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 $p_{corr.} = p + [RT/(v - \delta)]\gamma = [RT/(v - \delta)] - \phi$. $P_{corr.}$ 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.

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AN EQUATION OF STATE FOR GASEOUS CARBON DIOXIDE

BY OSCAR C. BRIDGEMAN[1]

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).

where ψ and ϕ are functions of volume only. However, this departure does not necessarily indicate a chemical association, for the derivation of Equation 1 from kinetic theory is based on the assumption that the time of encounter between molecules is independent of the temperature and if this is not true, then a change of complexity is simulated. Since no way of distinguishing these two effects is evident, the general term aggregation covering both of them will be used and departure from the above relation will be taken as a measure of this aggregation.

In the formulation of an equation of state which will accurately reproduce the P-V-T data, the problem in the first place resolves itself into finding a suitable correction term which, when added to the observed pressures, will give values which are linear functions of the temperature. The second phase of the problem, which consists in finding suitable volume functions for ψ and ϕ, will be considered later.

Thus, presumably, the equation for the isometric of any gas could be written

$$P + \Gamma = \psi T - \phi \tag{2}$$

where P is the observed pressure, Γ is a function of both volume and temperature, dependent upon the aggregation, and ψ and ϕ are, as before, functions of volume only. Rewriting Equation 2 by substituting for ψ the value given to it by Keyes,[4] there is obtained

$$P + \Gamma = (RT/V - \delta) - \phi \tag{3}$$

where δ is a volume function. Mathematically, the Γ term could originate in any of the R, δ or ϕ terms or in all of them, and physico chemical theory substantiates the latter possibility; but δ and ϕ enter only as correction terms, whereas R is a direct proportionality constant, so that it would seem reasonable that multiplication of R by a factor to take care of the number of moles present, would reproduce the whole effect with considerable accuracy if the association were small. In the other case, if the duration of encounters varies with the temperature, as has been shown to be probable by Jeans[5] on theoretical grounds, the molecular complexity would apparently vary, and if it is assumed that the laws which control this pseudo-variation of complexity are analogous to those which hold for thermodynamic equilibrium between species, here again the inclusion of a multiplying factor in the R term should account for most of this effect. Hence, to a first approximation, it seems reasonable that the phenomenon of aggregation can be accounted for by modifying Equation 1 as follows, to apply to actual gases,

$$P = \frac{RT\,(1 - y/2)}{V - \delta} - \phi \tag{4}$$

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[4] The Keyes equation of state is $p = (RT/V - \delta) - A/(V + 1)^2$, where $\delta = \beta e^{-\frac{\alpha}{v}}$.

[5] Jeans, *J. Chem. Soc.*, **123**, 3408 (1923).

where y is a function of volume and temperature, and this has the decided advantage of simplifying the thermodynamic derivatives. In this case, $\Gamma = RT\, y/2(V - \delta)$.

Both kinetic theory[6] and thermodynamics[7] indicate that for small amounts of aggregation, y should be an exponential function in inverse temperature, divided by the volume, that is,

$$ln\ y = ln\ g + a/T - ln\ V \tag{5}$$

and the problem becomes one of testing the applicability of this relation to the actual data and of finding the values of the constants a and g. The method of doing so is given below.

Expansion of either van der Waals' or Keyes' equation at constant temperature leads to a relation similar to that used by Onnes,[8] namely, $PV = RT + B\rho + C\rho^2 + D\rho^3 + \ldots\ldots$, where $\rho = 1/V$. Dividing through by RT, rearranging and multiplying by V, there is obtained

$$\Delta = V\left(\frac{PV}{RT} - 1\right) = B' + C'\rho + D'\rho^2 + \ldots\ldots \tag{6}$$

Deduced from the Keyes equation, B' has the value: $B' = \beta - A/RT$; whereas, if Equation 4 is similarly expanded, another term must be added as follows:

$$B' = \beta - \frac{A}{RT} - \frac{g \cdot f(T)}{2} \tag{7}$$

where $g \cdot f(T) = V\dot{y}$. Hence, if the value of B' is known for each isotherm, it can be ascertained whether or not the function of y as represented in Equation 5 is a suitable one and if so, constants for it should be determinable.

Of the available $P\text{-}V\text{-}T$ data on carbon dioxide, those of Amagat[9] are the most extensive, and accordingly were used for evaluating the constants of the equation of state. These PV values were multiplied by the factor[10] 505.87 to transform them into the desired units of cc.-atm. per gram, and values of Δ as defined by Equation 6 were then calculated[11] and plotted on a large scale against the density, the intercepts of the various isothermal curves on the Δ-axis giving the values of B'.

[6] Jeans, "Dynamical Theory of Gases," Cambridge University Press, 1921, p. 193.

[7] Keyes and Taylor, THIS JOURNAL, 49, 896 (1927).

[8] Onnes, *Proc. Acad. Sci. Amsterdam*, 4, 132 (1902). It differs from the expansion of Onnes in that it includes the terms ρ^{2n-1} where $n > 1$.

[9] Amagat, *Ann. chim. phys.*, 29, 109 (1893).

[10] Landolt-Börnstein's Tabellen, Julius Springer, Berlin, 1923, give the following values for the weight of 1 liter under standard conditions: Rayleigh, 1.9769; Leduc, 1.9763; Guye, 1.9768. See also Parr, THIS JOURNAL, 31, 237 (1909). Guye and Batuecas [*J. chim. phys.*, 20, 308 (1923)] give $(pv)_0/(pv)_1 = 1.00706$, which leads to a value of 1.9770 for the weight of 1 liter. Accepting the value 1.9768, the specific volume of carbon dioxide is 505.87 cc. at 0° and 1 atm.

[11] The value of $R = 1.8650$ in cc.-atm. per degree per gram was obtained by dividing 82.06 (International Critical Tables, McGraw-Hill Book Co., New York, 1926) by the molecular weight, which was taken as 44.000.

Since these curves are essentially deviation plots from the perfect gas law, they furnish an excellent means of obtaining accurate values of Δ and hence P, on each isotherm corresponding to convenient values of ρ, which can then be used to construct the isometrics of Equation 2. Such values were obtained for volumes ranging from 5 to 40 cc. per gram. These higher volumes lie on the extrapolated part of the Δ, ρ curves (which corresponds to an interpolation on the PV, ρ curves) but since Δ could be determined to 0.1%, and an error of 1% in it at 40 cc. per gram amounts to only 0.1% in the pressure, it is believed that these values are as accurate as those at lower specific volumes.

Reference to Equations 5 and 7 shows that the B', $1/T$ curve should consist of a straight line with an exponential superimposed upon it, if the reasoning outlined in the introduction is correct. A plot of B' against $1/T$ showed that there was such a curvature in the case of carbon dioxide over the entire range of B' values, so that in order to evaluate the constants of Equation 7, it was necessary to find the tangent to the extrapolated curve at its intercept with the B' axis. This in itself would be an extremely difficult matter, but fortunately the constants so obtained have to yield values of Γ which will make the resultant isometrics linear in pressure and temperature, according to the assumptions made in deriving the relations. By a few successive approximations, constants were obtained which satisfied both sets of data. Table I gives the calculated and observed values of B'. In Col. 2 are the observed values obtained by extrapolation of the Δ, ρ plot, while in Col. 3 are those calculated from the relation

$$B' = 2.6960 - \frac{3057.7}{T} - \frac{g \cdot f(T)}{2} \tag{8}$$

TABLE I

COMPARISON OF OBSERVED VALUES OF B' WITH THOSE CALCULATED FROM EQUATION 8

$B' = \beta - \dfrac{A}{RT} - \dfrac{g \cdot f(T)}{2}$; $\beta = 2.6960$, $A = 3057.7$, $R = 1.8650$; $T = t° + 273.13$;

$\log g \cdot f(T) = -3.7267 + 928.44/T$; $g \cdot f(T) = 1.8764 \times 10^{-4} e^{2137.8/T}$.

Temp., °C.	B', obs.	B', calcd.	$g \cdot f(T)$
0	−3.47[a]	−3.54	0.4705
10	−3.28	−3.27	.3569
20	−3.03	−3.04	.2758
30	−2.83	−2.82	.2168
40	−2.62	−2.63	.1731
50	−2.45	−2.45	.1401
60	−2.29	−2.28	.1149
70	−2.13	−2.13	.0953
80	−1.99	−1.99	.0799
90	−1.83	−1.85	.0676
100	−1.71	−1.73	.0577

[a] Only three points are given for the 0° isotherm in Amagat's table and hence this value of the intercept is uncertain.

where $\log g\cdot f(T) = -3.7267 + 928.44/T$; $g\cdot f(T) = 1.8764 \times 10^{-4}$ $e^{2137.8/T}$. In Col. 4 are listed values of $g\cdot f(T)$ obtained from the above relation which, when divided by V, give the corresponding amount of aggregation for any particular volume.

TABLE II

COMPARISON OF DEVIATIONS FROM LINEARITY IN THE ORIGINAL ISOMETRICS AND AFTER CORRECTION FOR AGGREGATION

Upper rows indicate curvature in original isometrics: lower rows show elimination of curvature by correction for aggregation; pressures in atmospheres.

Vol., cc./g.	10°	50°	100°
20	−0.05	+0.03	−0.01
	−.02	±.00	+.02
10	−.23	+.12	−.08
	−.05	+.03	+.03
5	−.30[a]	+.14	−.20
	+.01[a]	±.00	+.01

[a] Applies to 30°.

The extent of the curvature in the original isometrics is shown in Table II, where a comparison is made at three densities and temperatures between the observed pressures and those calculated on the assumption that Equation 1 represented the variation with temperature. At 20 cc. per gram, the curvature is small, but it increases at higher densities, becoming comparatively large at 5 cc. per gram. In the lower rows the observed pressures, corrected for the aggregation as expressed in Equation 2, are compared with those calculated from the best straight line through the resultant isometrics, and it is observed that this treatment introduces no curvature into the 20 cc. per gram isometric, whereas it eliminates the curvature in the others down to 5 cc. per gram. Thus it appears that the function for y as given in Equation 5, is a suitable one, within the experimental error of Amagat's data, and hence under these conditions, ψ and ϕ from the corrected isometrics are functions of volume only.[12]

The second phase of the problem of obtaining an accurate equation of state consists in finding appropriate volume functions for ψ and ϕ. and the solution of these was not so successful as was that of the first part. Using the method of averages, values of ψ were calculated for all of the volumes under consideration from 40 cc. per gram to 5 cc. per gram,

[12] In general, even if the isometrics are linear, it is possible to arrange ψ or ϕ as apparent temperature functions. Thus, at low pressures, van der Waals' equation can be written $PV^2 = RTV + RTb - a$, which is identical with $PV^2 = RTV + RT(b + c/T) - a'$, where $a' = a + Rc$. If now $(b + c/T)$ is called b', then it is evident that b' will be a function of the temperature, but the value of c cannot be obtained uniquely from P-V-T data, and in fact can have any desired value. Maass and Mennie [*Proc. Roy. Soc.*, **110**, 205 (1926)] use such an expression for their low-pressure data on carbon dioxide.

using pressures corrected for aggregation.   Assuming that $\psi = R/V - \delta$, values of δ were computed, and employing the Keyes exponential function, namely, $ln\ \delta = ln\ \beta - \alpha/V$, its constants were determined.   Taking the following numerical values for the constants,

$$\log \delta = 0.430719 - (1.2860/V); \quad \delta = 2.6960\ e^{-2.9701/V} \tag{9}$$

a satisfactory agreement was obtained between observed and calculated values of ψ down to 7 cc. per gram, but below that the departure was very marked.

Using these calculated values of ψ and substituting them in Equation 2, the average value of ϕ was obtained for each isometric.   Employing the functional form suggested by Phillips,[13] the constants were evaluated and the following relation obtained

$$\log \phi V^2 = 3.48539 - \frac{0.46108}{V}; \quad \phi = \frac{3057.7}{V^2} e^{-\frac{1.0617}{V}} \tag{10}$$

The agreement between the calculated and observed values of ϕ was fairly satisfactory down to 10 cc. per gram, but not at lower specific volumes.

<center>TABLE III</center>
<center>COMPARISON OF OBSERVED AND CALCULATED VALUES OF ψ AND ϕ</center>

$$\psi = \frac{R}{V - \delta}; \quad \log \delta = 0.430719 - \frac{1.2860}{V}; \quad \delta = 2.6960\ e^{-\frac{2.9701}{V}}; \quad \phi = \frac{A}{V^2} e^{-\frac{a}{V}};$$

$\log \phi\ V^2 = 3.48539 - (0.46108/V); \quad \phi = (3057.7/V^2)\ e^{-1.0617/V}.$

Vol., cc./g.	ψ, obs.	ψ, calcd.	Diff.	ϕ, obs.	ϕ, calcd.	Diff.
40	0.04978	0.04974	+0.00004	1.857	1.861	−0.004
30	.06775	.06768	+ .00007	3.277	3.279	− .002
25	.08257	.08250	+ .00007	4.691	4.689	+ .002
20	.10558	.10552	+ .00006	7.261	7.249	+ .012
15	.14588	.14585	+ .00003	12.689	12.661	+ .028
12	.18844	.18851	− .00007	19.462	19.436	+ .026
10	.23334	.23327	+ .00007	27.467	27.497	− .030
8	.30380	.30384	− .00004	41.503	41.839	− .336
7	.35642	.35633	+ .00009	52.804		
6	.43005	.42832	+ .00173	69.251		
5	.53664	.53151	+ .00513	94.218		

In Table III are listed the observed and calculated values of ψ and ϕ. The lack of agreement below 7 cc. per gram in the case of ψ and 10 cc. per gram in the case of ϕ may be due to two things.   In the first place, the functional forms used may not be the correct ones, but may hold over limited ranges only.   Thus the range from $V = \infty$ to $V = 10$ cc. per gram is equivalent to the range from 10 to 5 cc. per gram, since ψ and ϕ are functions of $1/V$, and hence a relation which held for the former part might show considerable deviation in the latter.   On the other hand,

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

the assumption was made that the aggregation was sufficiently small so that its effect on δ and ϕ was negligible, and at the high densities under consideration this assumption may not be justified.

Down to volumes of 10 cc. per gram, the equation of state for gaseous carbon dioxide as obtained from these data is, therefore,

$$P = \frac{1.8650 \; T \; (1 - y/2)}{V - \delta} - \phi \tag{11}$$

where $y = g \cdot f(T)/V$; $\log_{10} g \cdot f(T) = -3.7267 + 928.44/T$; $g \cdot f(T) = 1.8764 \times 10^{-4} \; e^{2137.8/T}$; $\log_{10} \delta = 0.430719 - 1.2860/V$; $\delta = 2.6960 \; e^{-2.9701/V}$; and $\log_{10} \phi V^2 = 3.48539 - 0.46108/V$; $\phi = (3057.7/V^2) \; e^{-1.0617/V}$

Pressures calculated from this relation are compared with the observed values in Table IV and it is seen that the agreement is very satisfactory, the average deviation being ± 0.02 atmosphere.

TABLE IV

COMPARISON OF THE OBSERVED PRESSURES OBTAINED FROM AMAGAT'S DATA AND THOSE CALCULATED FROM EQUATION 11

$$p = \frac{RT \; (1 - y/2)}{V - \delta} - \phi; \; \log_{10} y = -3.7267 + \frac{928.44}{T} - \log_{10} V; \; y = \frac{1.8764 \times 10^{-4}}{V}$$

$$e^{\frac{2137.8}{T}}; \; \log_{10} \delta = 0.430719 - \frac{1.2860}{V}; \; \delta = 2.6960 \; e^{-\frac{2.9701}{V}}; \; \log_{10} \phi V^2 = 3.48539 - \frac{0.46108}{V};$$

$$\phi = \frac{3057.7}{V^2} \; e^{-\frac{1.0617}{V}}.$$ Pressures in atm.; temperatures in °C.; $T = t + 273.13$.

Vol., cc./g.		0	10	20	30	40	50	60	70	80	90	100
40	obs.	11.16	12.15	12.67	13.17	13.69	14.19	14.69	15.19	15.69	16.19	16.70
	calcd.	11.64	12.16	12.67	13.18	13.68	14.18	14.68	15.19	15.69	16.19	16.69
		+0.02	−0.01	0.00	−0.01	+0.01	+0.01	+0.01	0.00	0.00	0.00	+0.01
30	obs.	15.08	15.76	16.47	17.15	17.86	18.54	19.22	19.91	20.58	21.28	21.96
	calcd.	15.06	15.77	16.47	17.16	17.85	18.54	19.22	19.91	20.59	21.27	21.95
		+0.02	−0.01	0.00	−0.01	+0.01	0.00	0.00	0.00	−0.01	+0.01	+0.01
25	obs.	17.66	18.48	19.35	20.19	21.06	21.90	22.73	23.56	24.39	25.24	26.07
	calcd.	17.63	18.50	19.36	20.21	21.05	21.89	22.73	23.57	24.40	25.23	26.06
		+0.03	−0.02	−0.01	−0.02	+0.01	+0.01	0.00	−0.01	−0.01	+0.01	+0.01
20	obs.	21.26	22.32	23.45	24.53	25.65	26.72	27.79	28.86	29.91	31.00	32.08
	calcd.	21.23	22.36	23.47	24.56	25.65	26.73	27.80	28.87	29.94	31.00	32.07
		+0.03	−0.04	−0.02	−0.03	0.00	−0.01	−0.01	−0.01	−0.03	0.00	+0.01
15	obs.	26.58	28.07	29.66	31.18	32.73	34.23	35.72	37.20	38.65	40.16	41.65
	calcd.	26.55	28.14	29.70	31.23	32.75	34.25	35.74	37.23	38.71	40.18	41.66
		+0.03	−0.07	−0.04	−0.05	−0.02	−0.02	−0.02	−0.03	−0.06	−0.02	−0.01
12	obs.	31.07	33.07	35.15	37.15	39.15	41.11	43.05	44.96	46.85	48.79	50.73
	calcd.	31.04	33.14	35.18	37.19	39.17	41.12	43.06	44.99	46.91	48.82	50.73
		+0.03	−0.07	−0.03	−0.04	−0.02	−0.01	−0.01	−0.03	−0.06	−0.03	0.00
10	obs.		37.35	39.96	42.48	44.97	47.41	49.83	52.20	54.54	56.94	59.35
	calcd.		37.37	39.94	42.45	44.91	47.35	49.77	52.16	54.55	56.92	59.29
			−0.02	+0.02	+0.03	+0.06	+0.06	+0.06	+0.04	−0.01	+0.02	+0.06

In addition to the data of Amagat, there are two other sets of P-V-T measurements on carbon dioxide. Andrews[14] compared a number of isotherms of carbon dioxide with those of air and published their relative

[14] Andrews, *Phil. Trans.*, **159**, 575 (1869); **167**, 421 (1877).

changes in volume under the same pressures. Ramsay and Young[15] calculated the actual pressures at various temperatures and volumes from these relative values, and their table gives the isometrics as linear even down to volumes of 3 cc. per gram. The author has recomputed all of Andrews' data, using recent measurements of the Reichsanstalt[16] on the isotherms of air, and the departure from linearity at high densities appears to be considerable. Table V gives a comparison of observed and calculated values between 30 cc. per gram and 10 cc. per gram for three isotherms. The agreement is fair, particularly in view of the indirect way in which the original data were obtained.

TABLE V

COMPARISON OF OBSERVED PRESSURES FROM ANDREWS' DATA WITH THOSE CALCULATED FROM EQUATION 11

Pressures in atm.; temperatures in °C.; $T = t + 273.13$.

Vol., cc./g.		6.5°	63.75°	100°	Vol., cc./g.		6.5°	63.75°	100°
30	obs.	15.51	19.49	21.94	15	obs.	27.83	36.43	41.66
	calcd.	15.52	19.48	21.95		calcd.	27.56	36.27	41.66
		−0.01	+0.01	−0.01			+0.17	+0.16	0.00
25	obs.	18.21	23.07	26.05	12	obs.		44.08	50.82
	calcd.	18.20	23.04	26.06		calcd.		43.76	50.73
		+0.01	+0.03	−0.01				+0.32	+0.09
20	obs.	22.00	28.19	32.05	10	obs.		51.16	59.53
	calcd.	21.96	28.25	32.07		calcd.		50.70	59.29
		+0.04	+0.06	−0.02				+0.46	+0.24

Recently Maass and Mennie[17] have published a series of P-V-T data at low pressures but over a considerable temperature range, in which they list the pressures, temperatures and volumes of various masses of carbon dioxide. Equation 11 was used to calculate corresponding pressures, and over the temperature range from 0 to 100° throughout which this equation holds, the agreement is good (0.06%), but below 0°, where the calculated values are extrapolated, the divergence is somewhat greater, the average deviation over the whole set of data being 0.17%.

Summary

1. The close approximation to linearity of the isometrics of carbon dioxide is used as the foundation for an equation of state based on Amagat's low-pressure data. Departure from linearity is defined as aggregation, and is quantitatively accounted for by a simple function of temperature and volume suggested by thermodynamics and kinetic theory.

[15] Ref. 3 a, p. 446. These values were used by Keyes in deriving an equation of state for carbon dioxide. Compare *Am. Soc. Refrigerating Eng. J.*, [4] **3**, 1 (1917); THIS JOURNAL, **46**, 1584 (1924).

[16] "Wärmetabellen der Physikalisch-Technischen Reichsanstalt," Friedr. Vieweg und Sohn, Braunschweig, **1919**, p. 44.

[17] Maass and Mennie, *Proc. Roy. Soc.*, **110**, 205 (1926).

2. The volume functions used for the constants of the various iso-metrics are those suggested by Keyes and Phillips which are found to be suitable down to volumes of 10 cc. per gram.

3. The resultant equation as based on Amagat's data between 0 and 100° is $P = [RT(1 - y/2)]/(V - \delta) - \phi$, where $y = g \cdot e^{a/T}/V$; $\log_{10} y = -3.7267 + 928.44/T - \log_{10} V$; $y = (1.8764 \times 10^{-4}/V)$ $e^{2137.8/T}$; $\delta = \beta e^{-\alpha/V}$; $\log_{10} \delta = 0.430719 - 1.2860/V$; $\delta = 2.6960$ $e^{-2.9701/V}$; and $\phi = (A/V^2)e^{l/v}$; $\log_{10} \phi V^2 = 3.48539 - 0.46108/V$; $\phi V^2 = 3057.7 e^{-1.0617/V}$; and a comparison is given between the ob-served values and those calculated from this equation for various iso-metrics down to 10 cc. per gram, the average deviation being ±0.02 atm., or 0.07%.

4. All of Andrews' data have been recomputed by the author and the agreement between his low-pressure values and those calculated from the above equation is fair. The recent data of Maass and Mennie at pressures around 1 atm. and below have been transformed into isometrics, and over the temperature range from 0 to 100° throughout which the proposed equation of state holds, the agreement between calculated and observed values is good.

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THE IODIMETRIC DETERMINATION OF VANADIUM

BY J. B. RAMSEY

In an alkaline solution or in a neutral buffer solution, tetravalent vanadium is oxidized by iodine to the pentavalent condition,[1] while in acid solution pentavalent vanadium is reduced by iodide ion. At very high concentrations of acid and iodide the reduction may be made to pro-ceed to the trivalent condition,[2] but over a wide range of acid and iodide concentrations at ordinary room temperatures, it stops at the tetravalent state. The effect of the concentration of the acid and iodide on the extent of the reduction has been discussed by Edgar.[3]

Methods of determining vanadium based on the determination of the iodine formed in the reduction of pentavalent vanadium to the tetrava-lent condition by iodide ion have been described by Perkins[4] and Edgar.[3] The iodine formed is determined in the one case[4] by converting it into silver iodide and weighing as such; in the other[3] by removing it from the vana-

[1] Browning, *Am. J. Sci.*, [4] **2**, 185 (1896).

[2] Friedheim and Euler, *Ber.*, **28**, 2067 (1895). Edgar, *Am. J. Sci.*, [4] **26**, 333 (1908); [4] **27**, 174 (1908).

[3] Edgar, THIS JOURNAL, **38**, 2369 (1916).

[4] Perkins, *Am. J. Sci.*, [4] **29**, 540 (1910).