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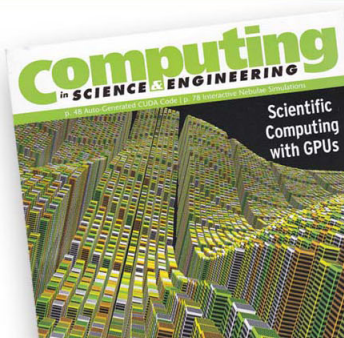
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Some Properties of van der Waals' Liquids

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A theoretical consideration of the volume of a van der Waals' liquid suggests some new rules, comparable to that of Trouton, relating coefficients of expansion and compressibility to heats of vaporization. According to the simplest and most reliable of these new relationships, the product of the coefficient of cubical expansion and the heat of vaporization, $\alpha\Delta H_v$, is the same for many liquids and equal to about 10 cal./deg. It is further shown that at a given temperature, $\Delta H_v^2\beta/V$ is also constant where β is the compressibility and V the volume of the liquid. Certain corollary rules are derived by combining the above two with each other and with Trouton's law. These new rules should prove of some value in estimating compressibilities and heats of vaporization from coefficients of expansion.

INTRODUCTION

IT has frequently been demonstrated that van der Waals' equation, although not quantitatively exact, can be used for the qualitative prediction of many phenomena exhibited by fluids. Although the equation has been most successfully applied to gases and vapors, it also appears to have considerable validity in describing the behavior of liquids. For example, it has been possible to derive from van der Waals' equation a vapor pressure relationship which has the correct functional form.¹ Moreover, it is possible to predict the orders of magnitude of the constants associated with certain empirical rules, such as those of Trouton or Guldberg and Guye. Numerous other conclusions can be drawn from van der Waals' equation; these have been summarized by van Laar,² who thoroughly investigated the equation.

The successful application of van der Waals' equation in deducing vapor pressure and related formulas leads one to suppose that still other relationships might be forthcoming, especially in connection with the liquid state. Thus from a consideration of the volume of a van der Waals' liquid, there can be derived some new general rules relating the coefficients of expansion and compressibility of liquids to their heats of vaporization or normal boiling points. The relationships are verified by comparison with published data, and are found to be about as reliable as Trouton's rule.

The conclusions of this paper do not constitute a verification of van der Waals' equation; instead they test the more general law of corresponding states. In fact, by using Pitzer's method for corresponding states, Guggenheim^{2a} made certain deductions closely related to some of those set forth in the present article.

COEFFICIENT OF THERMAL EXPANSION

In the aforementioned theory of vapor pressures based on van der Waals' equation,¹ use was made of the

¹ F. T. Wall, J. Chem. Phys. 16, 508 (1948).

² J. J. van Laar, *Die Zustandsgleichung von Gasen und Flüssigkeiten* (Leopold Voss, Leipzig, 1924); J. J. van Laar, *Zeits. f. anorg. u. angew. Chemie* 171, 42 (1928).

^{2a} K. S. Pitzer, J. Chem. Phys. 7, 583 (1939). E. A. Guggenheim, J. Chem. Phys. 13, 253 (1945).

molar volume of a van der Waals' liquid, the first approximation to which is

$$V = b + b^2 RT/a, \quad (1)$$

where a and b are van der Waals' constants. Employing the above expression for volume in connection with some basic thermodynamics, there was derived the following equation for the vapor pressure of a liquid:

$$\ln p = \ln(a/b^2) - a/(bRT). \quad (2)$$

From Eq. (2) it is readily seen that the heat of vaporization is simply equal to a/b .

Further examination of the volume of a van der Waals' liquid suggests that a simple relationship should exist between the coefficient of thermal expansion and the heat of vaporization. If α is used to denote the coefficient of thermal expansion, then the first approximation to α will be given by

$$\alpha = (1/V)(\partial V/\partial T)_p = bR/a. \quad (3)$$

Higher terms would involve the temperature and pressure, but such terms will be small compared to bR/a as long as a/b (the heat of vaporization) is large compared to RT and the pressure is well below the critical pressure. Recognizing that according to theory $\Delta H_v = a/b$, we see from (3) that

$$\alpha\Delta H_v = R \text{ (a constant)}. \quad (4)$$

Equation (4) suggests that the coefficient of thermal expansion multiplied by the heat of vaporization should be a constant for all liquids. This prediction is a reasonable one, for it implies that a liquid which expands readily upon heating also requires little energy for evaporation.

From a consideration of Trouton's rule,

$$\Delta H_v/T_0 = C, \quad (5)$$

where T_0 is the normal boiling point, it is apparent that the coefficient of thermal expansion should also be inversely proportional to the normal boiling temperature, or

$$\alpha T_0 = R/C \text{ (a constant)}. \quad (6)$$

To the best of our knowledge, Eqs. (4) and (6) have never been proposed as empirical relationships, so we have tested them by use of data contained in tables of physical constants. To provide a fair test of Eq. (4) it was felt desirable to utilize coefficients of thermal expansion and heats of vaporization for one temperature, say 25°C. Satisfactory data of this type, especially heats of vaporization which are usually given at the normal boiling point, are not generally available for all classes of compounds. Suitable data were found, however, for 37 hydrocarbons,^{3,4,5} and these are summarized in Table I. The product of α and ΔH_v for the 37 hydrocarbons is found to be quite constant, the average value being 10.1 ± 0.4 cal./deg. Although the empirical constant is about five times larger than predicted ($R = 2$ cal./deg.), the form of Eq. (4) is fully substantiated.

Equation (4) is further tested by use of data for 63 organic liquids^{4,5,6} appearing in Table II. For these compounds the heats of vaporization correspond to the normal boiling points of the liquids and not to 25°C. For this set the average value of the product $\alpha\Delta H_v$ is 9.4 ± 0.9 cal./deg. The principal reason for the greater variation in values (10 percent) is that the heats of vaporization were not all taken at the same temperature. The lower value (9.4 instead of 10.1) is largely due to the inclusion of highly associated liquids, such as formic and acetic acids, which are of an abnormal nature. On the other hand, the products for butyric acid and higher members of this series are close to the average value. Strangely enough, methyl and ethyl alcohol also appear to be quite normal on the basis of this criterion.

When relationship (4) is tested for inorganic liquids⁶ and for the elements in the liquid state⁷ (Table III) the agreement is not nearly so good. Water is definitely abnormal and certain metals such as zinc and mercury also show low values for the product $\alpha\Delta H_v$. Copper, hydrogen, and magnesium, on the other hand, show abnormally high values. This behavior is not unexpected as such substances generally do not conform to other relationships of a similar nature.

It is interesting to test Eq. (6) directly, although we would expect it to hold by virtue of Trouton's rule whenever Eq. (4) is valid. Values of αT_0 for 37 hydrocarbons are listed in Table I and the average is found to be 0.464 ± 0.032 . The quotient $\alpha\Delta H_v/\alpha T_0$, which should be Trouton's constant, is 22 or 20 cal./deg., depending on whether $\alpha\Delta H_v$ is taken as 10.1 or 9.4. This agreement with Trouton's constant is to be expected and does not

TABLE I. Values of $\alpha\Delta H_v$ for 37 hydrocarbons at 25°C.

Paraffins	ΔH_v^a cal.	$\alpha \cdot 10^{10b}$ per °K	$\alpha\Delta H_v$ cal/°K	T_0^c °K	αT_0
n-propane	3605	3.240	11.68	231.1	0.749
n-butane	5035	2.304	11.60	273.1	0.629
2-methyl butane	4570	2.304	10.53	271.5	0.602
n-pentane	6316	1.54	9.73	309	0.476
iso-pentane	5878	1.546	9.08	302	0.467
n-hexane	7540	1.35	10.18	341.9	0.462
2-methyl pentane	7138	1.476	10.54	333.5	0.492
2,3-dimethyl butane	6617	1.406	9.30	331.2	0.466
n-heptane	8735	1.222	10.67	371.6	0.454
2-methyl hexane	8318	1.259	10.47	363.3	0.457
3-methyl hexane	8385	1.228	10.30	365.2	0.470
2,2-dimethyl pentane	6969	1.268	9.83	352.4	0.447
2,3-dimethyl pentane	6617	1.220	9.30	331.2	0.404
2,4-dimethyl pentane	7860	1.268	9.97	353.7	0.448
3,3-dimethyl pentane	7892	1.223	9.65	359.3	0.439
2,2,3-trimethyl butane	7657	1.215	9.39	354.1	0.430
3-ethyl pentane	8419	1.222	10.29	366.7	0.448
n-octane	9915	1.116	11.06	398.9	0.445
2,5-dimethyl hexane	9048	1.19	10.77	382.3	0.455
2,2,3-trimethyl pentane	8823	1.118	9.86	383.0	0.428
3,3-diethyl pentane	10360	1.044	10.82	418.8	0.437
Cycloparaffins					
cyclopentane	6810	1.32	8.99	322.5	0.436
methyl cyclopentane	7560	1.25	9.45	345	0.431
cyclohexane	7895	1.20	9.47	353.7	0.424
methyl cyclohexane	8451	1.18	9.97	374	0.441
Olefins					
butene-1	4870	2.052	9.99	266.9	0.548
butene-2	5220	2.037	10.63	274.1	0.558
2-methyl propene	4920	1.954	9.61	266.3	0.520
Aromatic					
benzene	8090	1.215	9.83	353.3	0.429
toluene	9080	1.06	9.62	383.8	0.407
o-xylene	10380	0.9181	9.53	417.6	0.383
m-xylene	10195	0.999	10.18	412.3	0.412
p-xylene	10128	1.02	10.33	411.6	0.420
ethyl benzene	10100	0.955	9.64	409.4	0.391
pseudo cumene	11457	0.95	10.88	442.5	0.420
mesitylene	11346	0.937	10.63	437.9	0.410
propyl benzene	11049	0.97	10.72	432.4	0.419
Average					10.1 ± 0.4
					0.464 ± 0.032

^a See reference 3.

^b See reference 4.

^c See reference 5.

in any way test the validity of (4) or (6). Values of αT_0 for 63 miscellaneous organic liquids are given in Table II, and the average value of the product is 0.434 ± 0.027 .

The coefficients of thermal expansion are plotted against $1/\Delta H_v$ in Fig. 1, using the data of Table I, and it is seen that the points are well reproduced by a straight line passing through the origin and having a slope equal to 10.1. In Fig. 2 coefficients of thermal expansion are plotted against $1/T_0$. The points in the graph represent all liquids appearing in Table I for which the normal boiling temperatures exceed 250°K. Liquids boiling below that temperature exhibit large deviations, presumably because of irregularities in their α -values, which at 20°C must have been measured under high pressures. To establish more fully the trend for low boiling liquids, all compounds appearing in Table II having boiling points in the range 250–330°K are also included in Fig. 2. The solid line is drawn to pass through the origin and has a slope equal to 0.437. It is seen, however, that a better representation is given by the broken line, not passing through the origin, for which the equation is

$$\alpha T_0 = 0.61 - 4.4 \times 10^{-4} T_0. \quad (7)$$

Taking $\alpha\Delta H_v$ as 10.1, we can derive from (7) a modified

³ *Selected Values of Properties of Hydrocarbons* (American Petroleum Institute Project 44, National Bureau of Standards, Washington, D. C., 1945).

⁴ *Physical Constants of the Principal Hydrocarbons* (The Texas Company, New York, 1943), 4th edition.

⁵ *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1947), 30th edition.

⁶ N. A. Lange's *Handbook* (Handbook Publishers, Sandusky, 1946), 6th ed.

⁷ *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1926), Vol. 1, p. 102.

TABLE II. Values of $\alpha\Delta H_v$ for 63 organic liquids (ΔH_v at the normal boiling point).

A. Hydrocarbons	ΔH_v^a cal.	$\alpha \cdot 10^{3a}$ per °K	$\alpha\Delta H_v$ cal/°K	T_0^b °K	αT_0
Paraffins					
methane	2218	3.681	8.16	89.2	0.328
ethane	3515	3.750	13.18	101.2	0.380
decane	8878	1.06	9.41	447	0.473
undecane	9144	0.9678	8.85	469.0	0.454
dodecane	9351	0.9619	8.99	487.7	0.469
tridecane	9494	0.9166	8.70	507	0.465
tetradecane	9562	0.893	8.54	525.7	0.469
pentadecane	9537	0.8573	8.18	543.7	0.466
hexadecane	9487	0.8045	7.63	560.7	0.451
Bicyclic Aliphatic					
tetralin	10483	0.96	10.06	480.4	0.461
decalin (<i>cis</i>)	10575	(0.86)	9.09	(467.8)	(0.402)
decalin (<i>trans</i>)	10147		8.73		
(turpentine)	9330	0.973	9.08	429	0.417
Diolefins					
1,3-butadiene	5398	1.84	9.93	270	0.490
Aromatic					
<i>o</i> -cymene	8898	0.923	8.21	448	0.414
<i>p</i> -cymene	9073	0.96	8.71	449	0.431
methyl triisopropyl benzene	11355	0.975	11.07	527	0.514
ethyl triisopropyl benzene	11414	0.998	11.39	528	0.527
dimethyl triisopropyl benzene	11878	0.7855	9.33	548.8	0.431
1-phenyl-1-hexyl heptane	11980	0.885	10.60	551	0.488
tetraisopropyl toluene	11825	0.693	8.19	543	0.376
styrene	9050	0.849	7.68	419	0.356
Bicyclic Aromatic					
biphenyl	11472	0.935	10.73	527	0.492
1,2-diphenyl ethane	10662	0.85	9.06	557	0.473
Tricyclic Aromatic					
anthracene	13099	0.801	10.49	627	0.502
phenanthrene	12654	0.66	8.35	613.4	0.405
B. Other Organic Liquids	ΔH_v^a cal.	$\alpha \cdot 10^{3a}$ per °K	$\alpha\Delta H_v$ cal/°K	T_0^b °K	αT_0
Halogen Derivatives					
methyl iodide	6516	1.273	8.29	315.7	0.401
ethyl chloride	5949	1.706	10.15	285.4	0.487
ethyl bromide	6588	1.418	9.34	311.2	0.441
ethyl iodide	7113	1.179	8.39	345.4	0.407
amyl bromide	10498	1.102	11.57	402.1	0.443
amyl iodide	9428	0.986	9.30	429	0.423
ethylene chloride	8442	1.161	9.80	356.7	0.414
carbon tetrachloride	7138	1.218	7.80	349.9	0.426
chloroform	7044	1.236	8.82	334.5	0.413
chloral	7960	1.273	8.97	371	0.472
Ketones, Ethers					
acetone	7231	1.487	10.75	329.7	0.490
methyl ethyl ketone	7643	1.315	10.05	352.8	0.464
diethyl ketone	7821	1.233	9.64	375.9	0.463
ethyl ether	6220	1.656	10.30	307.8	0.509
Alcohols, Glycols					
methyl alcohol	8240	1.199	9.90	337.9	0.405
ethyl alcohol	9420	1.12	10.55	351.7	0.394
<i>n</i> -propyl alcohol	9885	0.956	9.42	370.4	0.354
isopropyl alcohol	9554	1.094	10.45	355.5	0.389
<i>n</i> -butyl alcohol	10451	0.950	9.93	390.9	0.371
<i>t</i> -butyl alcohol	9694	1.023	9.91	356.2	0.364
amyl alcohol	10596	0.902	9.56	404	0.364
allyl alcohol	9467	1.049	9.93	369	0.387
ethylene glycol	11855	0.6375	7.56	470	0.300
Acids, Esters					
formic acid	5524	1.025	5.66	374	0.383
acetic acid	5813	1.071	6.23	391.5	0.419
propionic acid	7319	1.102	8.07	412.5	0.455
<i>n</i> -butyric acid	10043	1.063	10.68	463.7	0.464
isobutyric acid	9852	1.068	10.50	427	0.456
<i>n</i> -valeric acid	10540	1.004	10.58	457.8	0.460
methyl formate	6360	1.563	9.92	304.5	0.476
ethyl formate	7110	1.417	10.10	326.5	0.463
methyl acetate	7310	1.427	10.43	330.3	0.471
ethyl acetate	8060	1.389	10.55	350.4	0.487
methyl propionate	7718	1.304	10.06	353.1	0.460
ethyl benzoate	9686	0.900	8.72	485.8	0.437
Miscellaneous					
carbon disulfide	6403	1.218	7.80	319.5	0.389
aniline	9657	0.858	8.29	457.6	0.393
Average					9.4 ± 0.9
					0.434 ± 0.027

^a See reference 4.^b See reference 5.^c See reference 6.

form of Trouton's rule, namely

$$\Delta H_v/T_0 = 16.6 + 0.012T_0. \quad (8)$$

Equation (8) is in excellent agreement with Bingham's modification⁸ of Trouton's rule, which is

$$\Delta H_v/T_0 = 17 + 0.011T_0. \quad (8a)$$

Since the same type of data was employed both for Bingham's calculations and our own, this agreement is also expected although it is not entirely trivial. It is significant that the modification involving a linear function of T_0 is not required for the $\alpha\Delta H_v$ relationship whereas it does improve both the rule for αT_0 and that of Trouton. This suggests that the constancy of $\alpha\Delta H_v$ is of greater reliability than Trouton's rule as ordinarily stated, although it is probably not as good as Hildebrand's modification.⁹

For practical purposes we suggest provisionally that the product $\alpha\Delta H_v$ be assumed equal to 9.4 cal./deg., using heats of vaporization at the normal boiling point. If the heat of vaporization is known at 25°C, then it would be better to use 10.1 cal./deg. for the constant. The rule should prove of some value, especially for hydrocarbons, for estimating heats of vaporization from coefficients of expansion.

COMPRESSIBILITIES OF LIQUIDS

As a first approximation, the volume of a van der Waals liquid depends upon the temperature but not upon the pressure, so such a liquid would be considered incompressible. Actually that is a reasonable prediction, for it is observed that the volume of a liquid is generally affected less by pressure than by temperature. To make any more detailed predictions concerning compressibilities, it is necessary to take recourse to higher approximations for the volume of a liquid. Unfortunately the higher approximations are of doubtful significance and the paucity of experimental data makes it difficult to rigorously test the predictions.

An effort in this direction has been made, however, by use of the second approximation¹ to the volume, namely:

$$V = b + \frac{b^2 RT}{a} + \frac{2b^3 R^2 T^2}{a^2} - \frac{b^4 RT p}{a^2}. \quad (9)$$

From Eq. (9) it can be shown that the first term for the compressibility will be

$$\beta = -(1/V)(\partial V/\partial p)_T = b^3 RT/a^2. \quad (10)$$

From (10) it can further be shown (neglecting higher powers of bRT/a) that

$$\Delta H_v^2 \beta / V = RT \text{ (a constant at a given } T). \quad (11)$$

Assuming Trouton's rule, Eq. (11) can be modified to

$$T_0^2 \beta / V = RT/C^2 \text{ (a constant at a given } T). \quad (12)$$

⁸ E. C. Bingham, J. Am. Chem. Soc. 28, 723 (1906).

⁹ J. H. Hildebrand, J. Am. Chem. Soc. 37, 970 (1915).

The equations have been subjected to test using such data as are available. From the data of Table IV^{5,10} it is found for a series of liquids that the expressions corresponding to (11) and (12) are fairly constant. In that table, β is the compressibility at 20°C measured over the pressure range 100–300 atmospheres. It is observed that $\Delta H_v^2\beta/V = 53.6 \pm 3.2$ (cal.)²/ml-atmos. and $T_0^2\beta/V = 0.105 \pm 0.007$ (degrees)²/ml-atmos. The square root of the quotient is 22.6 cal./deg., which is to be compared with Trouton's constant. These rules should be of some use in estimating compressibilities of normal liquids. Theoretically, $\Delta H_v^2\beta/VT$ (and $T_0^2\beta/VT$) should also be constant but the available data do not permit checking the effect of temperature and our rule is therefore restricted to 20°C.

By combining the rules expressed by Eqs. (4) and (11), the heat of vaporization can be eliminated and a relationship deduced between α and β , namely:

$$V\alpha^2/\beta = R/T \text{ (a constant at a given temperature).} \quad (13)$$

It will be recalled that the difference between the heat capacities at constant pressure and constant volume ($C_p - C_v$) is precisely $TV\alpha^2/\beta$, so from (13) it appears that this difference should be the same for all liquids. The predicted constant, R , is of course not numerically correct but the form of the law is approximately substantiated by the data of Table V, which includes all liquids appearing both in Tables I or II and in Table IV. (As indicated earlier, the lack of data restricts our test to one temperature, 20°C.)

It is found at 20°C that $V\alpha^2/\beta = 1.65 \pm 0.20$ ml-atmos./deg². This rule should find some application in estimating compressibilities from coefficients of cubical expansion, although it appears to be less reliable than the relationships involving ΔH_v .

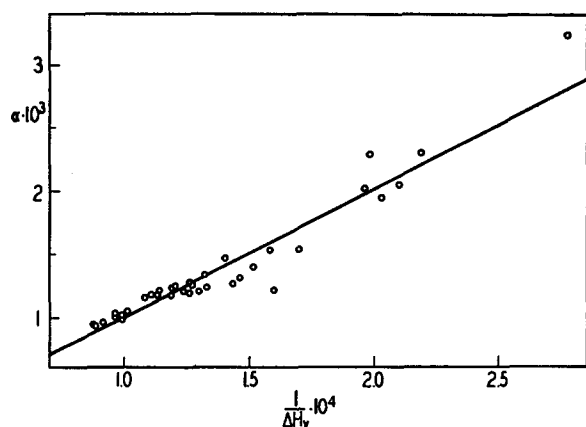


FIG. 1. Graph of coefficient of expansion (α) vs. reciprocal of heat of vaporization (ΔH_v). Solid line corresponds to Eq. $\alpha\Delta H_v = 10.1$ cal./deg.

¹⁰ *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1928), Vol. 3, p. 35.

TABLE III. Values of $\alpha\Delta H_v$ for some inorganic liquids.

A. Inorganic Liquids	ΔH_v^a cal.	$\alpha \cdot 10^{3a}$ per °K	$\alpha\Delta H_v$ cal/°K
phosphorus trichloride	7060	1.154	8.15
silicon tetrachloride	6133	1.430	8.77
stannic chloride	7894	1.178	9.30
sulfur monochloride	6684	0.968	6.47
water	9700	0.207	2.01
B. Elements in the Liquid State	ΔH_v^b cal.	$\alpha \cdot 10^{3b}$ per °K	$\alpha\Delta H_v$ cal/°K
A	1505	4.5	6.77
Ag	59490	0.11	6.54
Al	53750	0.113	6.07
Bi	46100	0.122	5.62
Br ₂	7168	1.100	7.88
Cd	26852	0.150	4.02
Cl ₂	4778	1.500	7.17
Cs	17440	0.37	6.45
Cu	11560	0.190	21.2
F ₂	(2867)?	3.00	(8.60)?
H ₂	2150	13.0	28.0
Hg	14166	0.182	2.58
I ₂	10512	0.800	8.41
K	20068	0.290	5.82
Li	40613	0.180	7.31
Mg	62600	0.380	23.7
N ₂	1338	6.0	8.02
Na	25080	0.280	7.02
O ₂	1632	4.10	6.69
O ₃	3498	2.00	7.00
P ₄	16108	0.52	8.36
Pb	46108	0.12	5.53
Rb	17680	0.340	6.01
S ₈	17162	0.430	7.38
Sb	45390	0.100	4.54
Sn	77643	0.100	7.76
Tl	(61158) (28670)?	(0.140)	(8.56) (4.01)
Zn	23700	0.150	3.55
Average 8.10 ± 2.07			

^a See reference 6.

^b See reference 7.

REDUCED VOLUME OF A VAN DER WAALS' LIQUID

The expression for the volume of a van der Waals' liquid can readily be put into reduced form by use of appropriate formulas for the critical constants. Denoting the reduced volume, V/V_c , by ϕ , and the reduced

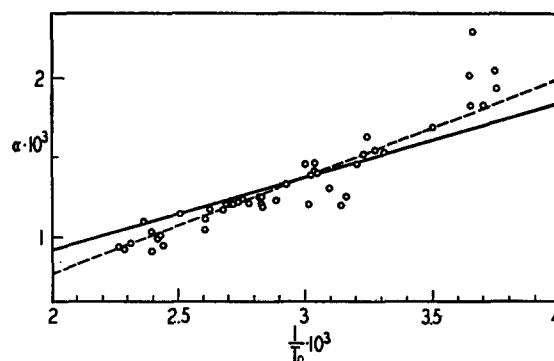


FIG. 2. Graph of coefficient of expansion (α) vs. reciprocal of normal boiling point (T_0). Solid line corresponds to Eq. $\alpha T_0 = 0.467$, and dotted line to Eq. (7) of text.

TABLE IV. Values of $\beta\Delta H_v^2/V$ and $\beta T_0^2/V$.

Hydrocarbons	V^a ml.	$\beta \cdot 10^{80}$ per atm.	ΔH_v^a cal.	$\beta\Delta H_v^2/V$ (cal) ² / ml. atm.	T_0^a °K	$\beta T_0^2/V$ deg ² /ml. atm.
<i>n</i> -octane	162.35	97.5	9915	59.0	399.1	0.096
2,5-dimethyl hexane	163.54	105	9048	52.6	381.6	0.093
3,4-dimethyl hexane	158.43	94.5			389.8	0.091
2-methyl heptane	162.51	101			389	0.094
3-ethyl hexane	159.34	96			392.2	0.093
cyclohexane	108.02	93	7895	53.7	354.7	0.108
benzene	88.82	78	8090	57.5	353.4	0.110
toluene	106.39	74	9080	57.3	384.1	0.103
ethyl benzene	122.46	71	10100	59.1	409.4	0.097
<i>n</i> -propyl benzene	139.43	69.7	11049	61.0	432.7	0.094
isopropyl benzene	139.11	70.3			425	0.091
<i>t</i> -butyl benzene	154.80	68			442.0	0.086
mesitylene	139.21	67	11346	62.0	437.9	0.092
pseudocumene	137.20	64	11049	56.9	443.1	0.092
Ketones, Alcohols						
acetone	73.3	82	7231	58.4	331	0.123
diethyl ketone	105.56	84	7821	48.7	376	0.112
cyclohexanone	103.55	58			430	0.104
<i>n</i> -butyl alcohol	91.53	76.5	10451	91.3	391.1	0.128
<i>t</i> -butyl alcohol	93.98	89	9694	89.0	356.1	0.120
isoamyl alcohol	108.56	84	10560	86.3	403.8	0.126
ethylene glycol	55.64	34	11855	85.7	470.5	0.135
benzyl alcohol	102.98	43	12142	61.6	478.5	0.096
<i>o</i> -cresol	103.33	44			464.8	0.092
<i>m</i> -cresol	104.57	45.5	10878	51.4	476.1	0.103
<i>p</i> -cresol	104.50	44			475.8	0.095
Acids, Esters						
<i>n</i> -butyric acid	108.42	77	10043	71.6	460	0.150
<i>n</i> -propyl formate	97.82	87	7762	53.6	354.6	0.112
isobutyl formate	112.13	86	8017	49.3	380.1	0.111
isoamyl formate	133.36	80	8549	43.8	396.8	0.095
methyl acetate	79.7	87.5	7310	58.7	330	0.120
ethyl acetate	97.8	90	8060	59.8	350	0.112
isobutyl acetate	133.33	87	8573	48.0	389.8	0.099
ethyl propionate	115.45	87.5	8181	50.7	372.4	0.105
methyl butyrate	113.73	84	8078	48.3	375.6	0.104
methyl isobutyrate	114.62	89	7976	49.4	365.9	0.104
ethyl butyrate	132.15	85	8677	48.4	394.6	0.100
ethyl isobutyrate	133.62	90	8375	47.2	385	0.100
Miscellaneous						
carbon tetrachloride	96.4	88	7138	46.5	350	0.112
chloroform	79.8	83	7044	51.6	334	0.117
ethylene chloride	78.74	67.5	8442	61.1	356.8	0.109
<i>o</i> -toluidine	106.72	44			473.1	0.092
<i>m</i> -toluidine	108.34	45			476.6	0.094
Average			53.6 ± 3.2		0.105 ± 0.007	

^a See reference 5.^b See reference 6.^c See reference 10.^d See reference 2.

temperature, T/T_0 , by θ , it is easily seen that for the first approximation

$$\phi = \frac{1}{3}\{1 + 8\theta/27\}. \quad (14)$$

The validity of Eq. (14) can be tested in part by comparison with the experimental results of Young¹¹ who investigated the volumes of 19 organic liquids all coexisting with their vapors at a reduced pressure

¹¹ S. Young, *Stoichiometry* (Longmans, Green and Company, London, 1908) p. 203.

TABLE V. Values of $V\alpha^2/\beta$ at 20°C.

Liquid	$\alpha \cdot 10^{20}$ per deg.	V^b ml.	$\beta \cdot 10^{80}$ per atm.	$V\alpha^2/\beta$ ml. atm./ deg ²
<i>n</i> -octane	1.116	162.35	97.5	2.07
2,5-dimethyl hexane	1.19	163.54	105	2.21
cyclohexane	1.20	108.02	93	1.67
benzene	1.215	88.82	78	1.68
toluene	1.06	106.39	74	1.61
ethyl benzene	0.955	122.46	71	1.57
mesitylene	0.937	139.21	67	1.82
<i>n</i> -propyl benzene	0.97	139.43	69.7	1.88
pseudocumene	0.95	137.20	64	1.93
acetone	1.487	73.3	82	1.98
diethyl ketone	1.233	105.56	84	1.91
<i>n</i> -butyl alcohol	0.950	91.53	76.5	1.08
<i>t</i> -butyl alcohol	1.023	93.98	89	1.10
ethylene glycol	0.6375	55.64	34	0.67
<i>n</i> -butyric acid	1.063	108.42	77	1.59
methyl acetate	1.427	79.7	87.5	1.85
ethyl acetate	1.389	97.8	90	2.10
carbon tetrachloride	1.218	96.4	88	1.63
chloroform	1.236	79.8	83	1.47
ethylene chloride	1.161	78.74	88	1.21

Average 1.65 ± 0.20 ^a See reference 4.^b See reference 5.^c See reference 10.^d See reference 2.

($\pi = p/p_0$) equal to 0.08846. Under these circumstances the 19 liquid-vapor systems all had very nearly the same reduced temperature, the average value being 0.7459 with a maximum variation therefrom of a few percent. Setting $\theta = 0.7459$ in Eq. (14) we calculate a reduced volume equal to 0.4069. This compares very favorably with the average value observed by Young, namely, $\phi = 0.4030$. This agreement is better than we might reasonably expect, for most reduced relationships derived from van der Waals' equation are only qualitatively correct. For example, the reduced vapor pressure equation corresponding to (2) is not nearly so good as (14) appears to be. Our test of Eq. (9) is so limited that the agreement may be coincidental; nevertheless it does appear that the equation is reliable.

Although the higher approximations¹ to the volume of a van der Waals liquid are of doubtful significance, we record here for the sake of greater completeness, the third approximation to the reduced volume:

$$\phi = \frac{1}{3} + \frac{1}{3}(8\theta/27) + \frac{2}{3}(8\theta/27)^2 - \frac{1}{3}(8\theta/27)(\pi/27) + 5/3(8\theta/27)^3 - 2(8\theta/27)^2(\pi/27) + \frac{1}{3}(8\theta/27)(\pi/27)^2 + \dots \quad (15)$$