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THE PRESSURE-VOLUME-TEMPERATURE RELATION FOR GASEOUS ETHYL ETHER. II

BY JAMES A. BEATTIE

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In a previous paper,[1] the author presented a set of measurements of pressures, volumes and temperatures for gaseous ethyl ether in which the experimental details were so arranged that the pressures were measured for the same series of specific volumes at each temperature, thus presenting data for isometrics as well as isothermals. It was pointed out that the constant-volume lines for the large specific volumes were practically straight, but as the specific volume was decreased the isometrics showed increasing curvature, which can be seen from an examination of Table I.

The data above 10 cc. per gram were used in the earlier paper for a study of the accuracy with which the Keyes equation of state reproduced the observed pressures. This equation

$$p = \frac{RT}{v - \delta} - \frac{A}{(v + l)^2}, \quad \delta = \beta e^{-\alpha/v} \tag{1}$$

was deduced for the case of a fluid of non-varying molecular species,[2] and since the degree of curvature of the isometrics was assumed by Keyes to be a measure of the association (or aggregation) effect, the equation should reproduce the measured pressures only in the region of straight isometrics. Above 15 cc. per gram the deviation between observed pressures and those calculated by Equation 1 was not over 0.05 atmosphere; for 12 cc. per gram the error was about 0.3 atmosphere, and for 10 cc. per gram, about 1.6 atmospheres.

In order to represent the pressures in the region in which the isometrics are curved it is necessary to introduce another temperature function into

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[1] Beattie, THIS JOURNAL, 46, 342 (1924).

[2] Keyes, *Proc. Nat. Acad. Sci.*, 3, 323 (1917).

Equation 1. This function must be so chosen that it straightens out the isometrics at the higher densities, without introducing any curvature into those isometrics which are already substantially linear. From an empirical standpoint this function could be introduced into either term of Equation 1 by multiplying any or all of the principal constants R, A and β by functions of the temperature and of the volume. It was shown in the previous paper that these three constants affect the calculated pressure decreasingly in the order named. Since R influences the pressure to the greatest extent, the effect of multiplying R by a function of t and v would affect the calculated pressure most directly.

Both Boltzmann[3] and Jeans[4] have suggested that the deviation of actual gases from the perfect gas law may be due to aggregation of the molecules, and have introduced into R that function of v and t which is obtained from kinetic theory considerations. The results expressed qualitatively the behavior of nitrogen dioxide, but the agreement is by no means quantitative. This is probably due to the fact that the perfect gas law is too simple an equation to use as a starting point for the addition of the idea of association, as was of course recognized by these writers.

The Keyes equation has been shown to represent the observed data quite well at not too great densities, and hence the use of this equation as a basis for applying the association principle should lead to much better chances of success. It is probable that under this assumption R, A and β would all be multiplied by functions of t and v, as well as the less important constants α and l. However, the introduction of a function of v and t into any of these three principal constants is approximately equivalent to its introduction into the others. Hence, for the first approximation, we can collect the whole effect and take care of it by throwing all the deviation into the gas constant R.

If it is assumed that the curvature of the isometrics is due to a change in the molecular species, the number of moles for a given mass of gas is changing and account must be taken of this variation of N, in R. This may be done to the first approximation by applying the mass-action equation (in its form for perfect gases) to the reaction consisting of an association of single to double molecules. Hence, the value of R becomes[5] $R = R_1\,(1 - y/2)$, where $(y/2)/(1 - y)^2 = (a/v)e^{b/T}$, and R_1 is the gas constant for the unassociated molecules, y the fraction associated, and a and b are constants usually identified with the chemical constant and the heat of association. When y is small we may neglect it in comparison with 1 and write

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[3] Boltzmann, "Vorlesungen über Gastheorie," Barth, Leipzig, vol. 2, chap. 6.

[4] Jeans, "Dynamical Theory of Gases," Cambridge University Press, 1916, 3rd ed., p. 193.

[5] Keyes, THIS JOURNAL, 49, 896 (1927).

$$R = R_1\left(1 - \frac{a}{v}e^{b/T}\right) \tag{2}$$

The values of y calculated from the equations above have now no physical significance, since Equation 2 represents a collective effect due to the variation with the number of moles, N, of both A and β, as well as R.

The equation of state then becomes

$$p = \frac{RT}{v - \beta e^{-\alpha/v}}\left(1 - \frac{a}{v}e^{b/T}\right) - \frac{A}{(v + l)^2} \tag{3}$$

or

$$p = \psi T(1 - \gamma) - \phi \tag{4}$$

where ψ and ϕ are functions of volume alone and not of the temperature, and γ is a function of both volume and temperature, that is, $(a/v)e^{b/T}$. This equation can be arranged to

$$p + \gamma\psi T = \psi T - \phi = p_{\text{corr.}} \tag{5}$$

and $p + \gamma\psi T$ can be called the "corrected pressure," which should now vary linearly with the temperature at constant volume. In order to test this treatment on experimental data, it is necessary to know ψ or $(\partial p_{\text{corr.}}/\partial T)_v$ in advance in order to obtain the correction to the measured pressures. This can be obtained very accurately by two successive approximations. The value of $\partial p/\partial T$ obtained from the best straight line through the original isometric (even though it shows curvature) is used to calculate a series of provisional corrected pressures. The value of ψ from these latter pressures, which now vary practically linearly with temperature, is used to calculate a new correction to be applied to the measured pressures for the final $p_{\text{corr.}}$. In the case of ether the convergence is rapid, and the greatest difference between the result of these two calculations was about 0.005 atmosphere.

In order to determine a and b, Equation 3 can be expanded in terms of $1/v$ after multiplying through by v, $pv = RT\ [1 + (\beta - A/RT - ae^{b/T})1/v + \ldots\ldots]$ and if this expansion is compared with the isothermal equation of Kamerlingh Onnes, $pv = RT\ (1 + B/v + \ldots\ldots)$, it is evident that

$$B = \beta - A/RT - ae^{b/T} \tag{6}$$

For each measured isotherm it is possible to determine a B either analytically or by plotting $[(pv/RT) - 1]v$ against $1/v$. This plot gives a curve which tends to straighten for small values of $1/v$, and the intercept on the $[(pv/RT) - 1]v$ axis gives directly the value of B.

From a consideration of the B values in the light of Equation 6 it is possible to obtain values for a and b. Plotting B against $1/T$ gives a curve which approaches a straight line, at higher temperatures, where the exponential is small, but at lower temperatures shows increasing curvature.

The difference ΔB between the experimentally determined B's and those obtained from an extension of the tangent to the high-temperature values gives a means of obtaining a and b, for $\Delta B = ae^{b/T}$ and $\log \Delta B =$

log $a + b/2.3\ T$. Unfortunately, a and b are not uniquely determined since a small variation in ΔB is due possibly to the use of judgment in drawing the tangent to the extension of the B plot. However, in the case of ethyl ether, a is very small so that although a and b are not determined absolutely by the method outlined above, the value of the whole exponential term $ae^{b/T}$ does not vary much with the different possible values of a and b for the temperature range of the data.

In Table I are given the values of $p_{\text{corr.}}$ compared with the pressures calculated from the best straight lines through the isometrics. $P_{\text{corr.}}$ was calculated by means of Equation 5, using the values of ψ, a and b obtained by the methods outlined in the preceding paragraphs. There are also included the deviations of the observed pressures from the best straight line through the original isometrics obtained from the former article. It can be seen that the observed pressures show curvature at the higher densities, while the corrected pressures are linear even down to 5 cc. per gram.

TABLE I

COMPARISON OF OBSERVED PRESSURES CORRECTED FOR THE "AGGREGATION EFFECT" WITH THOSE CALCULATED BY ASSUMING THE ISOMETRIC LINES TO BE STRAIGHT

The first line gives the observed "corrected pressures," the second those calculated from the linear equation given, and the third the observed minus the calculated pressures. The fourth line gives the deviation of the measured pressures from linearity.

$$P_{\text{corr.}} = P_{\text{obs.}} + T\left(\frac{\partial P_{\text{corr.}}}{\partial T}\right)_v \frac{0.00145}{v} e^{1596/T}$$

	Pressures, in atmospheres						
Vol., cc./g.	Temp., °C. 150	175	200	225	250	275	300	325
35				$p = 0.03685\ T - 4.374$				
	11.218	12.136	13.070	13.976	14.907	15.811	16.746	17.678
	11.218	12.140	13.061	13.982	14.903	15.825	16.746	17.667
	0.000	− 0.004	0.009	− 0.006	0.004	− 0.014	0.000	0.011
	.003	.000	.013	− .004	.005	− .014	− .002	.006
30				$p = 0.04400\ T - 5.923$				
	12.706	13.790	14.876	15.992	17.099	18.186	19.296	20.412
	12.695	12.795	14.895	15.995	17.095	18.195	19.295	20.395
	0.011	− 0.005	− 0.019	− 0.003	0.004	− 0.009	0.001	0.017
	.015	.000	− .013	.002	.008	− .007	.000	.014
25				$p = 0.05445\ T - 8.488$				
	14.537	15.909	17.273	18.643	19.993	21.354	22.737	24.077
	14.551	15.913	17.274	18.635	19.996	21.358	22.719	24.080
	− 0.014	− 0.004	− 0.001	0.008	− 0.003	− 0.004	0.018	− 0.003
	− .014	− .001	.002	.010	− .003	− .006	.013	− .012
20				$p = 0.07109\ T - 13.095$				
	16.975	18.759	20.542	22.313	24.095	25.893	27.649	29.434
	16.985	18.763	20.540	22.317	24.094	25.872	27.649	29.426
	− 0.010	− 0.004	0.002	− 0.004	0.001	0.021	0.000	0.008
	− .016	− .003	.005	− .001	.002	.020	− .005	− .001

Table I (*Concluded*)

	Pressures, in atmospheres							
Vol., cc./g.	Temp., °C. 150	175	200	225	250	275	300	325
15	$p = 0.10103\ T - 22.629$							
		22.646	25.171	27.698	30.228	32.737	35.284	37.797
		22.646	25.171	27.697	30.223	32.749	35.274	37.800
		0.000	0.000	0.001	0.005	-0.012	0.010	-0.003
		-.009	-.001	.005	.010	-.007	.012	-.005
12.5	$p = 0.12671\ T - 31.726$							
		25.057	28.226	31.394	34.562	37.734	40.891	44.057
		25.057	28.224	31.392	34.560	37.728	40.895	44.063
		0.000	0.002	0.002	0.002	0.006	-0.004	-0.006
		-.019	-.003	.005	.009	.012	-.001	-.009
10	$p = 0.16733\ T - 47.245$							
			31.913	36.105	40.296	44.482	48.655	52.847
			31.924	36.107	40.290	44.474	48.657	52.840
			-0.011	-0.002	0.006	0.008	-0.002	0.007
			-.010	.006	.013	.011	-.010	-.015
7.5	$p = 0.24181\ T - 78.257$							
			36.146	42.199	48.246	54.276	60.341	66.376
			36.151	42.196	48.241	54.286	60.332	66.377
			-0.005	0.003	0.005	-0.010	0.009	-0.001
			-.022	.009	.019	.001	.010	-.018
5	$p = 0.40638\ T - 151.876$							
			40.399	50.551	60.679	70.904	81.028	91.197
			40.395	50.554	60.714	70.873	81.033	91.192
			0.004	-0.003	-0.035	0.031	-0.005	0.005
			-.025	.020	.005	.059	-.009	-.050

$$T = t^\circ + 273.13$$

The values of ψ and ϕ of Equation 5 for each volume can be used to study the correctness of the volume function chosen, since the corrected pressures now vary linearly with the temperature, and hence ψ and ϕ are uniquely determined.[6] If in some special case it should happen that the functions suggested by Keyes do not fit, then other functions may be tried, but ψ and ϕ are now volume functions only, since all the temperature curvature has been removed by the exponential introduced into R.

Using the Keyes form for ψ, $\psi = R/v - \delta$, $\delta = \beta e^{-\alpha/v}$, we can calculate δ for each isometric, using the value of ψ from Table I, and these values of δ should be reproduced by an equation of the form $\log \delta = \log \beta - \beta/2.3\ v$. In Table II are given the deviations of the observed values from those calculated by the above equation.

For ϕ, Keyes used $\phi = A/(v + l)^2$, and it was shown in the former paper on ether that this is equivalent to $\phi = (A/v^2)e^{-l/v}$, the latter form holding

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[6] Using the "observed pressures" a considerable variation in ψ and ϕ is possible when the isometric is curved, depending upon how the straight lines are drawn.

perhaps slightly better than the former. Table II gives a comparison of the observed ϕ's from Table II with those calculated from the above equation. The check is not so satisfactory as in the case of the ψ function.

A new ϕ function was chosen, namely, $\phi = (A/v^2)e^{-l/v^2}$ or $\log \phi v^2 = A - l/2.3\, v^2$.

Table II

Comparison of Observed ψ's and ϕ's with those Calculated from the Equation of State

The observed values of ψ and ϕ are obtained from the linear equation given in Table I; the calculated values are from the following equation.

$$\psi = R/(v-\delta) = 1.10777/(v-\delta); \delta = 5.7630\, e^{-5.3397/v}; \log_{10}\delta = 0.76065 - 2.3190/v$$

$$\phi = \frac{5623.4}{v}\, e^{-1.4737/v};\ \log_{10}\phi v^2 = 3.75000 - 0.64/v$$

$$\phi' = \frac{5420.0}{v}\, e^{-13.797/v^2};\ \log_{10}\phi v^2 = 3.73400 - 5.992/v^2$$

R is in cc./atm. per °C. per gram; ψ in atm. per °C.; ϕ in atm.; v in cc. per gram.

v	$\Delta\psi \times 10^{-5}$ obs.—calcd.	$\Delta\phi$, obs.—calcd.	$\Delta\phi'$, obs.—calcd.
35	−1	−0.027	−0.001
30	0	−0.026	− .008
25	0	.006	.005
20	2	.035	.004
15	−2	− .025	− .027
12.5	−3	− .261	− .030
10	3	−1.284	.030
7.5	471	−3.882	+2.859

Table II gives a comparison of the observed and calculated ϕ values using this form of function. (In the table these values are designated by ϕ'.) It will be noticed that the values are reproduced satisfactorily over the same range that the ψ values are reproduced, that is, down to and including 10 cc. per gram. Both functions fail to about the same extent at 7.5 cc. per gram.

Table III

Comparison of Observed Pressures with Those Calculated by the Equation of State

The first line gives the observed pressures; the second those calculated from the equation of state given; and the third the observed minus the calculated pressures.

$$p = \frac{1.10777T}{v-\delta}(1-\gamma) - \phi;\ \log_{10}\delta = 0.76065 - 2.319/v;\ \log_{10} v\gamma = 693/T - 2.83900;\ \log_{10} v^2\phi = 3.73400 - 5.992/v^2.$$

	Pressures in atmospheres							
Vol., cc./g.	Temp., °C. 150	175	200	225	250	275	300	325
35	11.190	12.112	13.049	13.957	14.890	15.796	16.732	17.665
	11.194	12.119	13.044	13.967	14.891	15.814	16.737	17.659
	− 0.004	− 0.007	0.005	− 0.010	− 0.001	− 0.018	− 0.005	0.006
30	12.667	13.756	14.847	15.966	17.076	18.165	19.276	20.394
	12.648	13.753	14.858	15.961	17.064	18.166	19.267	20.369
	0.019	0.003	− 0.011	0.005	0.012	− 0.001	0.009	0.025

Table III (*Concluded*)

Vol., cc./g.	Pressures in atmospheres							
	Temp., °C. 150	175	200	225	250	275	300	325
25	14.479	15.859	17.229	18.604	19.958	21.322	22.708	24.050
	14.498	15.868	17.235	18.601	19.966	21.331	22.695	24.058
	− 0.019	− 0.009	− 0.006	0.003	− 0.008	− 0.009	0.013	− 0.008
20	16.880	18.678	20.471	22.250	24.038	25.841	27.601	29.390
	16.886	18.677	20.463	22.248	24.031	25.813	27.593	29.374
	− 0.006	0.001	0.008	0.002	0.007	0.028	0.008	0.016
15		22.492	25.036	27.578	30.120	32.639	35.194	37.713
		22.474	25.019	27.560	30.098	32.635	35.169	37.701
		0.018	0.017	0.018	0.022	0.004	0.025	0.012
12.5		24.825	28.023	31.214	34.400	37.586	40.755	43.930
		24.808	28.005	31.197	34.383	37.566	40.746	43.924
		0.017	0.018	0.017	0.017	0.020	0.009	0.006
10			31.579	35.808	40.028	44.238	48.430	52.638
			31.606	35.825	40.037	44.243	48.445	52.643
			− 0.027	− 0.017	− 0.009	− 0.005	− 0.015	− 0.005
7.5			35.502	41.626	47.730	53.805	59.908	65.973
			36.137	42.136	48.120	54.093	60.058	66.016
			− 0.635	− 0.510	− 0.390	− 0.288	− 0.150	− 0.043

$T = t° + 273.13$

In Table III is given a comparison of the original measured pressures with those calculated from the complete equation.

$$p = \frac{1.10777\ T}{v - \delta}(1 - \gamma) - \phi$$

$$\gamma = \frac{0.00145}{v} e^{1596/T} \qquad \log_{10} v\gamma = \frac{693}{T} - 2.83900$$

$$\delta = 5.7630\ e^{-5.3397/T} \qquad \log_{10} \delta = 0.76065 - 2.319/v$$

$$\phi = \frac{5420}{v^2} e^{-13.797/v^2} \qquad \log_{10} v^2\phi = 3.73400 - 5.992/v^2$$

This equation reproduces the measured pressures over the entire range above 10 cc. per gram. In only three cases are the deviations greater than 0.02 atmosphere and no deviation as great as 0.03 atmosphere occurs. This can be compared with the fit of the equation given in the earlier article in which the deviations were about 0.05 atmosphere at 15 cc. per gram and above, 0.3 atmosphere at 12.5, and 1.6 atmospheres at 10 cc. per gram. Part of the betterment is due to the introduction of the new function of t and v, but the greater part of the discrepancy is removed by the use of a new ϕ function, as can be seen by a comparison of Tables I and II.

Below 10 cc. per gram, different volume functions for ϕ and ψ (or δ) must be used. Series expansion of ϕ and ψ in appropriate powers of $1/v$ is probably the best method, at present, of representing the data in the region of high densities.

Summary

The isometrics of gaseous ethyl ether are sensibly straight for large specific volumes, but show increasing curvature as the specific volume decreases.

If the curvature is supposed due to an aggregation of the molecules of the fluid, and the effect of this association is taken account of only in R, we obtain an equation of the following form for gaseous ethyl ether, when the fraction of molecules aggregated is small: $p = RT/v - \delta(1 - \gamma) - \phi$, where $\delta = \beta e^{-\alpha/v}$, $\phi = (A/v^2)e^{-l/v^2}$, and $\gamma = (a/v)e^{b/T}$, Rearranging, this equation gives $p_{\text{corr.}} = p + [RT/(v - \delta)]\gamma = [RT/(v - \delta)] - \phi$. $P_{\text{corr.}}$ should now vary linearly with the temperature along an isometric. For gaseous ethyl ether this is the case down to 5 cc. per gram. The above equation reproduced all the data down to 10 cc. per gram, no single measurement deviating as much as 0.03 atmosphere from the calculated pressure.

A new form for ϕ, namely, $(A/v^2)e^{-l/v^2}$, has been suggested, and in the case of gaseous ethyl ether it represents the data better than forms previously used.

CAMBRIDGE, MASSACHUSETTS

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AN EQUATION OF STATE FOR GASEOUS CARBON DIOXIDE

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Equations of state have ordinarily been based on the perfect gas expression with the inclusion of appropriate correction terms to account for certain phenomena characteristic of actual gases, and these attempts[2] have met with considerable success both theoretically and practically. On the other hand, there is a relation which approximates much more closely the behavior of all actual gases than does the perfect gas equation and which from the standpoint of thermodynamics is almost as general, namely, the linear relation between the pressure and the temperature of a gas when the volume is maintained constant.[3] Departure from linearity becomes more marked at higher densities and lower temperatures, and association has been suggested[2b 3b] as the cause for the deviation from this relation which can be expressed mathematically as

$$P = \psi T - \phi \tag{1}$$

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[1] National Research Fellow in Chemistry.

[2] (a) van der Waals, "Die Kontinuität des gasförmigen und flüssigen Zustandes," Barth, Leipzig, **1881.** (b) Clausius, *Wied. Ann.*, **9**, 337 (1880). (c) Dieterici, *Ann. Physik*, [4] **5**, 51 (1901). (d) Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917).

[3] (a) Ramsay and Young, *Z. physik. Chem.*, 1, 440 (1887). (b) Keyes and Felsing, THIS JOURNAL, **41**, 589 (1919).