# van der Waals Equation of State Revisited: Importance of the Dispersion Correction

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Ⓢ *Supporting Information*

ABSTRACT: One of the most basic equations of state describing nonideal gases and liquids is the van der Waals equation of state, and as a consequence, it is generally taught in most first year undergraduate chemistry courses. In this work, we show that the constants a and b in the van der Waals equation of state are linearly proportional to the polarizability volume of the molecules in a gas or liquid. Using this information, a new

$$p(V - 8\pi N_A\alpha) = RTe^{\left[-\frac{5\pi}{128}\frac{IN_A\alpha}{RTV}\right]} + \frac{5\pi^2}{16}\frac{IN_A^2\alpha^2}{V^2}$$

thermodynamic one-parameter equation of state is derived that contains experimentally measurable variables and physics constants only. This is the first equation of state apart from the Ideal Gas Law that contains experimentally measurable variables and physics constants only, and as such, it may be a very useful and practical equation for the description of dilute gases and liquids. The modified van der Waals equation of state describes pV as the sum of repulsive and attractive intermolecular interaction energies that are represented by an exponential repulsion function between the electron clouds of the molecules and a London dispersion component, respectively. The newly derived equation of state is tested against experimental data for several gas and liquid examples, and the agreement is satisfactory. The description of the equation of state as a one-parameter function also has implications on other thermodynamic functions, such as critical parameters, virial coefficients, and isothermal compressibilities. Using our modified van der Waals equation of state, we show that all of these properties are a function of the molecular polarizability volume. Correlations of experimental data confirm the derived proportionalities.
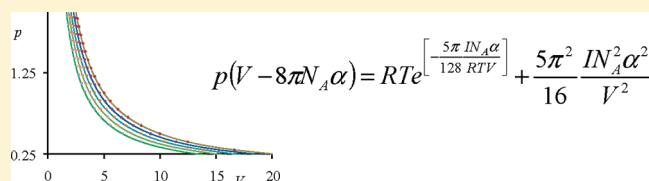
■ INTRODUCTION

At moderate temperature (T) and low pressure (p), gases are generally well-described by the Ideal Gas Law equation; however, significant deviations occur at higher pressure. For a long time, appropriate equations of state to describe real gases have been sought, but so far, none is universal. van der Waals[1] was one of the first to develop an equation of state (eq 1) that corrects the Ideal Gas Law for intermolecular interactions. Thus, the volume (V) of the gas was corrected for by the occupied volume of the molecules in the gas through the inclusion of a factor b reflecting the repulsive intermolecular forces, and a correction term to the pressure given by the coefficient a was introduced to account for the attractive intermolecular forces.

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT \tag{1}$$

Currently, the van der Waals parameters a and b do not correspond to physically measurable properties. In this work, we aim to provide suggestions for alternative coefficients of a and b that are based on fundamental physical constants and/or experimentally measurable coefficients.

In principle, the van der Waals parameter b corresponds to the sum of the volumes of the individual molecules in the system. Quantum mechanically, this is somewhat difficult to define because molecular volume is dependent on a probability function

of the electron cloud. However, using assigned probability functions for the molecular volume, this function was estimated from quantum chemical calculations, and it was found to correlate linearly with the polarizability volume (α) of the chemical system, which incidentally also has units of volume.[2] Therefore, polarizability volume seems to be a measure of the volume of a molecule and hence may also correlate with the above-mentioned van der Waals parameter b. To test this, we investigated this proportionality, which we will describe in the present work.

Atomic polarizability not only represents molecular volume but is also a measure of the electronegativity of the atoms due to its description of the electron density of the electron cloud.[3] In the past, we showed that reaction enthalpies correlate linearly with the change in polarizability volume during a reaction.[4] Furthermore, this was recently extended to correlations of barrier heights with the change in polarizability volume.[5] Therefore, these correlations seem to imply a proportionality of internal energy and polarizability volume of molecules. To gain further insight into thermodynamic relationships involving polarizability volumes, we investigated a direct correlation of the polarizability volume with van der Waals parameters a and b, and the results are presented in this work.

Table 1. van der Waals Parameters a and b, Polarizability Volume (α), and Ionization Energy (IE) of Selected Molecules Used in This Study^a

		a [bar L^2 mol^{-1}]	b [L mol^{-1}]	α [10^{-24} cm^3]	IE [eV]
BCl$_3$	boron trichloride	15.6	0.1222	9.38	11.6
BF$_3$	boron trifluoride	3.98	0.05443	3.31	15.56
BrH	hydrogen bromide	4.5	0.04415	3.32	11.66
Br$_2$	bromine	9.75	0.0591	7.02	10.515
ClH	hydrogen chloride	3.7	0.04061	2.77	12.747
Cl$_2$	chlorine	6.343	0.05422	4.61	11.48
FH	hydrogen fluoride	9.565	0.0739	2.46	16.044
F$_2$	fluorine	1.171	0.02896	1.38	15.697
F$_3$N	nitrogen trifluoride	3.58	0.05453	3.62	13
F$_4$Si	silicon tetrafluoride	5.259	0.07236	5.45	15.7
F$_6$S	sulfur fluoride	7.857	0.08786	6.54	15.33
HI	hydrogen iodide	6.309	0.05303	5.44	10.386
H$_2$O	water	5.537	0.03049	1.45	12.612
H$_2$S	hydrogen sulfide	4.544	0.04339	3.78	10.453
H$_3$N	ammonia	4.225	0.03713	2.81	10.16
H$_3$P	phosphine	4.696	0.05157	4.84	9.869
H$_4$Si	silane	4.38	0.0579	5.44	11.65
NO	nitric oxide	1.46	0.0289	1.7	9.26436
NO$_2$	nitrogen dioxide	5.36	0.0443	3.02	9.75
N$_2$	nitrogen	1.37	0.0387	1.7403	15.5808
N$_2$O	nitrous oxide	3.852	0.04435	3.03	12.886
O$_2$	oxygen	1.382	0.03186	1.5812	12.071
O$_2$S	sulfur dioxide	6.865	0.05679	4.28	12.32
O$_3$	ozone	3.57	0.0487	3.21	12.43
CClF$_3$	chlorotrifluoromethane	6.873	0.0811	5.72	12.39
CCl$_3$F	trichlorofluoromethane	14.68	0.1111	9.47	11.77
CCl$_4$	tetrachloromethane	20.01	0.1281	10.5	11.47
CF$_4$	tetrafluoromethane	4.04	0.06325	3.838	
CO	carbon monoxide	1.472	0.03948	1.95	14.0139
CO$_2$	carbon dioxide	3.658	0.04286	2.911	13.773
CHCl$_3$	trichloromethane	15.34	0.1019	8.23	11.37
CHF$_3$	trifluoromethane	5.378	0.06403	3.57	13.86
CHN	hydrogen cyanide	11.29	0.08806	2.59	13.6
CH$_2$Cl$_2$	dichloromethane	12.44	0.08689	6.48	11.32
CH$_3$Cl	chloromethane	7.566	0.06477	4.72	11.22
CH$_3$F	fluoromethane	5.009	0.05617	2.97	12.47
CH$_3$NO$_2$	nitromethane	17.18	0.1041	7.37	11.02
CH$_4$	methane	2.3	0.04301	2.593	12.51
CH$_4$O	methanol	9.472	0.06584	3.32	10.85
CH$_5$N	methylamine	7.106	0.05879	4.7	8.97
C$_2$H$_2$	acetylene	4.516	0.0522	3.93	11.4
C$_2$H$_2$F$_2$	1,1-difluoroethylene	6	0.07058	5.01	10.29
C$_2$H$_3$Cl$_3$	1,1,1-trichloroethane	20.15	0.1317	10.7	11
C$_2$H$_3$F$_3$	1,1,1-trifluoroethane	9.302	0.09572	4.4	12.9
C$_2$H$_3$N	acetonitrile	17.89	0.1169	4.48	12.194
C$_2$H$_4$	ethylene	4.612	0.05821	4.252	10.507
C$_2$H$_4$Cl$_2$	1,1-dichloroethane	15.73	0.1072	8.64	11.06
C$_2$H$_4$Cl$_2$	1,2-dichloroethane	17	0.108	8	11.04
C$_2$H$_4$O	ethylene oxide	8.922	0.06779	4.43	10.566
C$_2$H$_4$O$_2$	acetic acid	17.71	0.1065	5.1	10.66
C$_2$H$_4$O$_2$	methyl formate	11.54	0.08442	5.05	10.815
C$_2$H$_5$Br	bromoethane	11.89	0.08406	7.28	10.28
C$_2$H$_5$Cl	chloroethane	11.7	0.09	6.4	10.97

Table 1. Continued

		a [bar L^2 mol^{-1}]	b [L mol^{-1}]	α [10^{-24} cm^3]	IE [eV]
C_2H_5F	fluoroethane	8.17	0.07758	4.96	11.6
C_2H_6	ethane	5.57	0.06499	4.47	11.52
C_2H_6O	dimethyl ether	8.69	0.07742	5.84	10.025
C_2H_6O	ethanol	12.56	0.0871	5.41	10.47
C_2H_6S	ethanethiol	13.23	0.09447	7.41	9.285
C_2H_7N	dimethylamine	10.44	0.0851	6.37	8.23
C_2H_7N	ethylamine	10.79	0.08433	7.1	8.86
C_3H_5N	propanenitrile	21.57	0.1369	6.7	11.84
C_3H_6	propene	8.438	0.08242	6.26	9.73
C_3H_6	cyclopropane	8.293	0.0742	5.66	9.86
C_3H_6O	acetone	16.02	0.1124	6.33	9.705
C_3H_6O	propanal	14.08	0.09947	6.5	9.953
$C_3H_6O_2$	ethyl formate	15.91	0.1115	8.01	10.61
$C_3H_6O_2$	methyl acetate	15.75	0.1108	6.94	10.27
$C_3H_6O_2$	propanoic acid	23.49	0.1386	6.9	10.525
C_3H_7Cl	1-chloropropane	16.11	0.1141	10	10.82
C_3H_8	propane	9.385	0.09044	6.37	10.95
C_3H_8O	1-propanol	16.26	0.108	6.74	10.22
C_3H_8O	2-propanol	15.82	0.1109	7.61	10.12
C_3H_8O	ethyl methyl ether	12.7	0.1034	7.93	9.72
C_3H_9N	propylamine	15.26	0.1094	7.7	8.78
C_3H_9N	trimethylamine	13.37	0.1101	8.15	7.82
C_4H_4S	thiophene	17.21	0.1058	9.67	8.87
C_4H_6	1,3-butadiene	12.17	0.102	8.64	9.069
$C_4H_6O_3$	acetic anhydride	26.8	0.157	8.9	10
C_4H_7N	butanenitrile	25.76	0.1568	8.4	11.2
C_4H_8	1-butene	12.76	0.1084	7.97	9.58
C_4H_8O	2-butanone	19.97	0.1326	8.13	9.51
$C_4H_8O_2$	1,4-dioxane	19.29	0.1171	10	9.19
$C_4H_8O_2$	ethyl acetate	20.57	0.1401	9.7	10.01
$C_4H_8O_2$	methyl propanoate	20.51	0.1377	8.97	10.15
$C_4H_8O_2$	butanoic acid	28.18	0.1609	8.38	10.17
C_4H_{10}	butane	13.93	0.1168	8.2	10.53
C_4H_{10}	isobutane	13.36	0.1168	8.14	10.57
$C_4H_{10}O$	1-butanol	20.9	0.1323	8.88	10.06
$C_4H_{10}O$	2-methyl-1-propanol	20.35	0.1324	8.92	10.12
$C_4H_{10}O$	diethyl ether	17.46	0.1333	10.2	9.51
$C_4H_{10}S$	diethyl sulfide	22.85	0.1462	10.8	8.43
$C_4H_{11}N$	butylamine	19.41	0.1301	13.5	8.71
$C_4H_{11}N$	diethylamine	19.4	0.1383	9.61	8.01
C_5H_5N	pyridine	19.77	0.1137	9.18	9.25
C_5H_{10}	1-pentene	17.86	0.137	9.65	9.52
C_5H_{10}	cyclopentane	16.94	0.118	9.15	10.51
$C_5H_{10}O_2$	ethyl propanoate	25.86	0.1688	10.41	10
$C_5H_{10}O_2$	methyl butanoate	25.83	0.1661	10.41	10.07
C_5H_{12}	pentane	19.13	0.1451	9.99	10.35
C_5H_{12}	neopentane	17.17	0.141	10.2	10.21
C_6H_5Br	bromobenzene	28.96	0.1541	13.62	8.98
C_6H_5Cl	chlorobenzene	25.8	0.1454	12.3	9.06
C_6H_5F	fluorobenzene	20.1	0.1279	10.3	9.2
C_6H_5I	iodobenzene	33.54	0.1658	15.5	8.685
C_6H_6	benzene	18.82	0.1193	10	9.2459
C_6H_6O	phenol	22.93	0.1177	9.94	8.47
C_6H_7N	aniline	29.14	0.1486	12.1	7.72

Table 1. Continued

		a [bar L^2 mol^{-1}]	b [L mol^{-1}]	α [10^{-24} cm^3]	IE [eV]
C_6H_{12}	cyclohexane	21.95	0.1413	10.87	9.86
$C_6H_{12}O$	cyclohexanol	28.93	0.1586	11.56	9.75
C_6H_{14}	hexane	24.97	0.1753	11.9	10.13
$C_6H_{15}N$	triethylamine	27.59	0.1836	13.1	7.5
$C_6H_{15}N$	dipropylamine	24.82	0.1591	13.29	7.84
C_7H_5N	benzonitrile	33.89	0.1727	12.5	9.62
C_7H_8	toluene	24.89	0.1499	11.8	8.82
C_7H_{16}	heptane	30.89	0.2038	13.7	9.92
C_8H_{10}	ethylbenzene	30.86	0.1782	14.2	8.77
C_8H_{10}	o-xylene	31.06	0.1756	14.1	8.56
C_8H_{10}	m-xylene	31.41	0.1814	14.2	8.56
C_8H_{10}	p-xylene	31.54	0.1824	13.7	8.44
$C_8H_{10}O$	phenetole	35.7	0.1966	14.9	8.13
$C_8H_{11}N$	N,N-dimethylaniline	37.92	0.1967	16.2	7.12
C_8H_{18}	octane	37.86	0.2372	15.9	9.82
C_9H_7N	quinoline	36.7	0.1672	15.7	8.62
C_9H_{12}	propylbenzene	37.14	0.2073	16	8.72
C_9H_{12}	mesitylene	37.87	0.2118	15.5	8.41
C_9H_{20}	nonane	45.11	0.2702	17.4	9.72
$C_{10}H_8$	naphthalene	40.32	0.192	16.5	8.14
$C_{10}H_{14}$	butylbenzene	44.07	0.2378	17.2	8.69
$C_{10}H_{22}$	decane	52.88	0.3051	19.1	9.65
$C_{11}H_{24}$	undecane	60.88	0.3396	21	9.56
$C_{12}H_{26}$	dodecane	69.14	0.3741	22.8	

[a] Data obtained from ref.[6]
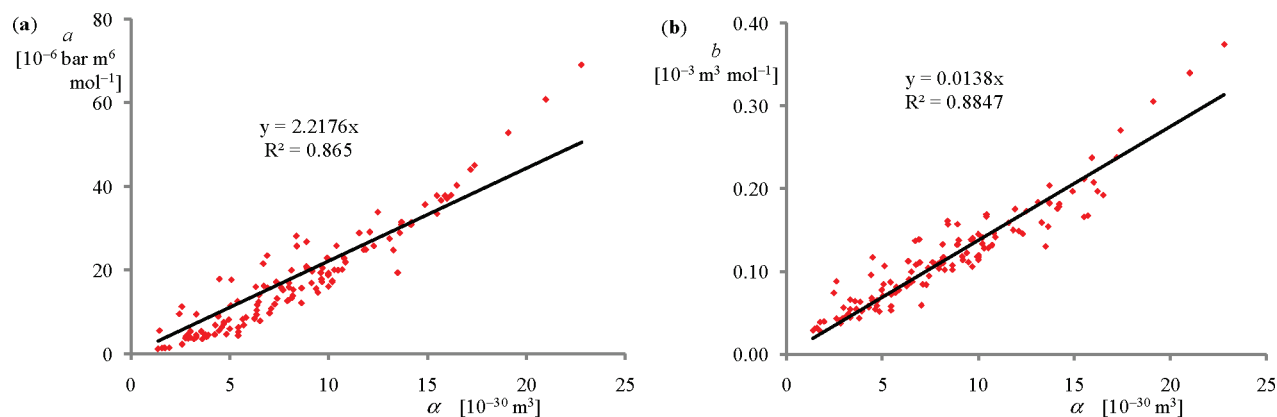
Figure 1. Correlation between the polarizability volume and van der Waals parameters a and b. Data for 130 molecules taken from ref 6.

■ RESULTS

In order to investigate the physical properties of the van der Waals coefficients a and b and their correlation with the polarizability volume (α), we selected a large data set of available systems with known values of a, b, and α from the literature.[6] Table 1 summarizes the literature data of the 130 molecules used in this study. The set of molecules includes apolar molecules, such as linear and branched alkanes and aromatic residues (benzene, toluene, xylene, etc.), as well as polar molecules including water, alcohols, amines, carboxylic acids, ethers, and haloalkanes. As such, this broad range of molecules with different physicochemical properties will enable us to investigate the intrinsic properties of the van der Waals parameters a and b.

Figure 1 displays the correlation between the polarizability volume and van der Waals parameters a and b as taken from this set of data representing 130 organic molecules. As follows from Figure 1, a satisfactory linear correlation is found with correlation coefficients of $R^2 = 0.87$ and 0.88 for the trend of polarizability against a and b, respectively. Inclusion of an intercept in the curve fitting, that is, fitting to the equation $y = cx + d$ rather than $y = cx$, gives only minor improvement of the correlation coefficient; therefore, Figure 1 implies a direct correlation between the two van der Waals parameters and the polarizability volume.

Note that for analogous compounds, for example, linear alkanes, linear alcohols, or amines, even better correlations are found (Supporting Information Figures S1–S3). For instance,

the fit through a series of linear alkanes ranging from methane to n-dodecane gives an $R^2 = 0.991$ for the fit between the polarizability volume and van der Waals parameter b. The reason the correlation coefficient for the complete set of data is only $R^2 = 0.88$ is probably because the tabulated data represents measurements at different temperatures, pressures, experimental conditions, experimental techniques, and so forth. Moreover, it is known that the polarizability volume contains a small temperature dependence.[7] Nevertheless, the correlation is satisfactory and implies a linear relationship between the polarizability volume and not only van der Waals parameter b but also parameter a. The former correlation was expected based on earlier studies that connected the polarizability with molecular or atomic size.[2] The linear correlation found between van der Waals parameter a and the polarizability volume seems surprising at first sight, but below, we will explain that it actually directly follows from the London dispersion equation and leads to a function resembling the Buckingham (exponent − 6) function.

■ DISCUSSION

The data in Figure 1 demonstrates a linear relationship between the polarizability volume and both van der Waals parameters a and b. Thus, Figure 1 shows that $a = k_1\alpha$ and $b = k_2\alpha$, with k_1 and k_2 as some physical constants. This implies that the van der Waals equation of state can be simplified from a two-parameter equation of state into a one-parameter equation of state with polarizability as the single dependent parameter. Substitution of $a = k_1\alpha$ and $b = k_2\alpha$ into the van der Waals equation of state gives the following

$$\left(p + \frac{k_1\alpha}{V^2}\right)(V - k_2\alpha) = RT \tag{2}$$

or rewritten in units of energy

$$p(V - k_2\alpha) = RT - \frac{k_1\alpha}{V} + \frac{k_1 k_2 \alpha^2}{V^2} \tag{3}$$

The last term in eq 3 resembles the London dispersion energy (E_{London}) expression for induced dipole−induced dipole interactions (eq 4), with I being the ionization potential of the molecules and r_{ij} the distance between the induced dipole moments of molecules i and j.[8]

$$E_{London} = \frac{3I\alpha^2}{4r_{ij}^6} \tag{4}$$

Technically, we should set up a Schrödinger equation and solve the energetic solutions here, but for the sake of this work and its comparison with the van der Waals equation of state, we will try to rewrite it into a van der Waals-type equation instead. As a first approximation, we take the ensemble average of the London dispersion equation, $\langle E_{London}\rangle$, which is equal to $(3I\alpha^2/4)\langle 1/r^6\rangle$. Mathematically, the average distance between two points within the unit sphere can be found from the triple integral over the distances of these points to the origin of the sphere and the angle between those two lines. Solving this triple integral gives $\langle r_{12}\rangle = (36/35)R$, with R being the radius of the sphere.[9] However, we do not have $\langle r_{ij}\rangle$ in the London dispersion equation but $\langle(1/r_{ij}^6)\rangle$. The latter is not solvable using this triple integral; therefore, we will abbreviate it, for the time being, as $(1/\langle r_{ij}^6\rangle)$. Using a similar triple integral as the one used to derive $\langle r_{12}\rangle = (36/35)R$, we can show that $\langle r_{ij}^6\rangle = (64/15)R^6$, which we insert into the London dispersion equation to get an

approximate dispersion correction to the Ideal Gas Law. Substitution of this radius with a volume ($V = (4/3)\pi R^3$) then gives $\langle r_{ij}^6\rangle = (64/15)(3V/4\pi)^2$, which transforms the London dispersion equation into an expression proportional to α^2/V^2 (eq 5), similar to the last contribution in eq 3. If the last term in eq 3 indeed represents the dispersion correction to the Ideal Gas Law, then the product of the constants k_1 and k_2 can be obtained from combination of the last term in eq 3 with eq 5 to give eq 6.

$$E_{London} = \frac{5\pi^2}{16}\frac{I\alpha^2}{V^2} \tag{5}$$

$$k_1 k_2 = \frac{5\pi^2}{16}IN_A^2 \tag{6}$$

The slope k_2 obtained from Figure 1b is dimensionless and is within the error of the correlation coefficient equal to $8\pi N_A$, where we prefer to use factors of π because we are dealing with volumes here. Inserting this value into eq 6 then gives $k_1 = (5\pi/128)IN_A$. Using the equation $k_2 = 8\pi N_A$, we predict $k_2 = 0.0151 \times 10^{-3}$ m^3 mol^{-1} from physics constants only, which is in good qualitative agreement with the slope obtained in Figure 1. In order to validate this value for k_2, we subsequently use $b = 8\pi N_A\alpha$ to estimate the polarizability volumes. Estimated polarizability volumes from $b = k_2\alpha$ for the set of 130 molecules in Table 1 are, on average, within 3% of those reported in the literature.

Replacing k_1 and k_2 in eq 3 by the physical constants that we just derived gives eq 7, which is the one-parameter modified van der Waals equation of state.

$$p(V - 8\pi N_A\alpha) = RT - \frac{5\pi}{128}\frac{IN_A\alpha}{V} + \frac{5\pi^2}{16}\frac{IN_A^2\alpha^2}{V^2} \tag{7}$$

The critical points for this equation (p_c, V_c, and T_c) can be found by locating $(\partial p/\partial V)_T = 0$ and $(\partial^2 p/\partial V^2)_T = 0$, which gives

$$\begin{cases} p_{c,\,eq7} = \dfrac{5}{221184}\dfrac{I}{\pi N_A\alpha} \\[2mm] V_{c,\,eq7} = 24\pi N_A\alpha \\[2mm] T_{c,\,eq7} = \dfrac{5}{3456}\dfrac{I}{R} \end{cases} \tag{8}$$

These critical parameters resemble those for the van der Waals equation of state but now are written as a function of physical constants, polarizability volume, and ionization potential only. As can be seen from eq 8, the critical volume is linearly proportional to the polarizability volume, whereas the critical temperature is proportional to the ionization potential of the molecules, while the critical pressure is dependent on both of these variables. Figure 2 displays the correlation between tabulated critical volumes and polarizability volumes for the molecules given in Table 1. As predicted, a linear relationship is found between the polarizability volume and the critical volume of a gas with an $R^2 = 0.906$. Using the relationship $V_c = 24\pi N_A\alpha$ from eq 8, we predict a slope of 45.4, which is in qualitative agreement with the slope of the line in Figure 2 and represents the upper limit of the data plotted in Figure 2. We also tested the correlation between the polarizability volume with either T_c or p_c (Supporting Information Figure S4), but as expected, no linear relationships were found. Therefore, these correlations confirm our derived critical parameter equations (eq 8).

Compressibility Derivation. The isothermal compressibility (κ_T) is dependent on the change in volume with a change in
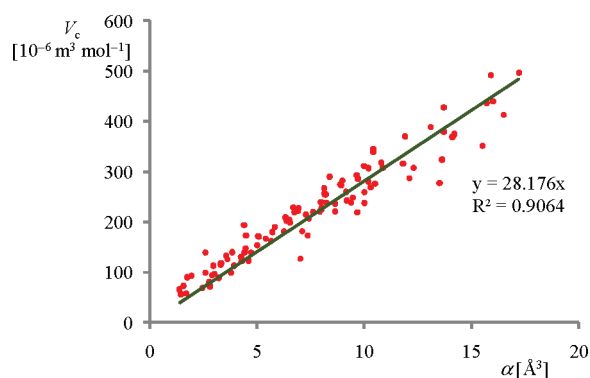
Figure 2. Correlation between the polarizability volume and critical volume V_c. Data for 103 molecules taken from ref 6.
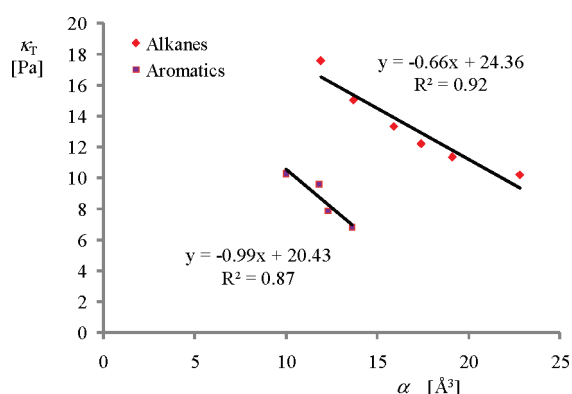

Figure 3. Correlation of the polarizability volume and the isothermal compressibility of liquids at a temperature of 30 °C and pressure of 10^5 Pa. Data taken from ref 6.

pressure at a constant temperature, eq 9

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{9}$$

We can derive $(\partial p/\partial V)_T$ from eq 7 above, which gives

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{1}{V - 8\pi N_A \alpha}\left[p - \frac{5\pi}{128}\frac{IN_A\alpha}{V^2} + \frac{5\pi^2}{8}\frac{IN_A^2\alpha^2}{V^3}\right] \tag{10}$$

This then leads to a compressibility function as described in eq 11

$$\kappa_T = \frac{V - 8\pi N_A \alpha}{pV - \frac{5\pi}{128}\frac{IN_A\alpha}{V} + \frac{5\pi^2}{8}\frac{IN_A^2\alpha^2}{V^2}} \tag{11}$$

Equation 11, of course, for an ideal gas with $V \gg 8\pi N_A\alpha$ and denominator equal to pV reduces to $\kappa_T = (1/p)$. In the situation in which the second and third terms in the denominator are small with respect to pV, the isothermal compressibility equation reduces to a linear relationship in polarizability volume via

$$\kappa_T \approx \frac{V - 8\pi N_A \alpha}{pV} \tag{12}$$

To test eq 12, we plot the polarizability volume versus the isothermal compressibility in Figure 3 for two series of liquids at
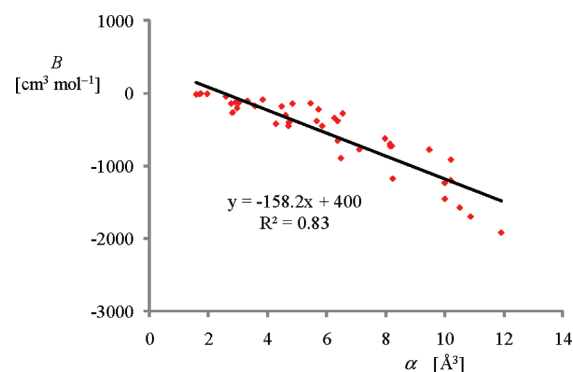

Figure 4. Literature data of the virial coefficient B at a fixed temperature of 300 K, plotted as a function of the polarizability volume for a selection of 42 molecules. Literature data taken from ref 6.

30 °C. The first set of liquids represents a series of linear alkanes, n-hexane, n-heptane, n-octane, n-nonane, n-decane, and n-dodecane, whereas the second set gives a series of aromatic residues, benzene, toluene, chlorobenzene, and bromobenzene. As can be seen, a reasonably linear correlation between κ_T and α is found with a negative slope, in agreement with eq 12. Therefore, Figure 3 confirms the relationship derived in eq 12 and implies that the modified van der Waals equation of state is applicable to the liquid state as well as the gas phase.

Comparison with the Virial Equation of State. A more general equation of state than the van der Waals equation of state is the Virial equation of state, in which the pressure essentially is described as a power series in $(1/V)$. Thus, expansion of the first two terms on the right-hand side of eq 7 into a Taylor series then converts the modified van der Waals equation of state into an equation that resembles the first three components of a Taylor series. The coefficient of $(1/V)$ in that equation is equal to the virial coefficient B. The value of B is derived from eq 7 and given in eq 13 as a function of physics constants, polarizability volume, and temperature. It is seen that the virial coefficient B is a function linear to the polarizability volume but also inversely proportional to the temperature. To find out whether literature data on the virial coefficient indeed correlate with the polarizability volume at a constant temperature, we plotted 300 K data of α versus B and, the result is given in Figure 4. Indeed, as predicted, a reasonable correlation between the polarizability volume and the virial coefficient B is found at constant temperature. The correlation coefficient of the trend is somewhat lower than those reported above in Figures 1 and 2 because we assumed a constant ionization energy for the selection of molecules, which obviously is not the case. Nevertheless, it appears that the correlations found in this work can be further generalized and applied to the virial equation of state as well.

$$B = \left(8\pi - \frac{5\pi}{128}\frac{I}{RT}\right)N_A\alpha \tag{13}$$

Exponential-Based van der Waals Equation of State. Because electron—electron repulsions are generally described by a Slater-type function, that is, proportional to $\exp(-\zeta r)$ with ζ as a constant, we assume that the $RT(1 - (5\pi IN_A\alpha/128RTV))$ contribution on the right-hand side of eq 7 are the first two terms of a power series $(e^x = \sum_{n=0}^{\infty} x^n)$ that can be replaced by an exponential function through the assumption that α/TV term is
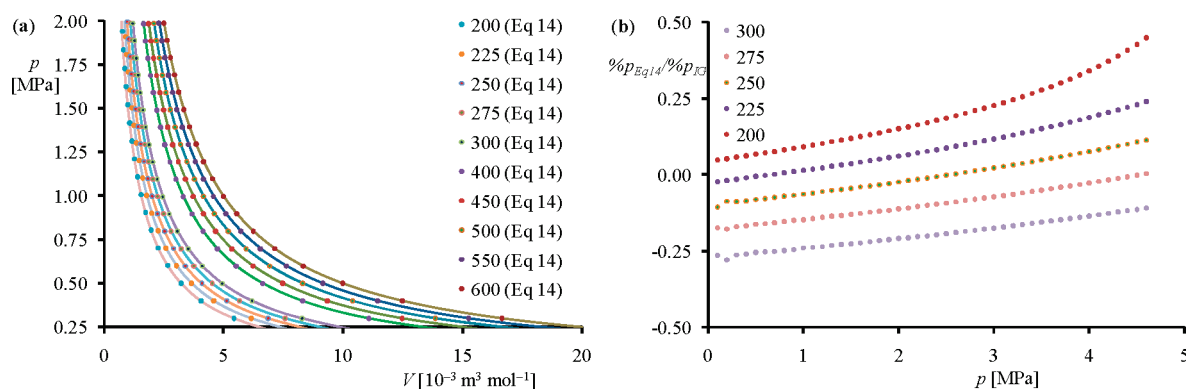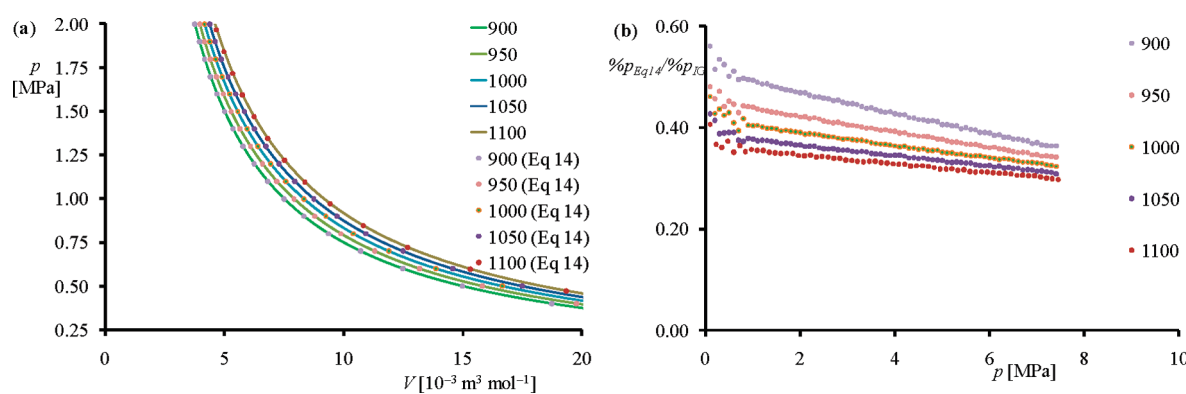
Figure 5. Methane pV diagram in the range of 200−600 K. Continuous lines are literature data,[12] while data points are calculated with eq 14 using $I_{methane} = 12.51$ eV and $\alpha_{methane} = 2.593 \times 10^{-30}$ m^3.

Figure 6. CO$_2$ pV diagram in the range of 900−1100 K. Continuous lines are literature data,[12] while data points are calculated with eq 14 using $I_{CO2} = 13.773$ eV and $\alpha_{CO2} = 2.911 \times 10^{-30}$ m^3.

small. This then gives eq 14, which is the exponential-based van der Waals equation of state

$$p(V - 8\pi N_A \alpha) = RT e^{[-(5\pi/128)(IN_A\alpha/RTV)]} + \frac{5\pi^2}{16} \frac{IN_A^2 \alpha^2}{V^2} \quad (14)$$

Equation 14 is empirically derived based on the correlations found above in Figure 1 and is a unique thermodynamic state function that includes experimentally measurable variables and physics constants only, in contrast to most reported equations of state in the literature that contain one or more fit parameters. As such, this state function may have uses in chemistry and chemical engineering problems.

The exponential-based van der Waals equation of state has some similarity with the well-known Buckingham (exponent − 6) function, which is a function describing the intermolecular interactions between molecules. The Buckingham potential is given in eq 15 and has an expression for the intermolecular repulsions that is exponential in r and another term for the intermolecular attractions, again resembling the London dispersion energy described above.[10] Between these functions, there are three fit parameters c_1, c_2, and c_3. The Buckingham potential is known to reproduce experimentally determined critical parameters and vapor pressure curves with better accuracy than, for instance, a standard Lennard-Jones potential.[11]

$$E_{Buckingham} = c_1 e^{-c_2 r} - \frac{c_3}{r^6} \quad (15)$$

To further validate the exponential-based van der Waals equation of state and test its performance against experimental data, we calculated the pV diagrams of several molecular systems and compared the results with available literature data from ref 12. Figure 5 displays the pV diagram of methane in the range of 200−600 K calculated using eq 14 with ionization energy and polarizability values from the literature,[6] $I_{methane} = 12.51$ eV and $\alpha_{methane} = 2.593 \times 10^{-30}$ m^3. The continuous lines shown in Figure 5 represent literature data, while our calculated values of the pressure using eq 14 are given with the inserted dots. As can be seen, the agreement between literature data and eq 14 is excellent, and generally, the deviation from the literature values is within 2%. Panel (b) displays the relative performance of eq 14 with respect to the Ideal Gas Law. First, we calculate the difference in pressure of the value obtained using eq 14 with the experimentally reported value ($\%p_{eq14}$). Subsequently, we calculate the Ideal Gas pressure (p_{IG}) using $p_{IG} = (RT/V)$ and the pressure difference with experiment ($\%p_{IG}$). The ratio ($\%p_{Eq14}/\%p_{IG}$) is plotted in Figure 5b as a function of experimental pressure. A value smaller than 1 implies that eq 14 gives data closer to experiment than the Ideal Gas Law. The figure shows that the performance of the exponential van der Waals equation of state is considerably better than the Ideal Gas Law, especially for low temperatures of dense gases.

Equation 14 was further tested for CO$_2$ gas in the range of 900−1100 K using $I_{CO2} = 13.773$ eV and $\alpha_{CO2} = 2.911 \times 10^{-30}$ m^3, and a similarly good agreement with experimental data was
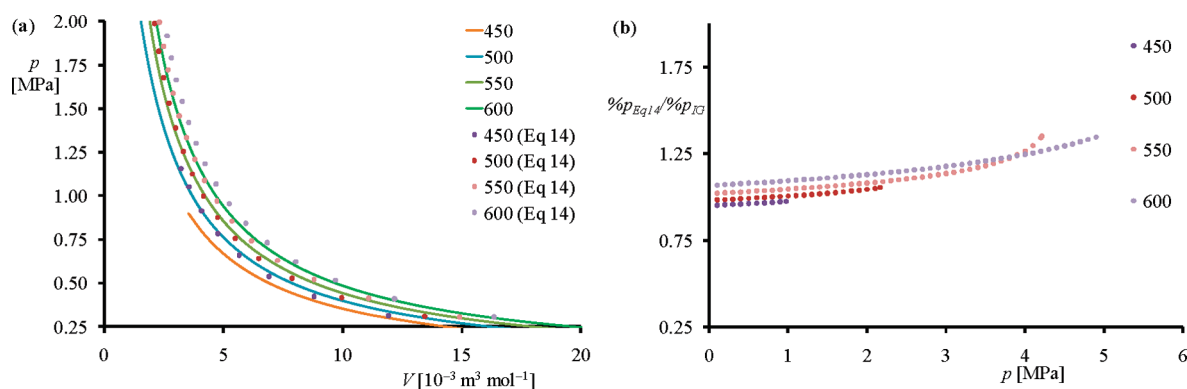
Figure 7. Benzene pV diagram in the range of 450–600 K. Continuous lines are literature data,[12] while data points are calculated with eq 14 using $I_{benzene}$ = 9.2459 eV and $\alpha_{benzene}$ = 10.0 × 10^{-30} m³.

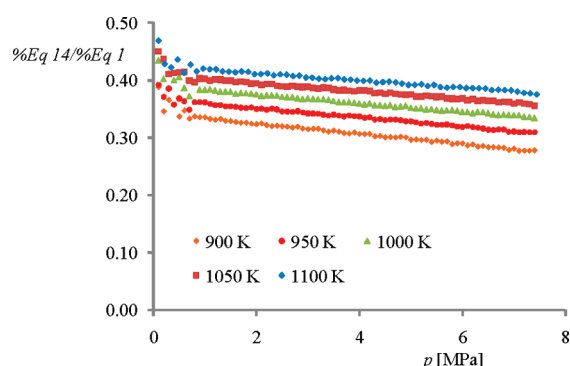**Figure 8.** Error ratio ($\%p_{eq14}/\%p_{eq1}$) of the exponential van der Waals equation of state relative to the original equation of state (eq 14 relative to eq 1) for the set of CO_2 data of Figure 6 using I_{CO2} = 13.773 eV and α_{CO2} = 2.911 × 10^{-30} m³. A value lower than 1 implicates that eq 14 is closer to experiment.

obtained (Figure 6). Also, the data for Figure 6 gave considerably better values with respect to experiment than those obtained from the Ideal Gas Law (panel b). In the case of the CO_2 plot, actually, the improvement with respect to the Ideal Gas Law increased with the pressure, which implies that it is a suitable equation for high-pressure systems as well.

Figure 7 gives the comparison of literature and calculated (eq 14) pressures for benzene in the range of 450–600 K. As follows from Figure 7, the modified van der Waals equation of state is able to reproduce experimental values of pV diagrams reasonably well but gives only minor improvement over the Ideal Gas Law (Figure 7b). At this stage, it is not clear why the pV diagram of benzene deviates from the literature curves. In this particular case, it may have to do with additional quantum chemical factors that stabilize benzene–benzene interactions or the inaccuracy of the reported values of either the polarizability volume or the ionization energy for benzene. Despite this, however, Figures 5–7 provide clear evidence that the equation of state of gases is a state function of the polarizability volume of the individual molecules involved.

To further ascertain the accuracy and reproducibility of eq 14 in calculating pV diagrams, we calculated the deviation of pressure ($\%p_{eq14}$) from the literature value for all systems described in Figures 5–7 and compared it with the value obtained using the original van der Waals equation of state (eq 1). Generally, the

deviation of the calculated pressure from experiment is small and on the order of about 5% or less. Subsequently, we used the original van der Waals equation of state (eq 1) to calculate these pV diagrams and also calculated deviations of these equations from experiment ($\%p_{eq1}$). We then divided $\%p_{eq14}$ by $\%p_{eq1}$ and plotted the ratio for the CO_2 data of Figure 6 in Figure 8. Also here, a value lower than 1 implies a better performance of eq 14 than eq 1 for this temperature and pressure range. As can be seen, all CO_2 calculated curves give an improvement over the original van der Waals equation of state by a factor of around 2 or better at low pressures. Furthermore, at larger pressures, the ratio drops even lower, which shows that eq 14 performs even better with respect to experiment than the original van der Waals equation of state. Therefore, eq 14 is probably a more realistic equation of state for the description of dispersion and repulsive interactions between molecules.

■ CONCLUSION

In summary, in this work, we present two new equations of state, one linear and one containing an exponential contribution, that are based on physics constants and experimentally measurable variables only. These equations of state are derived from correlations of the van der Waals parameters a and b with the polarizability volume. We show that the van der Waals equation of state can be reduced to a one-parameter equation of state. This correlation has further implications on various thermodynamic parameters, including critical parameters, isothermal compressibility, and so forth. Furthermore, it is shown that the critical parameters can be described as a function of the polarizability volume, ionization potential, and physics parameters, and it is shown that V_c is linearly proportional to the polarizability volume. We show that the exponential-based equation of state can reproduce experimental gas–liquid properties excellently and generally outperforms the original van der Waals equation of state and the Ideal Gas Law.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Tables with all data used in this work as well as three figures with correlations of analogous compounds and a pV diagram for CO_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) van der Waals, J. D. *Over de Continuiteit van den Gas- en Vloeistoftoestand (on the continuity of the gas and liquid state)*. Ph.D. Thesis, Leiden, The Netherlands, 1873.

(2) (a) Cohen, A. *Chem. Phys. Lett.* **1979**, *68*, 166–169. (b) Charney, E. *Chem. Phys. Lett.* **1980**, *75*, 599–601. (c) Gough, K. M. *J. Chem. Phys.* **1989**, *91*, 2424–2432. (d) Brinck, T.; Murray, J. S.; Politzer, P. *J. Chem. Phys.* **1993**, *98*, 4305–4306.

(3) Nagle, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4741–4747.

(4) de Visser, S. P. *Phys. Chem. Chem. Phys.* **1999**, *1*, 749–754.

(5) (a) de Visser, S. P. *J. Am. Chem. Soc.* **2010**, *132*, 1087–1097. (b) Kumar, D.; Karamzadeh, B.; Sastry, G. N.; de Visser, S. P. *J. Am. Chem. Soc.* **2010**, *132*, 7656–7667. (c) Kumar, D.; Sastry, G. N.; de Visser, S. P. *Chem.— Eur. J.* **2011**, 10.1002/chem.201003187.

(6) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, FL, 1996.

(7) See, for example: (a) Straty, G. C.; Younglove, B. A. *J. Chem. Phys.* **1972**, *57*, 2255–2259. (b) Hohm, U.; Kerl, K. *Mol. Phys.* **1987**, *61*, 1295–1298.

(8) London, F. *Trans. Faraday Soc.* **1937**, *33*, 8–26.

(9) Consider a unit sphere with two specific points 1 and 2 at a distance of R_{12} to each other inside of the sphere. The distances R_1 and R_2, respectively, connect points 1 and 2 with the origin (with $R_1 > R_2$), and the angle between R_1 and R_2 is θ. Then, the average distance between these two points can be calculated from the triple integral $\int_0^1 \int_{R_2}^1 \int_0^\pi R_{12} R_1^2 R_2^2 \sin\theta \, d\theta \, dR_1 \, dR_2$ divided by the triple integral over the weights $R_1^2 R_2^2 \sin\theta$. The former integral is $(4/35)$, while the latter is $(1/9)$, and their combination gives an average distance between two points inside of the unit sphere of $(36/35)$.

(10) Buckingham, R. A. *Proc. R. Soc. London, Ser. A* **1936**, *168*, 264–283.

(11) Errington, J. R.; Panagiotopoulos, A. Z. *J. Chem. Phys.* **1998**, *109*, 1093–1100.

(12) Lemmon, E. W.; McLinden, M. O.; Friend, D. G. Thermophysical Properties of Fluid Systems. In *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2008. http://webbook.nist.gov, (retrieved September 10, 2010).

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