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A NEW EQUATION OF STATE FOR FLUIDS.

II. APPLICATION TO HELIUM, NEON, ARGON, HYDROGEN, NITROGEN, OXYGEN, AIR AND METHANE

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In the preceding paper,² the authors proposed an algebraic equation of state whose constants are easily and uniquely determinable from pressure-volume-temperature data, and which can readily be used for evaluating the usual thermodynamic relations. This equation of state is

$$p = \frac{RT(1 - \epsilon)}{V^2} [V + B] - \frac{A}{V^2} \quad \begin{aligned} A &= A_0(1 - a/V) \\ B &= B_0(1 - b/V) \\ \epsilon &= c/VT^3 \end{aligned} \quad (1)$$

in which R is the gas constant and A_0 , a , B_0 , b and c are parameters which depend upon the kind of substance under consideration. It was shown that the data on gaseous ethyl ether and carbon dioxide were represented very satisfactorily by an equation of this form. A physical basis for this equation and the details of the method for the evaluation of the constants from the compressibility measurements will shortly be presented elsewhere.

In the present paper are given the results of the application of Equation 1 to the p - V - T data on eight gases extending over the temperature range from -252 to $+400^\circ$, and to pressures of about 100 to 200 atmospheres. The region of high pressures (1000 atmospheres or over) will be treated later. The data used for the present comparisons have resulted from the investigations of Kamerlingh Onnes and his associates,³ and of Holborn, Otto and Schultze⁴ on helium, neon, argon, hydrogen, nitrogen, oxygen and air; of Bartlett⁵ and Verschoyle⁶ on hydrogen and

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² Beattie and Bridgeman, *THIS JOURNAL*, **49**, 1665 (1927).

³ *Communications of the Physical Laboratory of Leiden*.

⁴ The data are summarized in *Z. Physik*, **33**, 1 (1925); **38**, 359 (1926).

⁵ Bartlett, *THIS JOURNAL*, **49**, 687, 1955 (1927).

⁶ Verschoyle, *Proc. Roy. Soc.*, **111A**, 552 (1926).

nitrogen; of Witkowski on hydrogen⁷ and air;⁸ of Smith and Taylor⁹ on nitrogen; of Koch¹⁰ and Amagat¹¹ on air; and of Keyes and Burks¹² on methane.

Within the density range studied, all of the measurements of the above observers were used for the determination of the values of the equation of state constants, and also in the comparisons given in Table II, with the following exceptions: helium, the isotherms below -252° for which the pressures even at large densities are small; argon, the 18.39° isotherm of Onnes and Crommelin; hydrogen, the data of Crommelin and Swallow (Leiden) which could not be correlated with the rest of the field, and the measurements of Verschoyle and Bartlett who made no observations below about 50 atmospheres; nitrogen, the 5 cc. per gram isometric of Smith and Taylor, which is possibly in error; and air, the -130 , -135 , -140 and -145° isotherms of Witkowski, which show large deviations from the rest of the field.

In order to determine the values of the equation of state constants for a substance, it is necessary to have data in the form of isometrics. Most investigators present their results in the form of isothermals; that is, they list a series of pressure-volume products together with the corresponding pressures (or volumes) for each of several different temperatures. To convert these results into isometrics, the quantity $[pV - RT]$ was calculated for each measurement on a given isothermal. A straight line was passed through the point of zero density (where $[pV - RT]$ is zero) and the highest measured density on the isotherm. Deviations of the observed values from those calculated by the linear equation were plotted against the density on a large scale. By use of the linear equation and the plot, values of $[pV - RT]$ and hence of the pressure (which are considered as the "observed pressures") could be interpolated for a set of evenly spaced densities, the same densities being used at each isotherm. Thus all of the original data were transformed into isometrics by a procedure which smooths with respect to volume; but no attempt was made to smooth for temperature, all of the original isotherms being preserved.

It has long been known¹³ that at constant volume the pressure of a gas varies almost linearly with the temperature, and many equations of state which make use of this property have been proposed. The experimental work indicates that the curvature $(\partial^2 p / \partial T^2)_V$ is always negative in the

⁷ Witkowski, *Krakauer Anzeiger*, 305 (1905); Landolt-Börnstein, "Tabellen," 1923, p. 105.

⁸ Witkowski, *Phil. Mag.*, [5] 41, 288 (1896).

⁹ Smith and Taylor, *THIS JOURNAL*, 45, 2107 (1923); 48, 3122 (1926).

¹⁰ Koch, *Ann. Physik*, 27, 31 (1908).

¹¹ Amagat, *Ann. chim. phys.*, [6] 29, 68 (1893).

¹² Keyes and Burks, *THIS JOURNAL*, 49, 1403 (1927).

¹³ Amagat, *Compt. rend.*, 94, 847 (1882).

gas region,¹⁴ but that the isometrics approach linearity as the density decreases, and as the temperature increases.¹⁵ It has been shown that the curvatures of the isometrics of nitrogen,¹⁵ ethyl ether,¹⁶ carbon dioxide,¹⁷ and methane¹⁸ could be represented by introducing into the Keyes¹⁹ equation of state a logarithmic function of the temperature.

The method used for the determination of the values of the constants of the new equation of state can be indicated by rearranging (1) into the form

$$p' = p + \frac{c\psi(V)}{VT^2} = T\psi(V) - \phi(V) \quad (2)$$

where $\psi(V) = R[V + B]/V^2$ and $\phi(V) = A/V^2$ both being functions of the volume alone. The quantity p' will be called the "corrected pressure." When c is positive, Equation 2 expresses the experimental findings concerning the curvature $(\partial^2 p/\partial T^2)_V$ mentioned above. If the volume and temperature functions used in (2) are satisfactory, there is one value of c which will cause the corrected pressure p' (calculated from p , c , and the volume and temperature functions given) to vary linearly with the temperature for all isometrics; this provides a method for determining c . With a chosen value for this parameter, the corrected pressures are calculated for a representative density; if too small a value of c has been used, all of the curvature is not removed from the corrected isometric, while too large a value causes the curvature of the p' , T lines to change sign. Ordinarily two or three approximations are sufficient to select a satisfactory value of c even when correlating different sets of data. This provisional value of c is then verified by a study of the linearity of the corrected isometrics over the entire density field. It is generally true that measurements by two different observers give isometrics having different curvatures over the same temperature range; hence the value of c chosen represents a compromise.

From each corrected isometric there is obtained a value of $\psi(V)$ and of $\phi(V)$ which appear as the slope and intercept on the p' axis, respectively, of the linear p' , T line. Since $V + B = V^2 \psi(V)/R$, and $A = V^2 \phi(V)$, it is possible to calculate a value of B and A for each isometric, and a plot of B against $1/V$ should give a straight line, the slope and intercept

¹⁴ (a) Keyes and Felsing, *THIS JOURNAL*, **41**, 589 (1919); (b) Keyes, Smith and Joubert, *J. Math. Phys., M. I. T.*, **1**, 191, 211 (1922) [methane]; (c) Smith and Taylor, *THIS JOURNAL*, **45**, 2107 (1923); (d) *ibid.*, **48**, 3122 (1926) [nitrogen]; (e) Beattie, *ibid.*, **46**, 342 (1924) [ethyl ether]; (f) Keyes and Burks, *ibid.*, **49**, 1403 (1927) [methane].

¹⁵ Keyes and Taylor, *THIS JOURNAL*, **49**, 896 (1927).

¹⁶ Beattie, *ibid.*, **49**, 1123 (1927).

¹⁷ Bridgeman, *ibid.*, **49**, 1130 (1927).

¹⁸ Keyes and Burks, ref. 14 f.

¹⁹ Keyes, *Amer. Soc. Refrig. Eng. Jour.*, **1**, 9 (1914); *Proc. Nat. Acad. Sci.*, **3**, 32² (1917); Phillips, *J. Math. Phys., M. I. T.*, **1**, 1 (1921).

of which are B_0b and B_0 , while A should also vary linearly with $1/V$, the slope and intercept being A_0a and A_0 . Thus, with the exception of c , all of the adjustable constants appear as the slopes or intercepts of straight lines in which all of the measured data are given weight.

The values of the constants for the gases studied are given in Table I, where for comparison those for ethyl ether and carbon dioxide are included. In the units chosen, R has the same value for all gases, namely, 0.08206, and T_0 was taken as 273.13. It was found necessary to use different values of the constants for the data of Smith and Taylor on nitrogen, which are very consistent among themselves but could not be correlated with the determinations of the other investigators. Therefore, in the Tables, N_2^a applies only to the Smith and Taylor data, while N_2 includes all of the other data; these latter are the accepted constants for nitrogen.

TABLE I

CONSTANTS OF THE EQUATION OF STATE FOR TEN GASES

$p = [RT(1 - \epsilon)]/V^2 [V + B] - (A/V^2)$. $A = A_0(1 - a/V)$. $B = B_0(1 - b/V)$. $\epsilon = c/VT^3$. $R = 0.08206$ for all gases. Units: pressures in atmospheres, volumes in liters per mole, temperatures in degrees Kelvin. $T^\circ K = t^\circ C + 273.13$.

Gas	A_0	a	B_0	b	c
He	0.0216	0.05984	0.01400	0.0	0.004 $\times 10^4$
Ne	0.2125	.02196	.02060	.0	0.101 $\times 10^4$
A	1.2907	.02328	.03931	.0	5.99 $\times 10^4$
H ₂	0.1975	-.00506	.02096	-.04359	0.0504 $\times 10^4$
N ₂	1.3445	.02617	.05046	-.00691	4.20 $\times 10^4$
N ₂ ^a	1.1440	.01788	.04314	-.01608	5.60 $\times 10^4$
O ₂	1.4911	.02562	.04624	.004208	4.80 $\times 10^4$
Air	1.3012	.01931	.04611	-.01101	4.34 $\times 10^4$
CO ₂	5.0065	.07132	.10476	.07235	66.00 $\times 10^4$
CH ₄	2.2769	.01855	.05587	-.01587	12.83 $\times 10^4$
(C ₂ H ₅) ₂ O	31.278	.12426	.45446	.11954	33.33 $\times 10^4$

^a Constants for Smith and Taylor's data alone.

In Table II is given a summary of the comparisons of the pressures calculated from the equation of state, using the constants listed in Table I, with the observed pressures. In this comparison the entire measured temperature range is included for all gases, with the few exceptions mentioned above. For some of the gases the entire measured density range at the lower temperatures was not used. This was partly due to the fact that in the low temperature high density region the data were too fragmentary to define the isotherm sufficiently to allow smoothed values of the pressure to be obtained, and partly to the difficulty of correlating this region with the rest of the field due to the large experimental error. In every case all of the isotherms were extended to the maximum density listed in Table II when any data existed.

The second and third columns of Table II give the average deviations in atmospheres and percentage between the observed and calculated

TABLE II
SUMMARY OF THE DEVIATIONS BETWEEN OBSERVED AND CALCULATED PRESSURES FOR
TEN GASES

Gas	Av. dev. to $1/V = 5.0$ Atm. %		Av. dev. over entire density range Atm. %		Max. press., atm.	Max. density, moles/liter	Temp. range, °C.	No. of observers	No. of points
He	0.067	0.133	0.071	0.133	102	10	400 to -252	2	183
Ne	.053	.147	.081	.209	106	8.5	400 to -217	2	229
A	.059	.170	.078	.203	114	6	400 to -150	2	209
H ₂	.053	.199	.068	.203	103	10	200 to -244	3	362
N ₂	.061	.155	.072	.190	134	5.5	400 to -149	4	214
N ₂ ^a	.033	.040	.033	.040	213	5.0	200 to 0	1	50
O ₂	.025	.069	.051	.115	103	9	100 to -117	2	137
Air	.095	.197	.113	.198	177	8	200 to -145	5	171
CO ₂	.079	.144	.128	.203	111	5.5	100 to 0	2	148
CH ₄	.039	.048	.045	.049	243	6	200 to 0	1	60
(C ₂ H ₅) ₂ O023	.076	90	2.7	325 to 150	1	64
Grand average	.060	.155	.077	.178					

^a Deviations for Smith and Taylor's data alone. These are not included in the grand averages; to do so would make the grand average deviations smaller.

pressures over the complete temperature range and to a density of 5 moles per liter, which corresponds to an Amagat density of approximately 110, that is, 110 times as dense as at 0° and 1 atmosphere. The fourth and fifth columns contain the same information over the total range of temperature and density considered, these ranges being given in the succeeding columns. The last two columns give the number of different investigators whose data were correlated and the total number of points at which comparisons of observed and calculated pressures were made.

In the evaluation of the constants for the gases and in the comparisons given in Table II, the data of all observers on any particular gas were correlated, if possible, since a better average was thus obtained. For this reason the errors between observed and calculated pressures were larger than if separate equations were used for each group of results. It is in general true that the consistency of one set of data taken by the same observer is much greater than the agreement between two different sets. In fact, the deviations shown in Table II would be about halved if separate equations were used for the measurements of each observer. This can be seen from the results on methane, ethyl ether and Smith and Taylor's nitrogen, which are obtained from the work of the individual investigators and, further, the derivation of individual equations for one experimenter's data in the case of some of the other gases has verified this conclusion. The values of the constants obtained from a consideration of all the data were about the mean of those derived from the individual sets of measurements and are thus the best values that can now be assigned to them. In the cases in which the constants were determined from a consideration

of the results of several investigators, the deviations between the observed and calculated values can be taken as an approximate estimate of the accuracy of the available data.

Summary

The new equation of state has been applied to the compressibility measurements on helium, neon, argon, hydrogen, oxygen, nitrogen, air and methane, and the values of the constants are given for these gases and for carbon dioxide and ethyl ether. A method is outlined for transforming the experimental pressure-volume-temperature data into isometric form, and a brief description of the procedure for evaluating the constants of the equation of state is given. Comparison of the observed pressures and those calculated from the equation have been made at 1777 points for these ten gases, the average deviation being 0.08 atmosphere or 0.18% over the entire temperature and density range considered. The average deviation is 0.06 atmosphere or 0.16% over the experimental temperature range and to a density of 5 moles per liter (an Amagat density of approximately 110).

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[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY OF VALIO, HELSINKI, FINLAND]

THE VOLATILITY WITH STEAM OF WATER-SOLUBLE ORGANIC SUBSTANCES

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Investigations on the determination of volatile fatty acids by means of steam (which from an analytical point of view is a very important mode of procedure) have in many ways explained our opinion as to the quantitative course of distillation by steam and have rendered it possible to express quantitatively in a simple manner the volatility of water-soluble substances with steam. When boiling the diluted solutions of fatty acids a certain percentage of acid is always distilled into a certain quantity of water, this percentage being different in the case of different acids. If there are several acids in the same diluted solution of acid, each acid is distilled independently of the others. Duclaux's¹ well known and purely empiric mode of procedure for the determination of volatile fatty acids is based on these facts. This procedure is, however, complicated and requires definite tables; it also applies only to fatty acids.

Among the investigations, the purpose of which has been to derive simple mathematical formulas in order to follow the course of distillation, should be mentioned Barrel, Thomas and Sidney Young's² differential equations,

¹ Duclaux, *Traité de Microbiologie*, 3, 384 (1900); 4, 685 (1901).

² Barrel, Thomas and Young, *Phil. Mag. and J. of Science*, (V) 37, 8 (1894).