tions given above. In place of (9), however, he gives the reaction (7a). The arguments given by Kassel seem to apply equally well if (9) is substituted. If (7a) were important at elevated temperatures, the yields of hydrogen peroxide should not parallel the water yields as was found for the photochemical reaction, but should depend primarily on the activation energy of (7a).

The modification proposed by von Elbe and Lewis[22] is identical with that proposed here, except that it admits the possibility of (7a) as well as (9), and also includes a reaction

$$H + O_2 + H_2 \longrightarrow H_2O_2 + H \qquad (11)$$

in order to explain the explosion limits. The present work gives no indication that such a reaction is of importance.

Acknowledgment.—The authors are grateful to the Roy R. Hornor Fund of Lehigh University for financial aid.

Summary

The photochemical oxidation of hydrogen has been studied by exposing mixtures of hydrogen and oxygen at room temperature to light of wave length 1719–1725 Å. The total pressure of the reaction mixture was varied from 1140 to 95 mm.

In general, with increasing oxygen content, the quantum yields of ozone increase while those of hydrogen peroxide and water decrease. Lowering of the total pressure tends to increase the water and peroxide yields, apparently at the expense of the ozone. At pressures of 190 mm. and less, the formation of water shows chain characteristics.

The temperature coefficients for the formation of the individual products have also been studied over the range 25 to 280°. The formation of ozone has a negative temperature coefficient while those of water and hydrogen peroxide are positive. At total pressures of 190 millimeters and in a 10–90% oxygen–hydrogen mixture, the temperature coefficients of water and hydrogen peroxide formation increase with great rapidity at temperatures above 230°.

A mechanism has been offered which explains satisfactorily the experimental results.

The relation of the direct photochemical reaction to the mercury sensitized and the explosive reactions has been discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Thermodynamic Properties of Substances. III. Vapor Volumes as Functions of Reduced Temperature Alone

BY HAROLD A. FALES AND CLARA S. SHAPIRO

In a previous article[1] we have shown that vapor volumes of chemically different substances can be expressed as a function of liquid volume and reduced temperature:

$$V_g = V_1 e^{k(1-\tau^2)^m/\tau^n} \qquad (1)$$

The same type of function was found to give correct values for vapor pressures of thirty liquids, including water, the parameters k', m', n', being very close in value to those of the above equation.[2,3]

$$P_s = P_{cr}\, e^{-k'(1-\tau^2)^{m'}/\tau^{n'}} \qquad (2)$$

An attempt was made[3] further to express vapor volumes as a function of reduced temperature alone by an analogous equation

$$V_g = V_{cr} e^{k''(1-\tau^2)^{m''}/\tau^{n''}} \qquad (3)$$

This equation was applied to water vapor and was found to hold for almost the entire saturation line (60–360°) with an average deviation under 0.2 volume per cent.

In view of the fact that equations (1), (2) and (3) represent the behavior of water and equations (1) and (2) apply to the various other substances as well, it seems reasonable to presuppose that equation (3) would also apply to the other substances; actual tests confirm this supposition in every one of the cases, as will be shown in detail in the following pages.[4]

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(1) H. A. Fales and C. S. Shapiro, THIS JOURNAL, **58**, 2418 (1936).

(2) H. A. Fales and C. S. Shapiro, *ibid.*, **60**, 794 (1938).

(3) H. A. Fales and C. S. Shapiro, *ibid.*, **60**, 784 (1938).

(4) After completing the test of equation (3) on all the various substances, we tried out (on water) the more general form

$$V_g/V_{cr} = \text{exp.}\ k''[(1+\tau)^{s''}(1-\tau)^{m''}/\tau^{n''}] \qquad (4)$$

as was done previously for the vapor pressure of water.[3] This was done in the hope that it would improve the agreement at both extremes of the saturation line, namely, near the melting point and near the critical point. We found that both forms (4) and (3) fit water volumes equally well at every point in the interval 60–360°, The substances selected for the present study are the same as before, except that argon has been replaced by krypton. The latter was chosen because its densities were recently measured by the Leiden Laboratories and checked by them up to highest coexistence temperatures against their new, very accurate mean diameter equation.[5]

In accordance with our earlier procedure, we have first made a graphical intercomparison of the observed vapor volume curves, which enabled us to answer two separate questions: (a) what is the shape and relative order of vapor volume curves of different liquids? (b) how are the three thermodynamic properties (vapor volume, vapor pressure and volume ratio) of any single substance related among themselves in the coördinate system?

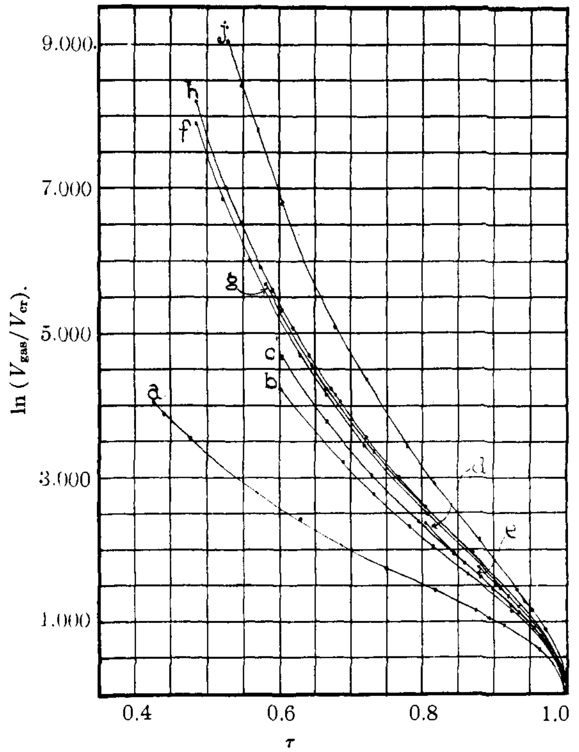

Fig. 1.—ln $(V_g/V_{cr}) = k''(1 - \tau^2)^{m''}/\tau^{n''}$: a, helium; b, krypton; c, ethane; d, acetylene; e, carbon monoxide; f, benzene; g, *n*-pentane; h, ammonia; j, ethyl alcohol.

For this purpose we have plotted the values ln V_g/V_{cr} obsd. against reduced temperature and have compared the ordinates of different curves at $\tau = 0.6000$ with each other as well as with the corresponding ordinates ln P_{cr}/P_s obsd., and ln V_g/V_{liq} obsd. of each substance.

We find here, as in the previous studies, that the ln of reduced vapor volume is represented by a family of curves, each of a form similar to that given earlier for water,[3] and very similar in shape to the curves ln V_g/V_{liq}. We see further that the order of the vapor volume curves, which is given herewith, is very close to that of the vapor pressures and is almost identical with the sequence of volume ratios[2,1]

1 Helium
2 Hydrogen
3 Neon
4 Krypton
5 Oxygen
6 Carbon monoxide
7 Nitrogen
8 Ethylene
9 Ethane
10 Hydrogen chloride
11 Nitrous oxide
12 Acetylene
13 Methyl ether
14 Carbon dioxide
15 Carbon tetrachloride
16 Benzene
17 *i*-Pentane
18 *n*-Pentane
19 Ammonia
20 Monofluorobenzene
21 Methyl formate
22 Ethyl ether
23 *n*-Hexane
24 Water
25 Acetic acid
26 Ethyl propionate
27 Sulfur trioxide
28 Methyl alcohol
29 Ethyl alcohol
30 Nitrogen tetroxide

As to the relative position of the above thermodynamic properties, we find that for every substance listed here their ascending order is the same as that shown for water:[3] ln P_{cr}/P_s; ln V_g/V_{cr}; ln V_g/V_{liq}.

An illustration of interrelation of different vapor volume curves is shown in Fig. 1, in which nine representative substances are plotted

(a) Helium
(b) Krypton
(c) Ethane
(d) Acetylene
(e) Carbon dioxide
(f) Benzene
(g) *n*-Pentane
(h) Ammonia
(j) Ethyl alcohol

For graphical comparison of different properties of a single substance the reader is referred to the article on water.[3]

Accuracy of the Proposed Equation.—The tolerance of the vapor volume equation for water was estimated earlier.[3,1] It was found to be affected by two sources of error: (a) errors in T_{cr} and (b) errors in vapor volume. The deviations in the critical volume were assumed negligible due to the precise method of extrapolation used by Keyes and his collaborators.[6] Hence the total accuracy of equation (3) for water was found

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the average deviation being: ΔV_g = 0.18 and 0.17%, respectively. At lower temperatures (0–40°) equation (4) deviates a trifle more than eq. (3).

As to the parameters, we find that both forms have practically equal values of k'', m'', n''; moreover, the constant s'' of eq. (4) is almost identical with its constant m'' (0.4708 and 0.4713). Since equation (4) did not show any appreciable improvement over eq. (3) in the case of water, there did not seem to be sufficient reason for investigating it any further.

(5) Literature on the new Leiden equation and on krypton densities is given below in Table V (bibliography).

(6) For corresponding literature see Table V below.

exactly equal to that of the volume ratio equation (1). In applying eq. (3) to other substances for which the critical densities are less accurately known, we can no longer neglect the effect of deviations in d_{cr} because for the majority of them the critical density is uncertain by at least 1–2% and for some liquids it may be in error by as much as 5–10%.[1]

The question of errors in critical density was discussed recently by Mathias and Crommelin of Leiden in connection with their new four-term diameter equation[5]

$$d_m = a + bT + cT^2 + dT^3 \tag{5}$$

These authors have shown that the critical densities of krypton and carbon monoxide calculated from eq. (5) are about 1% higher than the d_{cr} values obtained from the rectilinear diameter formula

$$d_m = a + bt \tag{6}$$

It seems to follow that many other substances for which the critical densities were extrapolated from the linear eq. (6) will be in error by about 1–2%.

Such will be the case with noble and permanent gases as well as with some organic and inorganic compounds. As to the reduced mean density formulas used by the "Int. Crit. Tables"

$$d_m = d_{cr}[1 + \gamma(1 - \tau) + \kappa(1 - \tau)^2] \tag{7}$$
$$d_m = d_{cr}[1 + \gamma(1 - \tau)] \tag{8}$$

it is obvious that they are less accurate than eq. (5) above, hence the critical densities given in Vol. III of these Tables may also deviate from true values by several per cent.

This situation raises a question: to what extent does an error of 1–5% in the critical density affect the total accuracy of the vapor volume equation?

To test this influence we have taken an actual case (carbon monoxide) and have made two sets of calculations using first the new and then the old d_{cr} values. In both sets of calculations the same reference points were used for evaluating the constants k'', m'', n''. A careful comparison of the results showed that, although the two sets of parameters I and II are different, the respective values of d_{gas} calcd. I and II are equal to each other at every temperature. In other words, a difference of 1% in d_{cr} produced no change in the calculations. Three other substances were tested similarly; these are krypton, ethyl ether, and ethane, with errors in d_{cr}, respectively, of 1, 1 and 5%. In each case we have found the two sets of calculated densities to be identical within 0.05%, which is a further proof that errors in d_{cr} of 1–5% have no effect whatsoever on the accuracy of the proposed equation.

In Table I we give the details of our calculations on carbon monoxide. This substance was chosen because of its long coexistence range (0.5–1.0 T_{cr}), and because its vapor densities are very accurately measured up to within 2° from the critical temperature. This affords an opportunity to test the proposed equation in the critical region (0.97–1.0 T_{cr}).

Table I is divided in two parts: the upper illustrates the agreement between experiment and the proposed equation. The lower part shows the effect of change in d_{cr} on the calculated values of d_{gas}. Here the calculations are given in detail for several temperatures and will be discussed first.

In columns 2 and 3 of the bottom part are given the two sets of observed ln V_g/V_{cr} data, the respective values of d_{cr} being 0.305 and 0.301. In columns 4 and 5 are given the corresponding sets of calculated ln V_g/V_{cr} values. In column 6 are shown the differences in per cent. between the observed ln values (Δ ln % obsd. I–II); in column 7 are given the corresponding differences between the two sets of calculated ln values (Δ ln % calcd. I–II). Examination of columns 6 and 7 shows clearly that at every temperature Δ ln % obsd. I–II is equal to Δ ln % calcd. I–II. From this fact it obviously follows that at each temperature the difference between observed and calculated ln values is the same for each set. This is very clearly demonstrated in the last two columns of the bottom part which contain the deviations Δ ln % obsd. − calcd. I and Δ ln % obsd. − calcd. II. We see that these are practically equal at every point both in sign and in value, averaging $\Delta \ln \phi = 0.62\%$ and 0.64%, respectively.

In the upper half of Table I are given: the Leiden data for vapor densities of carbon monoxide together with the two sets of calculated d_{gas} values I and II. At the very top of the table are given the corresponding two sets of parameters k'', m'', n''. In the last three columns are shown the two sets of deviations Δd_g % I and II, together with the corresponding deviations of the Leiden mean diameter equation (5). In examining this part of Table I we see again that the deviations Δd_g % obsd. − calcd. I and II are nearly identical at all temperatures. This shows that correct values for vapor densities can be obtained from the proposed equation even when the critical density is only approximately known.

As to the agreement between experiment and calculation, we see that it is quite satisfactory. The estimated tolerance of equation (3) for carbon monoxide is $\Delta \ln$ est. = 0.95% while the average deviation actually found is $\Delta \ln \phi = 0.62\%$. Considering the volumes themselves we see that the deviations Δd_g % are rather small and regularly distributed even in the critical range where the maximum is $\Delta d_g = 1.2\%$ at $\tau = 0.988$ (0.5° below T_{cr}). Here, as in the case of water,[3] we see that in the critical neighborhood (0.97–1.0 T_{cr}) the vapor densities deviate much less than

TABLE I

INFLUENCE OF ERRORS IN CRITICAL DENSITY ON THE ACCURACY OF THE PROPOSED EQUATION

$$\ln V_g/V_{c} = k'' \frac{(1-\tau^2)^{m''}}{\tau^{n''}} \quad \text{Carbon monoxide}$$

	d_{cr}	k''	m''	n''
I	0.305	2.5061	0.46404	1.5229
II	.301	2.5135	.47192	1.5182
	$\Delta d_{cr} = 1.3\%$	$\Delta k = 0.3\%$	$\Delta m = 2.0\%$	$\Delta n = 0.3\%$

T, °K.	τ	d_g, g./cc. obsd. data[a]	d_g, g./cc. proposed equation $d_{cr} = 0.305$ I	d_g, g./cc. proposed equation $d_{cr} = 0.301$ II	Δd_g, % Obsd. − calcd. proposed equation $d_{cr} = 0.305$ I	Δd_g, % Obsd. − calcd. proposed equation $d_{cr} = 0.301$ II	Δd_g, % Obsd. − calcd. Leiden equation[b] $d_{cr} = 0.305$
68.13	0.512603	(0.00080)	0.00074	0.000743	+ 7.5	+ 7.5	
73.56	.553457	(.00171)	.00167	.001673	+ 2.2	+ 2.2	
78.03^c	.587089	(.00296)	.00296	.00296	0^c	0^c	
82.25	.618840	(.00477)	.00476	.004758	+ 0.2	+ 0.25	
87.15	.655707	(.00774)	.00776	.007752	− 0.25	− .15	
90.28	.679257	(.01019)	.010289	.010283	− 1.0	− .95	
94.16	.708449	(.01422)	.014220	.014214	0.00	+ .04	
100.93	.759386	.02389	.023638	.023633	+ 1.0	+ 1.02	
103.50^c	.778723	.02824	.02824	.02824	0^c	0^c	
107.61	.809646	.03681	.037050	.037061	− 0.65	− 0.68	
109.05	.820480	.04014	.040624	.040639	− 1.20	− 1.24	
120.90	.909638	[.08202]	.084715	.084822	−(3.2)	−(3.34)	−(4.1)
125.60	.945001	.11607	.115829	.115960	+ 0.2	+ 0.1	+ 1.0
127.82	.961704	.13601	.137029	.137360	− .75	− .98	+ 0.15
129.81^c	.976676	.16357	.16357	.16357	0^c	0^c	− .25
130.56	.982319	.17767	.177058	.176951	+ .3	+ .37	− .10
130.86	.984576	.18462	.183348	.183190	+ .7	+ .78	+ .6
131.39	.988564	.19392	.19630	.19600	− 1.2	− 1.05	+ .3
132.91	1.000000	(.305, new)	.305	.301	0.0	0.0	.0
		(.301, old)		Av. diff. ΔV_g =	.9%	.9%	.34%
					range τ (0.55 − 1.0 T_{cr})		(0.9–1.0 T_{cr})

[a] d_{gas} in parentheses are calculated from the Leiden eq. of state. d_{gas} at T°K. = 120.90 is uncertain according to Leiden. [b] The mean density equation (5) was used to evaluate d_{gas} at very high T°. [c] Indicates reference points.

T, °K.	$\ln V_g/V_{cr}$ Obsd. $d_{cr} = 0.305$ I	$\ln V_g/V_{cr}$ Obsd. $d_{cr} = 0.301$ II	$\ln V_g/V_{cr}$ Calcd. $d_{cr} = 0.305$ I	$\ln V_g/V_{cr}$ Calcd. $d_{cr} = 0.301$ II	$\Delta \ln$ % Obsd. I–II	$\Delta \ln$ % Calcd. I–II	$\Delta \ln$ % Obsd. − Calcd. I	$\Delta \ln$ % Obsd. − Calcd. II
68.13	5.94347	5.93027	6.01912	6.00376	+0.2	+0.2	−1.2	−1.3
73.56	5.18383	5.17063	5.20650	5.19257	+ .25	+ .25	−0.4	−0.4
78.03^c	4.63514^c	4.62193^c	4.63514^c	4.62193^c	+ .3^c	+ .3^c	0^c	0^c
87.15	3.67392	3.66072	3.67168	3.65907	+ .35	+ .33	+ .06	+ .04
90.28	3.39891	3.38571	3.38918	3.37658	+ .4	+ .38	+ .27	+ .25
103.50^c	2.37957^c	2.36637^c	2.37957^c	2.36637^c	+ .5^c	+ .5^c	0^c	0^c
107.61	2.11455	2.10134	2.10805	2.09454	+ .63	+ .65	+ .30	+ .32
120.90	[1.31335]	[1.30015]	[1.28101]	[1.26656]	[+1.0]	[+1.1]	[+2.5]	[+2.6]
125.60	0.96612	0.95292	0.96820	0.95385	+1.4	+1.5	−0.2	−0.1
129.81^c	.62307	.60987^c	.62307^c	.60987^c	+2.0^c	+2.0^c	0^c	0^c
130.86	.50201	.48882	.50894	.49658	+2.6	+2.4	−1.4	−1.6
131.39	.45286	.43967	.44067	.42897	+3.0	+2.7	+2.7	+2.4
132.91	.0	.0	.0	.0	....	....	....	....
							0.62	**0.64**
							I	**II**

average Δ ln %
(0.55–0.96 T_{cr})

Comparison of equations
Average differences:
Tolerance of equations (1) and (3), $\Delta \ln$ % est. = **0.95%**
Average deviation of equation (3), $\Delta \ln V_g/V_{cr}$ = **0.62%**
Average deviation of equation (1), $\Delta \ln V_g/V_{liq}$ = **0.58%**

do the corresponding logs; this fact makes the equation applicable at these extreme temperatures.

In order to see how the proposed equation compares with other test equations, we have checked the above results against the Leiden eq. (5), which at very high temperatures can be used for evaluating vapor densities. We see that in the interval 0.9–0.98 T_{cr} the individual deviations are of the same order of magnitude for both eqs. (3) and (5), but at still higher temperatures the Leiden formula fits experimental data much better. On the whole we find that the proposed equation is valid in a long range 0.55–1.0 T_{cr} with an average accuracy $\Delta V_g = 0.9\%$. The Leiden eq. (5) applies to a short interval 0.9–1.0 T_{cr} within $\Delta V_g = 0.35\%$.

We have next proceeded to test other substances in a manner entirely similar to that described above. In each case we have compared the proposed equation with other vapor volume formulas. The intercomparison was done by a graphical method. For every substance the deviations of each equation from one and the same set of experimental data were calculated and plotted to the same scale so that the regional distribution and the average value of each set of deviations could be compared among themselves.

In Table II, which is similar in construction to Tables II of earlier articles,[1,2] we give the results of our calculations for the same nine typical substances portrayed in Fig. 1. The deviations are given up to the highest volumes known and are recorded in volume per cent. Average deviations are also given. In examining Table II we find certain points of interest with regard to individual substances which will be mentioned briefly.

Helium.—Its densities between 0.45–0.75 T_{cr} were evaluated from the latest form of the Leiden eq. of state[6]; the densities between 0.85–0.90 T_{cr} have been measured directly, while the value at 0.96 T_{cr} evidently has been calculated from the rectilinear diameter equation (6).[5] Examining our calculations we see that the proposed equation is in agreement with both the observed and calculated Leiden data, except at 0.96 T_{cr}. The average deviation $\Delta V_g = 0.5\%$ (0.45–0.92 T_{cr}) is much smaller than could be expected, as is evident from the fact that the tolerance for helium is $\Delta \ln \%$ estd. = 4.0%,[1] while the actually found deviation is $\Delta \ln \phi = 0.3\%$.

Contrasting the proposed equation with other formulas, we find that the volume ratio equation (1), when recalculated on the basis of the latest density data,[6] gives excellent agreement. At every point it runs parallel to the proposed equation and its average deviation is exactly the same as for the latter: $\Delta V_g = 0.5\%$. (In evaluating the averages the large discrepancies at 0.96 T_{cr} were omitted.) We have further checked our results against the standard Clapeyron equation for helium (available only between melting and boiling points) and against Meyers' equation (given for helium only at the high temperatures 0.8–0.9 T_{cr}).

Meyers' equation was discussed previously.[1,7] It is in good agreement with observed data of many liquids in the range melting point to 0.9 T_{cr}. At higher temperatures it is not valid. For helium its average deviation is $\Delta V_g = 1\%$ (0.8–0.9 T_{cr}). The Clapeyron equation has an equivalent accuracy at lower temperatures. We conclude from above that both the proposed and the volume ratio functions represent the helium data more closely and in a longer range than either the Clapeyron or Meyers' equation, the shortcoming of the former undoubtedly being due to inaccuracies in the data for latent heat of helium.

Krypton.—Its densities have been measured at Leiden up to 1° of T_{cr}. One value, however, for $\tau = 0.6000$, was calculated by them from their equation of state.[6] Contrary to the case of helium, we find that for this particular value the proposed and the volume ratio equations deviate enormously from the Leiden equation of state, while they fit remarkably well the other (observed) data for this substance. Both equations average $\Delta V_g = 0.23\%$ between 0.65–0.98 T_{cr}. The mean density equation (5) is equivalent to the other two between 0.85–0.98 T_{cr} ($\Delta V_g = 0.21\%$ on the average). In the immediate vicinity of the critical point the latter is definitely superior (average $\Delta V_g = 0.9\%$ as against 3.0% and 2.8%).

Ethane.—Its vapor densities between 0.65–0.90 T_{cr} are taken from the "Int. Crit. Tables" and are based on the experiments of Porter. The data at high temperatures (0.90–0.995 T_{cr}), as well as the critical constants, are from the new measurements of Sage, Webster and Lacey.[6] In our calculations the first two reference points were taken from the "Int. Crit. Tables" data and the third one from the data of Sage and co-workers. This was done purposely in order to test the consistency of the two sets of measurements. In fact we find exceptionally close agreement between the proposed equation and the experimental values of Porter and of Sage. With the exception of one value at 0.9 T_{cr}, the deviations in the range 0.65–0.96 T_{cr} are all under 0.2% and average 0.09 volume per cent. Even in the critical region (0.96–1.0 T_{cr}) the average $\Delta V_g = 0.6\%$. Comparing these results with the reduced diameter eq. (7), used by "Int. Crit. Tables," we see that the latter is much inferior, since its average is $\Delta V_g = 0.7\%$ (0.8–1.0 T_{cr}).[8]

As to the volume ratio equation, we find that calculations based on the new data of Sage, Webster and Lacey are less accurate than those based on the "Int. Crit. Tables" values alone. The average deviation is $\Delta V_g = 0.8\%$, as compared with 0.5% obtained previously.[1,9] The only explanation seems to be that the liquid densi-

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(7) C. H. Meyers, *Bur. Standards J. Research*, **11**, 691 (1933).

(8) We also notice that the "Int. Crit. Tables" diameter eq. (7), leads to a d_{cr} value which is 5% higher than that obtained by Sage and co-workers, or that selected by Pickering (see table of best critical data: "Int. Crit. Tables," Vol. III, 248 (1928)).

(9) Through oversight the critical temperature, the estimated tolerance and the actual and per cent. log deviations of the volume ratio eq. (1) for ethane were incorrectly given in the article on Orthobaric Densities.[1] These should be: T_{cr} = 305.3° K.; $\Delta \ln \%$ estd. = 0.5%; $\Delta \ln \rho$ = 0.0045 (actual) = 0.25%.

ties of Sage and collaborators are not quite consistent with the measurements of earlier observers recorded in the "Int. Crit. Tables." However, we find that the parameters of the recalculated volume ratio equation are of the same order of magnitude as before[1,9]: $K_{cr} = 3.638$ (Sage's critical data); $k = 3.681$; $m = 0.4175$; $n = 1.199$.

Acetylene.—In the case of this substance the question arises as to the correct value of the critical temperature. The different observed values range from 37.05° by Ansdell (1879) and by Mathias (1909) to 35.4° by Cardozo and Baumé (1912). In the "Int. Crit. Tables" the value 36.0° is used as the best average of the above. The vapor densities of acetylene are given in the "Int. Crit. Tables" to two significant figures only. The data for high temperatures are based on the experiments of Mathias (Leiden). The values at lower temperatures are evidently calculated from the reduced rectilinear diameter eq. (8). This equation is in agreement with Mathias' observed densities between −23° and +29° and leads to his value of d_{cr}, but in the interval +29° to +36.0° the discrepancy amounts to 2–3%. Remembering that the diameter equation is usually quite accurate in the critical region, one may ask whether the value 36.0° accepted as T_{cr} by "Int. Crit. Tables," might not be in error. In order to investigate this point we have turned to the original paper of Mathias.[6] It appears that his density values are much more consistent with the value $T_{cr} = 37.05°$, since the equation $d_m = a + bt°$ referred to this temperature agrees with his observations within 0.5% up to the highest temperatures.

In Table II we have applied the proposed equation both to the "Int. Crit. Tables" data and to Mathias' data for acetylene. For comparison we give the diameter equations (8), and (6), used by "Int. Crit. Tables" and Mathias, respectively. Examining the respective four sets of deviations, we notice that the densities of the "Int. Crit. Tables" cannot be represented by the proposed equation. The discrepancies amount to several volume per cent. and are especially large between 0.85–0.95 T_{cr}, which indicates the possibility of an error in T_{cr} greater than 0.5°.[1]

On the other hand, when referred to $T_{cr} = 37.05°$ and compared with the original d_{gas} values of Mathias, the proposed equation gives very good agreement. In the interval 0.9–0.98 T_{cr} it is slightly superior to Mathias' diameter eq. (6), ($\Delta V_g = 0.3\%$ against 0.5%). In the critical interval the reverse is true, the respective differences being $\Delta V_g = 1.5\%$ and 0.6%. We might add that the constants k'', m'', n'', obtained from Mathias' data, are quite in line with those of other substances.

Carbon Dioxide.—For this substance two sets of measurements are available, both in the short interval 0.9–1.0 T_{cr}. Those of Lowry and Ericson are checked against the cubic vapor density equation originally suggested by Jüptner.[6,12] The more recent measurements of Michels, Blaisse and Michels[6] are checked against the rectilinear diameter eq. (6). These authors have also given new critical constants for carbon dioxide, which are in good agreement with those of other observers. In our calculations we have used the critical data of Michels and collaborators, but the reference points were taken from the d_{gas} values of Lowry and Ericson, since we were interested in the numerical test of the cubic density equation. Our results show that both the proposed and the volume ratio equations deviate by less than 1% from the experimental densities of either observer, thereby indicating the high consistency of the two sets of measurements. On the other hand both equations are quite comparable to the cubic formula, the respective average deviations being $\Delta V_g = 0.8\%$, 0.8%, and 0.7% (0.9–0.99 T_{cr}). The rectilinear diameter eq. is much more accurate in this interval (average $\Delta V_g = 0.25\%$).

The remaining four substances: benzene, *n*-pentane, ammonia and ethyl alcohol are all checked in Table II against Meyers' equation discussed above. We find that **ammonia** shows excellent agreement both with the proposed and with Meyers' equations, the latter being superior at very low temperatures. In our calculations the three reference points were taken from the Bureau of Standards data. The deviations from these data are very small, averaging $\Delta V_g = 0.15\%$ and 0.04%, respectively (0.5–0.8 T_{cr}). The deviations from the d_{gas} values obtained from the Beattie and Lawrence equation of state[6] are larger: $\Delta V_g = 0.3$ and 0.4% on the average (0.8–0.9 T_{cr}). As to ***n*-pentane**, we see that Meyers' equation excels over the proposed equation at low and moderately high temperatures. ($\Delta V_g = 0.4\%$ as against 0.8% between 0.65–0.97 T_{cr}.) In the critical neighborhood Meyers' equation is not expected to hold and, accordingly, we find its deviation to rise to 15% at $\tau = 0.995$, where the proposed equation differs as little as 0.6% from observed value.

Ethyl alcohol is represented much more accurately by the proposed equation than by that of Meyers. We see that the former follows Young's data all along the line with an average $\Delta V_g = 0.5\%$ (0.6–0.96 T_{cr}). The latter deviates unevenly at different temperatures, averaging $\Delta V_g = 1.5\%$ between 0.5–0.8 T_{cr} and $\Delta V_g = 3\%$ between 0.8–0.99 T_{cr}. Substitution of the vapor densities evaluated by the Bureau of Standards (0–130°)[6] makes the agreement definitely worse for either formula, which suggests a lack of consistency between the two sets of d_{gas} data. **Benzene** shows a similar lack of consistency between Young's measured densities and those calculated by the Bureau of Standards from the latent heat (0–130°).[6] Since Young's values are extrapolated at low temperatures, we have used the Bureau of Standards values for the first reference point. We find that the proposed equation deviates from the calculations of the Bureau of Standards by $\Delta V_g = 1.5\%$ (0.6–0.8 T_{cr}). On the contrary, the densities measured by Young are in close agreement with our calculations, the deviations averaging $\Delta V_g = 0.5\%$ (0.8–0.97 T_{cr}). The equation of Meyers shows a reverse picture: it fits the Bureau of Standards values within $\Delta V_g = 0.1\%$ and differs from those of Young by $\Delta V_g = 2\%$ on the average.

The inspection of the foregoing nine typical substances shows that the proposed equation expresses vapor densities of different liquids very accurately (within one volume per cent. or less) in the range boiling point to 0.97 T_{cr}. Near the critical temperature the majority of substances show larger differences, but only a few give as much as 5–6% deviation even at those very high temperatures. When compared with other formulas, the proposed equation is found equivalent to the volume ratio function, as regards precision. It is also found comparable and in some cases superior to other vapor volume equations recorded in the literature. Only in the critical region it is less accurate than the mean density formulas (5)–(8) of Cailletet and Mathias.

TABLE II

COMPARISON OF THE PROPOSED EQUATION WITH OTHER VAPOR VOLUME EQUATIONS, AS SHOWN BY THE DIFFERENCES: ΔV_g % OBSD. − CALCD.

Substances:	(a) Helium			(b) Krypton			(c) Ethane			(d) Acetylene			
Equations:	Proposed	Volume ratio	Clapeyron and Meyers	Proposed	Volume ratio	Diameter eq. (6)	Proposed	Volume ratio	Diameter eq. (7)	Proposed	Diameter eq. (6)	Proposed	Diameter eq. (8)
τ	ΔV_g %			ΔV_g %			ΔV_g %			ΔV_g %			
0.400	...	...	...										
.450	0.9[a]	0.5[a]	1.5[c]										
.500	.1	.08	...										
.550	.25	.22	...	....	....	....							
.600	.42	.38	...	(27.0)[a]	(28.0)[a]		....	...	...			...	
.650	.40	.38	1.3	0.08[b]	0.22[b]		0.1[f]	1.2[f]				1.6[j]	
.700	.20	.20	...	.28	.50		.1	1.5				0.9	
.750	.00	.00	0.7	.22	.20		.03	0.9		...	...	0.22	
.800	.00[b]	1.00[b]	1.5[d]	.02	.10		.01	0.2		0.00[i]	5.00[i]	1.0	
.850	.95	1.2	1.25	.12	.08	0.20[b]	.06	1.5	0.9[f]	...	...	4.0	1.3[j]
.900	.18	0.5	0.85	.30	.15	.09	.8	4.2	0.4	.10	1.00	3.5	0.8
.910	.05	0.2	...	.45	.35	.12	....	...	...	.04	0.20	3.4	.75
.920	...	...	...	.58	.50	.15	....	...	...	.06	0.6	3.4	.65
.930	...	...	...	.60	.55	.15	....	...	...	.25	0.9	2.7	.5
.940	...	...	...	.45	.30	.18	....	...	...	.4	1.0	2.2	.4
.950	...	...	...	.35	.15	.20	.2[g]	0.25[g]	...	.3	0.6	1.7	.2
.960	(4.0)[e]	(8.0)[e]	...	.15	.03	.25	.1	0.2	2.0[g]	.9	.6	...	...
.970	...	...	...	.10	.07	.25	.5	1.4	0.5	.3	.6	...	...
.980	...	...	...	.30	.13	.20	.5	1.7	0.7	.00	.00	0.00	.10
.990	...	...	...	....	....	....	.7	0.7	1.0	1.5	.6	...	...
.995	...	...	...	3.2	2.8	0.90	.6	...	...	...	...	...	...
.999	...	...	...	....	....	....	....	...	...	...	...	...	...
1.000	0.00	0.00	7.00[d]	0.00	0.00	0.00	0.00	0.00	5.00[h]	0.00	0.00	0.00	0.00
Av. ΔV_g =	0.5%	0.5%	1.0%	0.23%	0.23%	0.21%	0.09%	0.8%	0.7%	0.3%	0.5%	1.6%	0.6%

Substances:	(e) Carbon dioxide				(f) Benzene		(g) n-Pentane		(h) Ammonia		(j) Ethyl alcohol	
Equations:	Proposed	Volume ratio	Jüptner's cubic eq.	Diameter eq. (6)	Proposed	Meyers' eq.	Proposed	Meyers' eq.	Proposed	Meyers' eq.	Proposed	Meyers' eq.
τ	ΔV_g %				ΔV_g %		ΔV_g %		ΔV_g %		ΔV_g %	
0.450					....	....			....	....		
.500					20.0[n]	....			2.7[q]	0.01[q]	...	...
.550					5.0	0.1[n]	...	...	.7	.02	8.2[s]	1.0[s]
.600					1.9	0.1	(1.4)[p]	...	.07	.02	0.4	1.1
.650					0.9	0.05	0.2[o]	0.4[o]	.08	.05	.52	1.3
.700					1.9	0.35	.7	.08	.08	.07	.7	1.2
.750					1.7[o]	1.4[o]	.5	.3	.12	.08	.5	1.6
.800					0.25	2.5	.05	.6	.25[r]	.05[r]	.30	2.2
.850	...	...	...	....	0.08	2.5	.28	.18	.4	.5	.7	3.3
.900	0.4[k]	0.55[k]	0.4[k]		0.6	2.4	1.6	.4	.55	.9	.55	3.9
.910	0.9[l]	1.0[l]	1.1	0.00[l]	....	....	...	...	....	....	...	...
.920	2.2[k]	2.5[k]	1.9	.10	....	....	2.4	.2	....	....	...	...
.930	1.0[l]	1.2[l]	1.0	.15	....	....	...	...	....	....	.3	3.5
.940	0.4[k]	0.4[k]	0.5	.18	....	....	...	...	....	....	...	...
.950	1.0[k]	1.0[k]	.07	.19	0.55	2.4	1.2	.75	....	....	.05	3.3
.960	1.2[l]	1.6[l]	.10	.20	0.2	2.3	0.85	0.9	....	....	1.0	3.0
.970	0.4[k]	0.7[k]	.30	.20	0.1	2.2	.4	...	....	....	2.0	2.0
.980	0.4[l]	0.6[l]	...	.20	1.8	2.2	.1	...	....	....	3.0	1.2
.990	0.6	0.45	...	.00	2.5	2.1	.6	...	....	....	...	...
.995	2.0	1.4	...	1.2	....	....	...	15.0	....	....	6.0	0.6
.999	3.4	3.4	...	0.8	....	....	...	...	....	....	...	...
1.000	0.00	0.00	0.3[m]	0.00	0.00	19.0	0.00	17.0	0.00	not given	0.00	not given
Av. ΔV_g =	0.8%	0.8%	0.7%	0.25%	1.0%	1.2%	.8%	0.4%	0.25%	0.15%	0.5%	2.1%

[a] d_g values (0.45 − 0.75 T_{cr}) taken from Leiden equation of state. [b] d_g (0.80 − 0.91 T_{cr}) taken from Leiden measurements. [c] ΔV_g % by Clapeyron equation (0.45 − 0.75 T_{cr}). [d] ΔV_g % by Meyers' equation (0.80 − 1.00 T_{cr}). [e] d_g (0.96 T_{cr}) taken from diameter equation (6). [f] d_g (0.65 − 0.90 T_{cr}) taken from "Int. Crit. Tables." [g] d_g (0.95 − 1.00 T_{cr}) obsd. by Sage, Webster and Lacey. [h] Equation (7) leads to $\Delta V_{cr} = 5\%$. [i] All values of d_g obsd. by Mathias, t_{cr} = 37.05°. [j] All values of d_g from "Int. Crit. Tables," t_{cr} = 36.0°. [k] d_g obsd. by Lowry and Ericson at various points (0.90 − 0.97 T_{cr}). [l] d_g obsd. by Michels, Blaisse and Michels at various points (0.91 − 1.00 T_{cr}). [m] The cubic equation leads to $\Delta V_{cr} = 0.3\%$. [n] d_g taken from Bureau of Standards calculations (0.50 − 0.70 T_{cr}). [o] d_g obsd. by Young (0.75 − 1.00 T_{cr})(0.65 − 1.00 T_{cr}). [p] d_g extrapolated by Young (0.60 T_{cr}). [q] d_g taken from Bureau of Standards observations. [r] d_g values taken from Beattie and Lawrence equation of state (0.80 − 0.90 T_{cr}). [s] All values of d_g from Young's data only.

In Table III we give, as in previous papers, a brief summary of our calculations on thirty liquids. The table is constructed in the same way as before.[1,2] The arrangement of liquids is in the order of ascending $\ln V_g/V_{cr}$ values at $\tau = 0.6000$.

In part 1, column 3 of this table we give numbers to literature references, which are listed in Table V below. The fourth column gives values of critical densities which in all cases, except that of ethyl ether, were obtained by extrapolation from mean density equations. The critical density of ethyl ether was obtained by direct measurement (Schröer[6]). In column 5 are given the observed values of $\ln V_g/V_{cr}$ which were read directly from the graph at $\tau = 0.6000$. In the last three columns we compare the average deviations of the proposed equation ($\Delta \ln \phi$ %) with the estimated tolerances ($\Delta \ln$ % estd.) and with the corresponding average deviations of the volume ratio equation ($\Delta \ln \rho$ %). The figures in the columns ($\Delta \ln$ % estd. and $\Delta \ln \rho$ %) are the same as in the article on orthobaric densities[1] with few corrections, namely: two new substances, krypton and carbon dioxide, have been added and three old ones, helium, ethane and acetylene, have been recalculated on the basis of more reliable data.

Table III

Summary of Results

Substances in the table are arranged in the ascending order of curves

	Substances	Literature[a]	$d_{crit.}$[b] g./cc.	$\ln V_g/V_{cr}$ Obsd. $\tau = 0.6000$	Average per cent. differences[c] $\Delta \ln \phi$ % found	$\Delta \ln \rho$ % found	$\Delta \ln$ % estd.
1	Helium	2, 1, 10	0.06930	2.60	0.3	0.26[d]	4.0
2	Hydrogen	2, 1	.03102	3.29	.21	.54	0.9
3	Neon	2, 1, 10	.4835	4.07	.86	.61	1.0
4	Krypton	2, 1	.9191	4.22	.15	.09	1.0
5	Oxygen	2, 1	.4299	4.32	.55	.54	1.0
6	Carbon monoxide	2, 1	.305	4.42	.62	.58	1.0
7	Nitrogen	2, 1	.311	4.42	.63	.37	1.0
8	Ethylene	2, 1	.21597	4.60	.57	.52	0.7
9	Ethane	3	.21216	4.70	.07	.35[d]	.5
10	Hydrogen chloride	5	.424	4.78	.48	.32	.7
11	Nitrous oxide	5	.451	4.85	.35	.40	.7
12	Acetylene	2	.230	below triple pt.	.20	.16[d]	1.0[e]
13	Methyl ether	5	.2714	5.09 extrap.	.63	.50	0.5
14	Carbon dioxide	4	.467	. .	.74	.56[d]	.7[e]
15	Carbon tetrachloride	6	.5576	5.13	.35	.14	.5
16	Benzene	6, 10	.3045	5.22	.25	.18[f]	.5
17	*i*-Pentane	6	.2343	5.23	.07	.06	.5
18	*n*-Pentane	6, 10	.2323	5.35	.53	.40	.5
19	Ammonia	7, 10	.23635	5.35	.10	.05[f]	.25
20	Monofluorobenzene	6	.3541	5.35	.10	.10	.5
21	Methyl formate	6	.3489	5.42	.34	.18	.5
22	Ethyl ether	6	.265	5.48	.24	.24	.5
23	*n*-Hexane	6, 10	.2344	5.52	.38	.07	.5
24	Water	8, 10	.31274	5.75	.09	.26	.25
25	Acetic acid	6	.3506	5.75	.37	.11	.5
26	Ethyl propionate	6	.2965	6.00	.13	.05	.5
27	Sulfur trioxide	5	.630	6.20 extrap.	.25	.73	.5
28	Methyl alcohol	6, 10	.2722	6.70	.19	.08	.5
29	Ethyl alcohol	6, 10	.2755	6.95	.20	.20	.5
30	Nitrogen tetroxide	9	.570	7.00 extrap.	.20	.20	.5

[a] The numbers in column 3 indicate the corresponding references on observed vapor densities and critical densities listed in Table V. [b] The critical densities are all extrapolated from corresponding equations, except that of ethyl ether which is the value actually measured by Schröer. [c] The per cent. deviations given in the last three columns refer to the range of reliable densities (0.6–0.95 T_{cr}) with the following exceptions: helium, hydrogen, ethylene (0.45–0.95); oxygen and sulfur trioxide (0.75–0.95); acetylene and carbon dioxide (0.90–0.99); and nitrogen tetroxide (0.65–0.75). [d] The average deviations of the volume ratio equation, $\Delta \ln \rho$ %, for helium, ethane, carbon dioxide and acetylene are recalculated in accordance with the new data for these substances (see Tables II and V for details). [e] The tolerances of the proposed equation, $\Delta \ln$ % estd., for acetylene and carbon dioxide refer to the range 0.9–0.95 T_{cr} and are evaluated according to the method given in the article on orthobaric densities.[1] [f] The average deviations $\Delta \ln \rho$ % for benzene and ammonia were evaluated from Young's, respectively, Bureau of Standards data only.

TABLE III (*Concluded*)

Proposed equation: $\ln V_g/V_{cr} = k''(1 - \tau^2)^{m''}/\tau^{n''}$ V_g = vapor volume (cc./g.)

	Substances	K_{cr}[a]	k''[b]	m''	n''	Average differences ΔV_g %[c] Proposed equation	Volume ratio eq.	Meyers' eq.	Diameter eq.
1	Helium	3.264	(1.8967)	(0.43255)	(0.98753)	0.5	0.5	1.0	1.8
2	Hydrogen	3.273	2.3567	.51218	1.0880	.6	1.4	...	0.6
3	Neon	3.245	2.3301	.44312	1.4955	1.5	1.9	1.4	1.7
4	Krypton	3.480	2.5458	.46526	1.4115	0.23	0.23	...	0.21
5	Oxygen	3.421	(2.2973)	(.40623)	(1.5792)	(.7)	(1.0)	...	(.5)
6	Carbon monoxide	3.440	2.5061	.46404	1.5229	.6	1.6	...	.3
7	Nitrogen	3.426	2.5798	.44696	1.4428	1.0	1.2	...	2.8
8	Ethylene	3.527	(2.6454)	(.46750)	(1.4949)	0.9	2.0	...	2.6
9	Ethane	3.638	2.8023	.48283	1.4300	.09	0.8	...	0.7
10	Hydrogen chloride	3.801	2.8032	.46448	1.4569	1.0	1.0	...	1.1
11	Nitrous oxide	3.630	2.8326	.48209	1.4808	0.8	1.0	...	0.86
12	Acetylene	3.647	(2.8785)	(.49507)	(1.4520)	.3	0.35	...	.5
13	Methyl ether	3.719	(2.7887)	(.45821)	(1.6070)	1.4	1.7	...	.8
14	Carbon dioxide	3.639	(2.9412)	(.46665)	(1.1753)	0.8	0.8	0.7[d]	.25
15	Carbon tetrachloride	3.680	2.8831	.46394	1.5088	.7	.5	...	.52
16	Benzene	3.755	2.9982	.47406	1.4850	1.0	.8	1.2	1.4
17	*i*-Pentane	3.735	2.9148	.47063	1.5466	0.25	.2	...	0.23
18	*n*-Pentane	3.766	2.9233	.46216	1.5727	.8	.4	0.4	.4
19	Ammonia	4.125	(3.1678)	(.49408)	(1.4770)	.25	.4	.15	..
20	Monofluorobenzene	3.796	2.8669	.45069	1.6231	.2	.4	...	.5
21	Methyl formate	3.922	2.9612	.45990	1.5872	.7	.5	...	.5
22	Ethyl ether	3.878	2.9216	.45221	1.6219	.5	1.0	...	1.9
23	*n*-Hexane	3.830	3.0092	.46273	1.5946	.8	0.6	1.0	1.0
24	Water	4.234	3.2813	.47169	1.5190	.17	1.7	0.1	0.03[e]
25	Acetic acid	4.991	3.1956	.47403	1.5677	1.3	0.6	...	.7
26	Ethyl propionate	3.923	3.1312	.46283	1.6627	0.6	.4	...	.35
27	Sulfur trioxide	3.805	(4.1556)	(.55677)	(0.8308)	.6	1.7	...	.25
28	Methyl alcohol	4.559	3.5527	.46455	1.6338	1.0	0.4	1.2	1.2
29	Ethyl alcohol	4.026	3.5420	.48701	1.7438	0.5	1.0	2.1	1.0
30	Nitrogen tetroxide	4.385	(4.3281)	(.52971)	(1.3151)	.9	1.0	...	..

[a] The critical coefficient $K_{cr} = (RT_{cr})/(P_{cr}V_{cr})$ is given for comparison. The values are the same as in the previous papers, except those of ethane, carbon dioxide, acetylene, ethyl ether. For these substances K_{cr} was recalculated in accordance with the new values for the critical constants (see Table V). [b] The values of k'', m'', n'', in brackets are not reliable, the range of known densities being too short, or the data at the reference points being uncertain. [c] The average deviations for the proposed equation and the volume ratio equation refer in general to the range: 0.6–0.97 T_{cr}. Exceptions: see footnote *c* in the first half of Table III. The average deviations for Meyers' equation refer to the range 0.6–0.9 T_{cr}. Exceptions: helium (0.8–0.92 T_{cr}); water (0.42–0.95 T_{cr}); ammonia (0.5–0.9 T_{cr}); benzene (0.7–0.95 T_{cr}); methyl and ethyl alcohols (0.55–0.97 T_{cr}). The average deviations for the mean density equation refer in general to the range: 0.85–1.0 T_{cr}. Exceptions: helium, ethyl ether, *n*-hexane, methyl formate (0.75–1.0 T_{cr}); hydrogen, ethane, hydrogen chloride, benzene (0.7–1.0 T_{cr}); neon; nitrous oxide, methyl ether (0.6–1.0 T_{cr}); Acetylene and carbon dioxide (0.9–1.0 T_{cr}) (for literature see Table V). [d] The equation for carbon dioxide in column 9 is that of Jüptner and used by Lowry and Ericson (0.9–0.97 T_{cr}). [e] The equation for water in column 10 is that by Keyes, Smith and Gerry (0.45–0.95 T_{cr}).

Examining the three sets of deviations, we see that in all cases, except that of carbon dioxide, the $\Delta \ln \phi$ % of the proposed equation are smaller than the estimated tolerances and are very close to the $\Delta \ln \rho$ % of the volume ratios.

We conclude that the proposed equation holds with required accuracy in twenty-nine cases out of thirty and that it has the same reliability as the volume ratio equation.

In part 2 of Table III we give the constants k'', m'', n'' of the proposed equation together with the critical coefficients (for the purpose of comparison). The latter values are the same as given before, except a few new data: the K_{cr} of ethane, carbon dioxide, acetylene and ethyl ether. In the last four columns the precision of the proposed equation is compared with the precision of other vapor volume functions, the deviations V_g obsd. − V_g calcd. being in volume per cent.[10] The literature references on the different equations are given under individual substances in Table V below.

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(10) The ΔV_g % of the volume ratio equation are taken from the article on orthobaric densities; ref. 1, Table III$_2$, column 6. To obtain the volume per cent. deviations the actual log differences were multiplied by 100.

In examining individual liquids with regard to the accuracy of the proposed equation, we notice, as in the case of pressures, that the best agreement with experiment is found for those substances recently measured, the average deviations being between 0.09–0.6%. These are: water, ammonia, krypton, carbon dioxide, helium and ethane. Of the substances measured by Young, *i*-pentane, monofluorobenzene, ethyl ether, ethyl propionate and ethyl alcohol fall in the same category, while *n*-pentane, *n*-hexane, carbon tetrachloride, methyl formate, methyl alcohol, acetic acid and benzene deviate from experiment by about 1% on the average. Of the substances listed in the "Int. Crit. Tables," only one, acetylene, has a set of adjusted vapor densities less consistent than the original data (of Mathias). In all other instances, methyl ether, hydrogen chloride, sulfur trioxide and nitrous oxide, the adjusted vapor densities of "Int. Crit. Tables" were found in close agreement with the proposed equation, the average deviations ranging between 0.5–1.0 volume per cent., while the original data of the respective observers were found inconsistent with both the "Int. Crit. Tables" data and with our calculations.[11]

Comparison of the Constants k'', m'', n'' of the Proposed Vapor Volume Equation.—These constants possess the same general characteristics as the corresponding parameters for vapor pressures and for volume ratios.[2,1] Thus we find that helium and nitrogen tetroxide have extreme values of k'', m'' and n''. We also notice that the parameters change but little from substance to substance, the limits being: k'', from 1.89 (He) to 4.32 (N_2O_4); m'', from 0.4062 (O_2) to 0.5568 (SO_3); and n'', from 0.8809 (SO_3) to 1.744 (C_2H_5OH). Where two substances are located on adjacent curves, their parameters become very close, as was found for other properties. For instance: ethyl ether and *n*-hexane have k'' = 2.9216 and 3.0012; m'' = 0.4522 and 0.4627; n'' = 1.622 and 1.595; similarly water and acetic acid have k'' = 3.281 and 3.196; m'' = 0.4717 and 0.4740; and n'' = 1.519 and 1.568; etc.

We notice further (as before) that the constant k'' varies more than m'' or n''. The increase of the constant k'' from substance to substance is parallel to the rise of the critical coefficient and to the order of curves $\ln V_g/V_{cr}$. For each substance it stands in almost constant ratio to its critical coefficient, the values K_{cr}/k'' lying within narrow limits, 1.14–1.39. Since the same parallelism was observed with regard to the curves $\ln P_{cr}/P_s$ and $\ln V_g/V_{liq.}$, we conclude that the critical coefficients exert a directing influence on the arrangement of the above three thermodynamic properties. To what extent this influence is alike for all of them can be seen by comparing Table III of the present paper with Tables III of the earlier articles.[1,2] We find that the first eighteen and last three of the vapor volume curves (helium to *n*-pentane and methyl alcohol to nitrogen tetroxide) have identical positions with the volume ratio curves. Carbon dioxide is placed just below carbon tetrachloride, which is different from its position in the pressure table; this, however, is provisional inasmuch as accurate measurements of its densities at low temperatures are not available. Krypton is placed just below oxygen in all three tables. The nine remaining substances exhibit slight shifts in their position: for instance, monofluorobenzene is removed from benzene even further than in the volume ratio table, ammonia entering between it and *n*-pentane. Acetic acid, ethyl propionate and sulfur trioxide follow each other as in the volume ratio table. Water, on the contrary, occupies the same place as in the pressure table, just above *n*-hexane.

In summarizing we can say that the three properties, vapor pressures, vapor volumes and volume ratios of different substances show almost identical behavior for the equilibrium liquid–vapor, as demonstrated by the relative succession of their curves and by the close correspondence of their k and n parameters. As appropriate examples we can cite in addition to that of water[3] two other substances, nitrogen tetroxide and carbon monoxide. The former has respective k values 5.4, 4.33, 4.0, while its n values are 1.24, 1.31, 1.22; the latter has k values 2.77, 2.51, 3.25, and n values 1.48, 1.52, 1.32.

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(11) The case of nitrous oxide is typical in this regard. Its densities and critical data have been measured many times, but with little concordance. Only recently Quinn and Wernimont[6] have carried out new measurements over a long temperature range. On checking these data against the cubic equation of Jüptner (same as used for carbon dioxide by Lowry and Ericson), they have found complete lack of agreement, the deviations ranging from 2–50% and averaging 17%.[6] The proposed equation fits their values much closer than that of Jüptner, since the average deviation is only 5.5%; however, this cannot be considered a satisfactory agreement, especially since the constants of k'', m'', n'' acquire abnormal values. The agreement of the proposed equation with the adjusted vapor densities of nitrous oxide and with the "Int. Crit. Tables" diameter equation is within $\Delta V_g = 0.8\%$ in the range 0.6–0.97 T_{cr}. Accordingly, the parameter values obtained are in line with those of other substances, suggesting high consistence of the "Int. Crit. Tables" d_{gas} data for nitrous oxide.

TABLE IV

Ratio average		Per cent. deviations 0%		0.2–5.0%		6–10%		11–15%		20–100%	
		number of substances									
		Δa	Δu	Δa	Δu	Δa	Δu	Δa	Δu	Δa	Δu
k'/k''	1.076	0	0	25	7	0	15	3	3	1	4
m'/m''	2.087	0	0	21	20	5	6	1	0	2	3
n'/n''	0.9816	0	0	26	25	0	1	1	1	2	2

In closing this discussion we wish to point out that the parameters k'' and n'' for vapor volume are in no instance exactly equal to the constants k' and n' for pressure, although at first sight the ratios k'/k'' and n'/n'' appear to be close to unity. Similarly, the ratios m'/m'' are never exactly equal to the integer 2. In order to make this clear, we have computed the averages for the ratios k'/k'', m'/m'', n'/n'', on the basis of all the liquids studied, except those with bracketed parameters. In Table IV we show how many substances deviate from those averages (Δa), as well as from the integral ratio values (Δu). On the top of the table we mark per cent. deviations divided into groups. In the vertical columns marked Δa and Δu we give the number of substances contained in each one of these groups:

Table IV shows that the deviation from unity or from 2 is never zero, but for the majority of substances the difference is small. It is also clear that for nearly all thirty liquids the constant k' for pressure is slightly larger than k'' for volume; the reverse is true for the constant n, with but few exceptions; the constant m'' for volume is almost half that of pressure. This regularity is followed by the majority of liquids within 5% or less.

It must be added that of thirty substances only one, sulfur trioxide, has very abnormal ratios k'/k'', m'/m'', and n'/n'' which equal 0.657, 1.54 and 2.67, respectively. The cause of this abnormality lies in the pressure constants which form a very peculiar set of values.[2] The volume parameters of sulfur trioxide are quite within the range of normal values.

Intercomparison of Different Vapor Volume Equations.—Historically there appear to be only four original attempts to express vapor density as function of temperature alone. Cailletet and Mathias observed many years ago that at high temperatures the densities of nitrous oxide, sulfur dioxide and other substances can be expressed by a parabolic equation, which in ordinary and in reduced units is[6,12]

$$d_{\text{gas}} = a - bt - c\sqrt{t_{\text{cr}} - t} = d_{\text{cr}}[1 + B(1 - \tau) - C\sqrt{1 - \tau}] \text{ range: } 0.8\text{–}1.0\ T_{\text{cr}} \qquad (9)$$

Later van Laar and also Jüptner developed on the basis of respective theoretical considerations the relationships

$$d_{\text{gas}} = f(-\sqrt{1-\tau}) = d_{\text{cr}}[1 - \alpha(1-\tau)^{0.5} + \gamma(1-\tau) - \phi(1-\tau)^{1.5} + \kappa(1-\tau)^{2.0} - \nu(1-\tau)^{2.5} + \ldots] \qquad (10)$$

$$d_{\text{gas}} = F(-\sqrt[3]{1-\tau};\ 1+\tau) = d_{\text{cr}}[1 - \omega(1-\tau)^{1/3} + \beta(1-\tau)^{2/3} - \left(\frac{\delta}{1+\epsilon\tau} - 1\right)(1-\tau)] \qquad (11)$$

These were found, however, to be in complete disagreement with experiment.[12]

Finally, Jüptner offered an empirical cubic equation, which was considered by van Laar an artificial relationship,[12] yet was found to give good results at high temperatures[6,12]

$$d_{\text{gaa}} = d_{\text{cr}} + b'(t_{\text{cr}} - t) - c'\sqrt[3]{t_{\text{cr}} - t} = d_{\text{cr}}[1 + B'(1-\tau) - C'\sqrt[3]{1-\tau}] \text{ range: } 0.8\text{–}0.95\ T_{\text{cr}} \qquad (12)$$

In this equation the constants B' and C' are characteristic for each substance.

All other vapor density formulas recorded in the literature and used here for comparison, express d_{gas} in terms of two or more variables. To the category $d_{\text{gas}} = f(d_{\text{liq}}, t)$ belong, besides the volume ratio eq. (1), the different modifications of the mean density equation (5)–(8). Recently two formulas of the type: $V_{\text{gas}} = f(p, t)$ were

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(12) We give the literature on variation of vapor density with temperature: (a) parabolic d_{gas} equations, Cailletet and Mathias, *J. phys.*, **5**, 549 (1886). Further elaboration of same: Mathias, *ibid.*, **1**, 53 (1892). (b) Van Laar's equation of state and the function: $d_{\text{gas}} = f(-\sqrt{1-\tau})$; expansion of it into series and numerical tests, showing disagreement: van Laar; "Die Zustandgleichung," Leipzig, 1924, pp. 132–139, 327–328, 332–333. 344–345. (c) Jüptner's vapor pressure equation and the function: $d_{\text{gas}} = F(-\sqrt[3]{1-\tau}, 1+\tau)$ also numerical test on fluorobenzene (Young's data), showing poor results: Jüptner, *Z. physik. Chem.*, **63**, 355. 360 (1908); **73**, 173 (1910). (d) Cubic d_{gas} equation: Jüptner, *ibid.*, **80**, 299, 307–311 (1912); numerical test on fluorobenzene showing poor agreement when $C' = 2$ is a universal constant: *ibid.*, pp. 309–310; discussion of the cubic equation (assuming B' and C' to be characteristic constants), van Laar, "Die Zustandgleichung." pp. 345–348; numerical tests on carbon dioxide showing good results when equation is applied to high temperatures only and the constants have characteristic values: Lowry and Ericson, THIS JOURNAL, **49**, 2729 (1927). Numerical tests on nitrous oxide showing disagreement when equation is applied to the whole saturation line: Quinn and Wernimont, *ibid.*, **51**, 2002 (1929). (e) Modification of the cubic equation, assuming the coefficient $C' = f(1-\tau)$; also numerical test on fluorobenzene, showing no improvement over $C' = 2$: Jüptner, *Z. physik. Chem.*, **80**, 299, 309 (1912). Further modification of cubic equation, assuming the first term, unity, to be replaced by T/T_{cr} and the constants B' and C' to be equal to each other: $d_{\text{gas}} = d_{\text{cr}}[B''(1-\tau) - B''(1-\tau)^{1/3} + \tau]$; no direct numerical tests are given here, Jüptner, *Z. physik. Chem.*, **85**, 1, 55–57 (1913).

TABLE V

BIBLIOGRAPHY ON EXPERIMENTAL DATA FOR VAPOR VOLUMES AND CRITICAL PROPERTIES; INCLUDING EMPIRICAL TEST EQUATIONS USED BY DIFFERENT OBSERVERS

(1) The new scale of temperature: (Absolute zero = −273.144°C.); improved equation for mean diameter (in ordinary and reduced units); corrected critical temperatures, critical densities and critical coefficients for: helium, hydrogen, neon, oxygen, nitrogen, carbon monoxide, and ethylene (Mathias and Crommelin, *Ann. phys.*, **5**, 137, 143, 144 (1936)); for krypton (Mathias, Crommelin and Meihuizen, *ibid.*, **8**, 467 (1937)); improved equation of state (Leiden), "Leiden Lab. Comm. No. 234e."

(2) Substances observed at the Leiden Laboratories: Helium and carbon monoxide; vapor densities calcd. (eq. of state) and observed; also the corresponding mean diameter equations, *Ann. phys.*, **5**, 137, 143 (1936).

Helium: vapor density at 5°K. (0.96 T_{cr}), also Clapeyron eq. (melting to boiling point), "Leiden Lab. Comm. No. 179c."

Hydrogen, oxygen, nitrogen: vapor densities calcd. (eq. of state) and observed; also corresponding rectilinear diameter equations, *Ann. phys.*, **17**, 416 (1922).

Neon: same, *ibid.*, **19**, 231 (1923).

Ethylene: same, *ibid.*, **11**, 344 (1929).

Krypton: vapor densities calcd. (eq. of state) and observed: *ibid.*, **8**, 467 (1937).

Acetylene: vapor densities observed (−23.75° to t_{cr}); t_{cr} = 37°.05; also the rectilinear diameter equation, Mathias, *Compt. rend.*, **148**, 1102 (1909). Critical density: "International Critical Tables," Vol. III, 230 (1928). Adjusted vapor densities (normal b. p. to t_{cr}); t_{cr} = 36.0°; also the reduced rectilinear diameter equation: *ibid.*, "Int. Crit. Tables," III, 230 (1928).

(3) Ethane: adjusted vapor densities (from Porter) between: normal b. p. and +10° also at +20 and +30°, together with the reduced mean diameter equation of second degree: "Int. Crit. Tables," Vol. III, 230 (1928); observed vapor densities (from isotherms) between +17.6° and t_{cr}; also all critical data, Sage, Webster and Lacey, *Ind. Eng. Chem.*, **29**, 658 (1937).

(4) Carbon dioxide: vapor densities observed (−5.8 to +22.9°); also the cubic equation for d_{gas} as function of temperature alone: Lowry and Ericson, THIS JOURNAL, **49**, 2729 (1927). Vapor densities (from isotherms) between +2.8° and t_{cr}; also all critical data and the rectilinear diameter equation: Michels, Blaisse and Michels, *Proc. Roy. Soc.*, **A160**, 358 (1937).

(5) Substances recorded in the "International Critical Tables" (1928). Hydrogen chloride, methyl ether, sulfur trioxide: adjusted vapor densities (normal b. p. to t_{cr}); all critical data; mean diameter eq.; *ibid.*, Vol. III, p. 228–236. Nitrous oxide: adjusted vapor densities (normal b. p. to t_{cr}); reduced rectilinear diameter equation; all critical data, "International Critical Tables," Vol. III, p. 228 (1928). Original observed vapor densities; corresponding T_{cr} values and test equations: (a) Cailletet and Mathias, *J. phys. radium*, **5**, 549 (1886); (b) Villard, *Compt. rend.*, **118**, 1096 (1894); (c) Quinn and Wernimont, THIS JOURNAL, **51**, 2002 (1929).

(6) Substances observed by Young: *n*-hexane, carbon tetrachloride, monofluorobenzene, methyl formate, ethyl propionate, acetic acid, ethyl alcohol, methyl alcohol: vapor densities observed (0° to t_{cr}): also all critical data and corresponding mean density equations; Young, *Proc. Roy. Dublin Soc.*, **12**, 374 (1910). The cubic equation applied to fluorobenzene; Jüptner, *Z. physik. Chem.*, **80**, 309, 310 (1912).

Ethyl and methyl alcohols: vapor densities calculated from the Clapeyron equation (0–130°); *Bur. Standards J. Research*, **6**, 881 (1931).

Benzene: vapor densities calculated from the Clapeyron equation between 0 and +130°; Fiock, Ginnings and Holton, *Bur. Standards J. Research*, **6**, 881 (1931). Vapor densities observed between +140° and t_{cr}; also all critical data and mean diameter equation of second degree: Young, *Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

i-Pentane and *n*-pentane: vapor densities observed (0° − t_{cr}); also all critical data; Young, *Proc. Roy. Dublin Soc.*, **12**, 374 (1910). Mean density equations of second degree (same range): Timmermans, *ibid.*, **13**, 310 (1912).

Ethyl ether: vapor densities observed (0° − t_{cr}); also t_{cr}; P_{cr}; and the mean diameter eq. of second degree; Young, *ibid.*, **12**, 374 (1910). Critical density (observed): Schröer, *Z. physik. Chem.*, **129**, 79 (1927); **140**, 241 (1929).

(7) Ammonia: vapor volumes observed between −77.5 and +60°; also all critical data and an empirical test equation: (a) Circular Bur. Standards, No. 142, (1923); and (b) the ammonia table in the article by Meyers, *Bur. Standards J. Research*, **11**, 699 (1933). Vapor densities calculated from the eq. of state of Beattie and Lawrence between +60° and +95.6°; ammonia table in the article of Meyers, *ibid.*; equation of state; Beattie and Lawrence, THIS JOURNAL, **52**, 6 (1930). (Vapor densities calculated from the Clapeyron equation between −50 and +50°: *Bur. Standards* Sci. Papers, No. 18, 707 (1923).)

(8) Water: vapor volumes calculated from the empirical equation for water at saturation between 0–340°: Keyes, Smith and Gerry, *Proc. Am. Acad. Arts and Sci.*, **70**, 319 (1936). Vapor volumes between 340° − t_{cr}, calculated by the Clapeyron equation (Bureau of Standards data) *ibid.*, table of saturated volumes. Values of T_{cr} and d_{cr}: Smith and Keyes, *ibid.*, **69**, 285 (1934). Vapor volumes calculated from the Clapeyron eq. between 0–360° (details). Preliminary report, *Bur. Standards;* Osborn, Stimson and Fiock, *Mech. Eng.*, **57**, 162 (1935).

(9) Nitrogen tetroxide: vapor densities observed between +3 and +55°: Mittasch, Kuss and Schleuter, *Z. anorg. Chem.*, **159**, 29 (1927). Vapor densities observed between +60° − t_{cr}; also T_{cr} and d_{cr}; (also mean rectilinear diameter eq. in this interval): Bennewitz and Windish, *Z. physik. Chem.*, **A166**, 401 (1933).

(10) Meyers' equation: C. H. Meyers, *Bur. Standards J. Research*, **11**, 691 (1933).

suggested for water and ammonia by Keyes and collaborators and by the Bureau of Standards, respectively. The Clapeyron equation gives vapor volume as a function of V_{liq}, dp/dT and T; while Meyers' equation

$$\log_{10} (1 - pv_{\text{gas}}/RT)(1 - pv_{\text{liq}}/RT) = A \log_{10} p/p_{\text{cr}}\ 2.718 \text{ (range: } 0.5\text{–}0.9\ T_{\text{cr}}) \qquad (13)$$

expresses vapor volume in terms of V_{liq}, P_{sat} and T.

In the last two columns of Table III are given the summarized results on intercomparison of the proposed equation with the several volume functions listed above. For every one of the thirty substances the average deviations of each equation were evaluated (in volume per cent.) by a graphical method, as described under Table II.

Examining the equations (9)–(12) of the type $d_{\text{gas}} = f(\tau)$, we see that only two, the first and the last, have any applicability, and this over a limited range. The proposed equation was found to be superior to each of them, inasmuch as it expresses correctly the whole saturation line rather than a portion of it, with an accuracy equal to or better than that of equations (9) or (12).

Comparing the deviations of the proposed equation with those of the volume ratios, we find that twenty-three out of thirty liquids have smaller or equal average deviations. The seven substances which show inferior results are: *n*-pentane, *n*-hexane, carbon tetrachloride, ethyl propionate, methyl formate, acetic acid and methyl alcohol. As to the distribution of deviations, they run for most liquids parallel in both equations. Water, sulfur trioxide, hydrogen and a few organic liquids are exceptions, but here the difference is not so great as to be of importance. On the whole we feel justified to conclude that the proposed and the volume ratio equations are entirely equivalent as regards accuracy, range of validity and extent of applicability to different substances.

Considering the different modifications of the mean density equation, we see that they are of no practical value at lower temperatures, but in the region 0.9–1.0 T_{cr} they are invariably superior to the proposed equation (ethane and methyl alcohol being the only exceptions so far encountered).

The functions $V_{\text{gas}} = f(p, T)$ of Keyes and coworkers and of the Bureau of Standards are extremely accurate (V_{gas} = 0.03% and 0.1%). On the other hand, they are very cumbersome in form (7 or 8 constants), and seem to be of specific rather than general applicability.

Meyers' equation was tested on eight liquids. At low and moderate temperatures it was found equivalent or slightly better than the proposed equation in all cases except that of ethyl alcohol. The fact that it does not hold above 0.9 T_{cr}, as well as the large number of independent variables necessary for its evaluation make this relationship inferior to the proposed equation. However, at temperatures below the boiling point it is most reliable.

Clapeyron's equation was contrasted with the proposed equation on ammonia, water[3] and helium. Both equations apply about equally well to the first two substances (ΔV_g = 0.1–0.2%). The inferior accuracy of the Clapeyron equation for helium is subject to revision, pending more accurate data for the latent heat of helium.

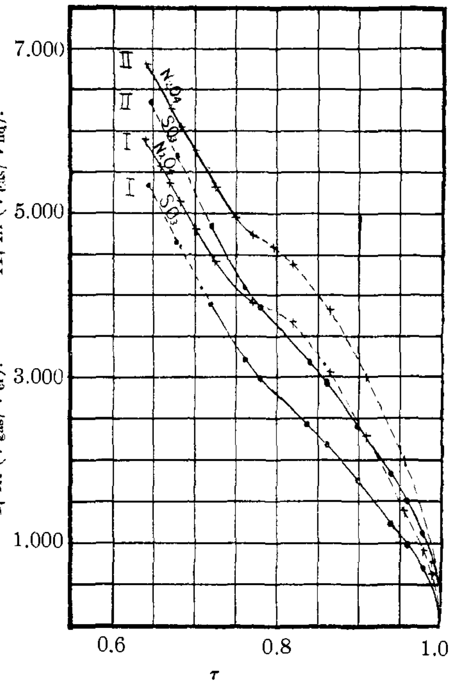

Fig. 2.—Curves I give ln (V_g/V_{cr}), obsd. Curves II give ln (V_g/V_{liq}), obsd. ———— Parts of experimental curves I and II which follow the equations; -------- parts of experimental curves I and II which deviate from the equations. ●, SO_3; +, N_2O_5.

As the result of the above comparative study of equations, we can say that both the proposed and the volume ratio functions have a definite advantage over the other vapor volume expressions here discussed, because, having equivalent or, sometimes, better accuracy, they fit a larger variety of liquids over a longer temperature interval than any of the others. In addition, we see that the proposed equation is the only rather satisfactory attempt to express V_{gas} in terms of a single independent variable, reduced temperature.

Before leaving the subject we wish to add a few words regarding sulfur trioxide and nitrogen tetroxide. Both were previously found to have abnormally shaped experimental curves ln V_{gas}/V_{liq}.[1] The deviating portion of either curve was found in disagreement with the volume ratio equation, while the portion regularly shaped was found to follow this equation within expected limits. A corresponding behavior is to be noted for the vapor volume curves of these substances. In Fig. 2, the observed curves ln V_g/V_{cr} of SO_3 and N_2O_4 are plotted alongside the observed values of their ratios, ln V_g/V_{liq}. We see that for either substance the two functions have deviating portions (dotted lines) very similar both in direction and in length of temperature interval. As to the proposed equation, we find that it follows the experiment in the normal region of the vapor volume curves ($\Delta V_g = 0.6\%$ and 1.0% for SO_3 and N_2O_4, respectively). On the other hand, in the abnormal section of these curves the vapor volume equation deviates enormously from observed data, and this behavior is in accordance with that observed for the volume ratio.[1]

Summary

1. The reduced vapor volume of chemically different substances is found to be an exponential function of reduced temperature alone. The form of this function is identical with those for vapor pressure and for volume ratio

$$\ln V_g/V_{cr} = k''(1 - \tau^2)^{m''}/\tau^{n''} = x \qquad (14)$$

$$V_{gas} = V_{cr}\cdot e^{x} \qquad (15)$$

2. The accuracy of this equation is well within experimental limits; it is in good agreement with vapor volume equations of other investigators.

3. When compared with the volume ratio equation it is found to give analogous results as regards average and regional accuracy and range of application. Its advantage lies in the fact that V_{gas} is expressed as a function of one independent variable only.

4. The parameters k'', m'', n'' of this equation have the same characteristics as the constants of the vapor pressure and of the volume ratio equations; they vary only slightly with chemical properties of substances; the constant k'' increases in the same order as the critical coefficient and the heights of ordinates ln V_g/V_{cr}, but there is no simple mathematical relationship between K_{cr} and k''.

5. The three properties, vapor pressure, vapor volume and volume ratio, exhibit striking similarity along the whole saturation line, since not only the mathematical expressions of these functions are identical, but the respective parameters are of the same order of magnitude; further, the geometrical shape of the curves ln P_{cr}/P_s, ln V_g/V_{cr}, ln V_g/V_{liq} is similar and their relative order to each other is identical for every substance here studied; finally, for each one of these properties the successive order of liquids in the coördinate system is the same with but few exceptions.

6. The constants k'' and n'' for vapor volume are nearly equal to the respective constants for pressure and the constants m'' are nearly half the others. However, in no case have the ratios k'/k'', n'/n'', m'/m'' assumed the integral values 1, or 2. Their averages for 30 liquids are respectively: 1.08; 0.98; and 2.09.

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