \quad (6)$$

when

$$T ds = (\text{slope}) s dT \quad (7)$$

Therefore, from eq. (7) one may write

$$\frac{ds}{s} = (\text{slope}) \frac{dT}{T}$$

which is eq. (3).

Equation (1) follows directly from eq. (3), thus: rearrange eq. (3) to

$$\frac{dT}{T} = K_1 \frac{ds}{s} \quad (3a)$$

By integration,

$$\ln T = K_1 \ln s + \ln K_2 = \ln K_2 s^{K_1} \quad (8)$$

and

$$T = K_2 s^{K_1} \quad (8a)$$

Substituting in eq. (6),

$$d\epsilon = K_2 s^{K_1} ds \quad (9)$$

Integration of eq. (9) gives

$$\epsilon = K_2 K_1 s^{K_1-1} + K_3 \quad (10)$$

where $K_2 K_1 = f_1$, $K_1 - 1 = f_2$, $K_3 = f_3$. The volume-dependent functions are defined by their derivatives as

$$f_1 = c_2 \quad (11)$$

$$f_2 = 0 \quad (12)$$

$$f_3'' = u^p e^w \quad (13)$$

where p is a constant and $w = \phi u$, and

$$u^{-1} = v^{1/3} - v_0^{1/3} \quad (14)$$

where v is the specific volume, and v_0 is the specific "occupied" volume.³

The volume-dependent functions are now seen to be

$$f_1 = f_1(u) = c_1 + c_2 u \quad (15)$$

$$f_2 = f_2(u) = c_3 \quad (16)$$

$$f_3 = f_3(u) = \iint u^p e^w du \quad (17)$$

Since eq. (17) is difficult to integrate and introduces several additional parameters, and the exact value adds nothing to our understanding of the liquid state, we prefer to use the following approximation equation:

$$\ln f_3 = c_4 + c_5 \ln u \quad (18)$$

Equation (18) gives excellent agreement with measured values except in the neighborhood of T_{crit} , but its derivatives are not accurate. Should it ever be necessary to have the exact values of f_3 , these may be obtained readily from velocity of sound measurements.

The final form of our VSE equation of state for liquids is thus written

$$\epsilon = f_1 s^{c_3} + f_3 \quad (19)$$

This equation is valid only in the "region of regular performance." Corrections must be applied to f_1 , f_2 , and f_3 for calculations made in the "region of irregular performance."

The point that divides these two modes of behavior is determined by the average separation of the molecules and is characteristic of the substances. We call this distance $1/ud$, and the corresponding temperature we call T_{ud} . For members of homologous series, such as the n -alkanes, ud has the same value, although T_{ud} differs.

CALCULATION OF PARAMETERS c_1 , c_2 , c_3 , c_4 , AND c_5

There are many ways to calculate the parameters of eq. (1), but the simplest is from heat capacity measurements. Two points, taken in the region of regular performance, are sufficient to characterize all five of the above parameters, provided the quantities are known with high accuracy. Since heat capacity measurements are usually made over a range of temperatures, it is generally more convenient to use several points. In this way, one may be certain of T_{ud} , and use only points lying between T_{ud} and T_{crit} .

If two or more values of v , c_p , and δ , plus one value of ϵ are known accurately in the regular region, all other thermodynamic quantities pertaining to the system can be calculated from eq. (19), with high accuracy. This can be done because, in the regular region, v , c_p , and s , are substantially linear with T . Therefore, one can calculate α , c_v , s , and ϵ from

$$c_v = c_p - Tv\alpha\gamma \quad (20)$$

$$s = \int \frac{c_p}{T} dT \quad (21)$$

and

$$\epsilon = \int T ds \quad (22)$$

The integration constant of eq. (21) is zero, that of eq. (22) is determined from the experimental value of ϵ .

CALCULATION OF c_3

The slope of c_v vs. s is related to c_3 as follows:

$$c_3 = 1/\text{slope} + 1 \quad (23)$$

CALCULATION OF c_1 AND c_2

At constant volume,

$$T = \left(\frac{\partial \epsilon}{\partial s} \right)_v = f_1 c_3 s^{c_3-1} \quad (24)$$

and

$$f_1 = T/c_3 s^{c_3-1} \quad (24')$$

However, from eq. (13),

$$f_1 = c_1 + c_2 u \quad (15)$$

where u is defined by eq. (14). Thus, with two points, c_1 and c_2 are determined.

CALCULATION OF c_4 AND c_5

From eq. (19), one may write

$$f_3 = \epsilon - f_1 s^{c_3} \quad (19a)$$

The values of c_4 and c_5 are obtained from eqs. (14) and (18).

CALCULATION OF THERMODYNAMIC QUANTITIES

All thermodynamic quantities can be expressed as derivatives of energy. Thus, from eq. (19), the following equations may be derived (only those thermodynamic quantities are listed here that have been measured by others and published; therefore, this list does not include all possible thermodynamic quantities):

$$\ln s = \frac{\ln T - \ln f_1 - \ln c_3}{c_3 - 1} \quad (25)$$

$$T = \left(\frac{\partial \epsilon}{\partial s} \right)_v = f_1 c_3 s^{c_3 - 1} \quad (26)$$

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p = \frac{1}{F v f_3'' - T c_v (c_2/f_1)^2} \quad (27)$$

$$-F = \frac{du}{dv} \quad (28)$$

$$F = (u/v^{1/3})^2 \div 3 \quad (29)$$

$$\beta_T = \frac{1}{v} \left(\frac{\partial v}{\partial p/10} \right)_T = \frac{1}{F v f_3'' - T c_v (c_2/f_1)^2} \quad (30)$$

$$\gamma = \frac{\alpha}{\beta_T} = \left(\frac{\partial p/10}{\partial T} \right)_v = \left(\frac{\partial s}{\partial v} \right)_T = F c_v (c_2/f_1) \quad (31)$$

$$c_v = \left(\frac{\partial \epsilon}{\partial T} \right)_v = \frac{s}{c_3 - 1} \quad (32)$$

$$c_p = \left(\frac{\partial \epsilon}{\partial T} \right)_p = c_p + T v \alpha \gamma \quad (33)$$

$$\frac{p}{10} = - \left(\frac{\partial \epsilon}{\partial v} \right)_s = F \left(\frac{\partial s}{\partial u} \right)_s \quad (34)$$

$$\frac{p_i}{10} = \left(\frac{\partial \epsilon}{\partial v} \right)_T = -F \left(\frac{\partial \epsilon}{\partial u} \right)_T \quad (35)$$

Note: Values of α and β from eqs. (27) and (30) were calculated for only one substance, *n*-heptane, since accurate calculation of derivatives of f_3 can be made only from eq. (17) which involves additional parameters.

VERIFICATION OF THE EQUATION

Calculation of various thermodynamic quantities pertaining to the following liquids have been made and compared with corresponding measured quantities. All of these results are summarized in Table I. The standard percentage error (SPE) (assuming that the measured quantities were correct in each case) of the 1034 calculations made was less than $\frac{1}{3}$ of 1%.

TABLE I
Summary of Results VSE Equation of State for Liquids, Parts I-VI

Compound	T		$P = 1$		ϵ	
	Range (K)	SPE	Range (K)	SPE	Range (K)	SPE
<i>n</i> -Heptane	273.16-473.16	39 ^b 0.0407	273.16-473.16	39 0.0457	273.16-473.16	273.16-473.16
<i>n</i> -Pentane	160.00-290.00	14 0.6161	160.00-290.00	14 0.3460	143.47-290.00	143.47-290.00
<i>n</i> -Hexane	177.83-341.50	15 0.6233	177.83-341.50	15 0.3444	177.83-300.00	177.83-300.00
<i>n</i> -Heptane	182.56-480.00	37 0.2886	182.56-480.00	37 0.1749	182.56-470.00	182.56-470.00
<i>n</i> -Nonane	219.65-320.00	12 0.5881	219.65-320.00	12 0.3550	219.65-320.00	219.65-320.00
<i>n</i> -Heptadecane	295.14-390.00	11 0.2588	295.14-390.00	11 0.1674	295.14-390.00	295.14-390.00
Benzene	273.16-403.16	15 0.0301	273.16-403.16	15 0.0169	273.16-403.16	273.16-403.16
Mercury	273.16-1273.16	11 0.9499	273.16-1273.16	11 0.2463	373.16-1073.16	373.16-1073.16
Water	393.16-563.16	18 1.4322	393.16-563.16	18 0.7729	393.16-563.16	393.16-563.16
<i>n</i> -Heptane			280.00 ^a -540.16	13 0.0604		
Sodium	1473.16-1773.16	4 0.0633	1473.16-1773.16	4 0.0239	1473.16-1773.16	1473.16-1773.16
Poly(tetrafluoroethylene)	600.00-725.00	6 0.0132	600.00-725.00	6 0	600.00-725.00	600.00-725.00
Polymethylene ^e	500.00-650.00	4 0.0013	500.00-650.00	4 —	500.00-650.00	500.00-650.00

SPE	α		c_p		β_T		Range (K)
	Range (K)	SPE	Range (K)	SPE	Range (K)	SPE	
39	297.55-450.00	32 0.6395	297.55-450.00	32 0.3121	297.55-371.59	3 1.4595	297.35-371.59
0.0690					Part II (T_{mp}^d to max temperature of measurement)		
16			160.00-290.00	14			
0.2160				0.5603			
14			177.83-341.90	15			
0.2114				0.3744			
36			182.56-390.00	28			
0.0489				0.2975			
12			219.65-320.00	12			
0.4681				0.3701			
11			295.14-390.00	11			
0.1288				0.2421			
15			273.16-353.86	10			
0.1084				0.1094			
8			234.28-1273.16	12			
0.5394				0.4926			
18			323.16-553.16	24			
0.6383				0.2729			
					Part III (Regular region from $U_d = 10$ to T_{crit} for <i>n</i> -heptane)		
			280.00-540.17	13			
				0.2466			
4					Part IV (Regular region of liquid sodium)		
0.0850							
6			600.00-725.00	6			
0.0119				0.4149			
					Part V (Regular region of a liquid polymer)		
4			500.00-650.00	4			
—					Part VI (Regular region of a hypothetical liquid polymer)		500.00-650.0

TABLE I (Continued from previous page)

<i>E</i>	<i>P_i</i>		<i>T</i>		<i>s</i>	
	Range (K)	SPE	P Range (bar)	T range (K)		P range (bar)
14	297.55-371.59	1.1262	14	303.16-540.17	24	303.16-540.16
0.485	50-500 ^c	0.1798	50-500 ^c		50-500 ^c	

<i>24</i>	<i>c</i>		<i>c₀</i>		<i>γ</i>	
	P range (bar)	T range (K)	Range (K)	SPE		Range (K)
0.967	50-500 ^c	303.16-540.17	24	0.1965	14	160.00-290.00
					0.4284	15
					0.2929	28
					0.2310	12
					0.2992	11
					0.2052	10
					0.0771	12
					0.3927	24
					0.1935	13
					0.3104	4
					0.5282	4
					—	—

The liquids studied were 5 *n*-alkanes,⁴ benzene,⁴ mercury,⁴ water,⁴ sodium,⁵ poly(tetrafluoroethylene),⁶ and polymethylene of 75,000 molecular weight.⁷

Three sets of calculations were made on *n*-heptane. The first⁸ involved the exact equation for f_3 , but carried some of the calculations only as high as γ obtained from literature values of β_T , which was 372 K. The second set of calculations⁴ carried the results from T_{mp} to the highest experimental value of γ obtained from internal pressure data, which was 390 K. The third set of calculations⁹ were carried from T_{ud} to T_{crit} , using values of γ obtained from very accurate PVT data,¹⁰ which went to 540 K.

^a The regular region (see below) for *n*-heptane starts at $ud = 10$ (280 K).

^b The number of points taken is listed just above the SPE values.

^c At 303.16 K, the highest pressure listed is 300 bar. All others are listed up to 500 bar. This is because the value for u at 303.16 K and 300 bar is about $ud = 10$.

^d Values of T_{mp} and ud for the liquids studied in this series are

Compound	T_{mp} (K)	ud	(corresponding T_{ud}) (K)
<i>n</i> -Pentane	143.99	10	250
<i>n</i> -Hexane	177.81	10	270
<i>n</i> -Heptane	182.55	10	280
<i>n</i> -Nonane	219.64	10	310
<i>n</i> -Heptadecane	295.14	10	360
Benzene	278.69	12.31	323
Mercury	234.29	35.73	1073
Water	273.16	9.72	533
Sodium	370.66	4.2	1200
Poly (tetrafluoroethylene)	600.16	2.09	625
Polymethylene	407.21	10	475

The irregular region is from T_{mp} to T_{ud} , and the regular region is from T_{ud} to T_{crit} . Most of the liquids examined in ref. 4 are studied from T_{mp} to their highest temperature of measurement. Equations requiring additional parameters are given in ref. 4 for correcting the volume-dependent functions in the irregular region. In the regular region, the volume-dependent functions f_1 and f_2 are very simply defined and require only three parameters. The potential energy function f_3 is more complicated, but can be closely approximated by a simple equation requiring only two parameters. In ref. 8, the exact equation for f_3 was used. In all other calculations in this series, the approximation equation is used for simplicity. Since several additional parameters are required for correcting f_1 , f_2 , and f_3 in the irregular region, and such empirical calculations add nothing to our understanding of the liquid state, all calculations in this series of papers refer to liquids in the *regular* region except those in ref. 4. The behavior of every liquid becomes irregular when $u > ud$. The value of u increases as the temperature is lowered or as the external pressure is raised or both. In all cases, the volume-dependent functions f_1 , f_2 , and f_3 can be corrected empirically in the manner described in ref. 4.

^e Although a hypothetical polymethylene of MW = 75,000 is assumed for the calculations of ref. 7, so that no actual thermodynamic measurements are available in this case, nevertheless, temperature can be calculated from

$$T_{calc} = f_1 c_3^8 c_3^{-1} \quad (3)$$

The SPE₄ in T_{calc} , over the range 500–650 K, based on $\Delta T = T_{calc} - T$, is 0.0013%, which is listed, although the calculations are not shown in the article. The grand average SPE for all 1034 points calculated in this series of six articles is 0.32%.

CONCLUSIONS

The lessons that have been learned from this study should prove useful in directing further research on plastics made of chain polymers. These include the following:

(1) All liquids have a region of regular performance that is defined by the average distance of separation of the molecules. If this average distance is represented by $1/u$, given by eq. (14), then the regular regions lie between values of u from 0 to u_d .

In the irregular region the simple equations for f_1 , f_2 , and f_3 fail, so a correction must be applied. The form of this correction is the same for all liquids examined [eqs. (6)–(8) of ref. 4], but the agreement in the irregular region of calculated with experimental values is not as good with highly polar liquids (such as water and mercury) as it is with the other liquids studied by us.

This suggests that, in the neighborhood of the melting point, certain cohesive forces come into play that are greater with highly polar liquids than with nonpolar liquids.

(2) In the regular region, the fractional change in entropy is directly proportional to the fractional change in temperature just as it is in gases. The only difference is that in gases, one deals with entropy at constant volume, whereas with liquids one uses saturation–pressure values. The proportionality constants are not the same for both phases.

(3) A van der Waals-type PVT equation of state applies to liquid polymers in the regular region.

(4) Volume, entropy, and energy of polymers are all substantially linear with absolute temperature in the regular region, as is the case with gases.

(5) The point at which deviation from regular behavior begins is clearly evident visually in polyethylene. This suggests that u_d corresponds to the temperature at which all crystallites have melted. In liquids of lower molecular weight, these crystallites are not visible, but there is no reason to suppose that they do not exist and become more dense as the freezing temperature of the liquid is approached. This phenomenon could also contribute to the failure of uncorrected calculated thermophysical quantities to correspond to the observed values in the irregular region.

Table I lists all thermodynamic quantities that have been calculated from our equation of state in this series of articles that have been compared with measured values obtained from the literature. The ranges of temperature and of pressure over which the comparisons are made are also listed as well as the SPE. This quantity is defined as follows:

$$[\% \text{ error}] = 100 \times \frac{\Delta y}{y_{\text{obs}}} = \frac{100 (y_{\text{obs}} - y_{\text{calc}})}{y_{\text{obs}}} \quad (36)$$

SPE_n = standard percentage error for n points

$$= \{\sum [\%]^2\}^{1/2}/2 = \{\sum [100(y_{\text{obs}} - y_{\text{calc}})/y_{\text{obs}}]^2\}^{1/2}/n \quad (36a)$$

where y_{calc} is the calculated value, y_{obs} is the observed value, and n is the number of points. The grand average SPE for all 1034 points is 0.32%.

As soon as the calculations on polymeric systems^{6,7} were completed, a possible improvement in the manufacture and application of paint was envisioned that

would have been very unlikely to have been discovered had this scientific study not been made. If patents can be obtained and the idea can be successfully adapted to commercial practice, it should afford great savings in certain areas of the paint industry.

Therefore, it appears that one of the goals sought in undertaking this research program may be realized.

The author has been given a great deal of help in pursuing the VSE equation of state program over the past 20 years by his associates in the Arcadia Institute. The assistance of S. S. Kurtz, Jr., M. L. Huggins, and E. B. Bagley is acknowledged with thanks. Likewise, the officers and trustees of the corporation have contributed liberally of their time and advice. Of these, L. D. Price, General Counsel, and R. A. Pew, Chairman of the Executive Committee, deserve particular mention.

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Received October 8, 1979

Accepted February 19, 1980