20); nevertheless, numerically the linear relation does hold rather closely over temperature range 375 to 500° (Fig. 1).

CAMBRIDGE, MASSACHUSETTS

THE ISOMETRICS OF GASEOUS METHANE

BY FREDERICK G. KEYES AND HARRY G. BURKS

Introduction

The interest which attaches to an accurate knowledge of the properties of methane is two-fold. First, it belongs to that class of substances, of which nitrogen, hydrogen and oxygen are further examples, which in the sense of their dielectric behavior[1] may be said to possess no natural or permanent electrical moment. Secondly, relative to the other members of the above class of substances, the constants A, β, α and l of the equation of state are large, making it very suitable as a component with, for example, nitrogen in binary mixtures. Molecular simplicity and freedom from the possibility of chemical action in binary mixtures are indeed most important in attempting to determine the equation-of-state constants in mixtures as functions of the constants of the equations of state of the pure components of the binary mixtures.

The present measurements represent a repetition of work already carried out for methane some years ago.[2] However, in the interval, the apparatus has been much improved in many particulars, not the least of which is an increase in the size of the methane container or piezometer. Thus the present container has a maximum volume of about 13.337 cc. at 0°, whereas the earlier had a volume of 7.657 cc. In principle, however, the method remains the same as that in use for this class of work for a number of years.

The earlier work gives smaller pressures for corresponding volumes and temperatures, although above 30 cc. per g. the differences are practically insignificant. At about 10 cc. per g., however, the differences are larger than would have been anticipated in spite of the small size of the piezometer employed in the earlier survey. Thus at 0° the

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[1] The importance of the dielectric constant in relation to the cohesive pressure constant A has been made clear by Debye [*Physik. Z.*, **21**, 178 (1920)]. A recent paper by Keyes and Marshall [THIS JOURNAL, **49**, 156 (1927)] shows that for substances of the simple character referred to, the ratio of the equation-of-state constants A and β (in per mole units) is approximately proportional to the Lorentz constant P_0 in the dielectric equation $V(D - 1)/(D + 2) = P_0$, where V is the molecular volume and D the dielectric constant.

[2] Keyes, Smith and Joubert, *J. Math. Phys. Mass. Inst. Techn.*, **1**, 191 (1922).

difference in pressure for specific volume 10.03 cc. amounts to about 0.3%, while at 200° it is somewhat more than 1%. The accumulating experience indicates that to obtain a uniform degree of precision over a range of densities it is best to keep the actual volumes of material whose pressures and temperature are being measured as nearly the same as possible by varying the mass of material in the piezometer. The latter procedure involves, of course, much more manipulation, but the high precision required for the solution of many aspects of the equation-of-state problem can be attained by no other procedure.

The range of temperatures used in the measurements herewith recorded is from 0 to 200°, and the specific-volume range 40 cc. per g. to 10 cc. per g., corresponding to a lowest pressure of about 32 atm. and a highest pressure of about 254 atm.

Quality of the Methane Employed.—The supply of methane was prepared as described earlier.[2] Dry sodium acetate was decomposed by heat, the evolved gases being passed slowly through 20% fuming sulfuric acid, concd. sulfuric acid, sodium hydroxide solution, solid sodium hydroxide and phosphorus pentoxide. Repeated fractional distillation finally gave a product which a special analytical method indicated to be pure to one part in 1300, about the limit of sensitiveness of the apparatus.

Experimental Method

The details of the method of loading the piezometer and making the measurements have been fully described in earlier work.[2] The method consists in confining a definite mass of methane in the piezometer at constant temperature by means of mercury. The volume of methane, owing to the apparatus design, may be accurately varied and, by obvious manipulation of the mercury injector, the volume of the methane under measurement may be kept constant in spite of distention of the steel piezometer.

Experimental Data

The data obtained are given in Table I, in which Col. 1 contains the volumes in cubic centimeters per gram. Corresponding to these volumes there are given in the horizontal rows the observed pressures, beneath which are pressures calculated for the volumes given in Col. 1, and for the temperatures at the top of each vertical column of pressures. The latter computed pressures will be referred to more explicitly below.

The isometrics of methane show a small curvature which, however, is much greater for the same range of temperature than for nitrogen.[3] The earlier work also indicated curvature but the precision of the data was insufficient to permit a quantitative examination of the effect. In Table II will be found the successive differences in pressure at constant volume divided by the temperature intervals (50°) corresponding thereto.

³ Smith and Taylor, THIS JOURNAL, **45**, 2107 (1923); **48**, 3122 (1926).

TABLE I

METHANE

Pressure in atmospheres

Vol., cc./g.		0°	50°	100°	150°	200°
40	obs.	32.297	39.418	46.474	53.486	60.486
	calcd.	32.291	39.388	46.429	53.444	60.459
35	obs.	36.514	44.760	52.935	61.040	69.158
	calcd.	36.515	44.742	52.898	61.025	69.142
30	obs.	42.003	51.809	61.510	71.139	80.752
	calcd.	42.013	51.794	61.496	71.138	80.766
25	obs.	49.441	61.504	73.445	85.260	97.050
	calcd.	49.478	61.511	73.432	85.289	97.126
20	obs.	60.129	75.980	91.240	106.540	121.806
	calcd.	60.198	75.831	91.274	106.632	121.967
15	obs.	76.879	99.004	120.854	142.426	163.973
	calcd.	77.006	99.152	120.991	142.723	164.344
12	obs.	92.689	121.949	150.883	179.407	207.951
	calcd.	92.740	122.093	151.017	179.736	208.357
10	obs.	107.950	145.076	181.840	218.122	254.266
	calcd.	107.801	145.017	181.713	218.121	254.396

$$p_{\mathrm{atm.}} = \frac{5.1173\, T\, (1 - y/2)}{v - \delta} - \frac{9370\, (1 - 0.586\, y)}{(v + 0.42)}$$

$$\log_{10} \delta = 0.5611 - 0.978/v$$

$$\log_{10} (v - \delta)\, \frac{y}{(1 - y)^2} = \frac{527}{T} - 1.25 \log_{10} T + 0.813$$

TABLE II

METHANE

$\dfrac{\Delta p}{\Delta T}$ per degree from the 50° intervals of each isometric in Table I

Vol., cc./g.		0–50°	50–100°	100–150°	150–200°
40	obs.	0.14242	0.14111	0.14024	0.14000
	calcd.[a]	.14194	.14082	.14030	.14030
35	obs.	.16492	.16348	.16210	.16237
	calcd.	.16454	.16312	.16254	.16234
30	obs.	.19612	.19402	.19258	.19226
	calcd.	.19562	.19404	.19284	.19256
25	obs.	.24127	.23881	.23630	.23584
	calcd.	.24064	.23842	.23714	.23674
20	obs.	.31301	.30920	.30603	.30529
	calcd.	.31266	.30886	.30716	.30670
15	obs.	.44250	.43701	.43143	.43095
	calcd.	.44292	.43678	.43464	.43242
12	obs.	.58520	.57869	.57048	.57087
	calcd.	.58706	.57848	.57438	.57242
10	obs.	.74242	.73528	.72563	.72289
	calcd.	.74432	.73392	.72816	.72550

[a] The calculated numbers are obtained from the 50° intervals of the computed pressures in Table I.

Inspection of the tabulated values of $\Delta p/\Delta T$ corresponding to each volume indicates clearly that there is a curvature diminishing steadily in degree as the temperature increases.[4] This means that as the temperature increases the isometrics are becoming more exactly linear, an effect common to all substances in the gaseous phase excluding temperatures high enough to cause chemical decomposition.

The method by which the equation used to compute the pressures in Table II was obtained has not been hitherto described. The assumptions on which it rests are first, that the isometrics are exactly linear at sufficiently high temperatures, and second, that the cause of the increasing departure of the isometrics from linearity as lower temperatures are approached is a quasi-association of the molecules.[5] The equation of state[6] for the region where the isometrics are substantially linear has already been published and need not be discussed beyond remarking that a good representation of the *pressures* may often be obtained by neglecting a slight curvature of the isometrics. Where derived quantities are required (as, for example, in calculating the Joule-Thomson effect or the specific heat at constant volume as a function of the pressures), the equation-of-state constants obtained by neglecting the curvature must be used with due caution.[7]

The hypothesis that a quasi-association or molecular aggregation[8] exists is chiefly based on the fact that the departure from linearity of the isometrics as lower temperatures are approached displays the same general characteristics that would be exhibited by a gas such, for example, as nitrogen dioxide. In addition, a rather severe test of the hypothesis has already been described in a paper by one of the writers dealing with the dependence of the Joule-Thomson effect for carbon dioxide[7] on temperature. A further exacting test lies in the direction of accounting for the dependence of the constant-volume heat capacity on temperature. Indeed, unpublished treatment of the latter kind of data for ammonia obtained at the Bureau of Standards indicates that the constant-volume specific heat can be well represented as a function of the density.

The method of obtaining the constants of the equation of state for the high-temperature linear isometric state of methane consisted in first

[4] The last column contains numbers corresponding to 35 cc. per g. and 12 cc. per g. for which this statement is not true. The reversal of sign is evidently due to experimental error corresponding to an error (if assigned to a single pressure) in the 150° pressure of one part in 4000 in the former volume and half of this for the latter.

[5] Keyes and Felsing, THIS JOURNAL, **41**, 589 (1919).

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

[7] Keyes, THIS JOURNAL, **46**, 1584 (1924).

[8] A description of what is meant by quasi-association or aggregation sufficiently similar to the conception of the authors is given by Jeans in his "Dynamical Theory of Gases," Cambridge University Press, **1925**, p. 193.

using the four series of $\Delta p/\Delta T$ values given in Table II to calculate four values each of the "constants" β and α. This procedure amounts to assuming that the isometric curvature is constant for each 50° interval. The four values each of the "constants" β and α were next treated graphically in relation to the temperature for the purpose of obtaining β and α "constants" corresponding to each of the five temperatures at which pressures were measured along each isometric. The latter "constants" were next employed to compute five values of the equation-of-state term $A/(v + l)^2$ corresponding to each of the five temperatures for each isometric. The final result is a series of values of the constants given in Table III.

TABLE III

VARIATION OF "CONSTANTS" WITH TEMPERATURE

	0–50°	50–100°	100–150°	150–200°	
β	4.426	4.000	3.698	3.648	
α	3.80	2.86	2.35	2.26	
	0°	50°	100°	150°	200°
A	11283	10453	9810	9419	9382
l	0.844	0.571	0.486	0.330	0.422

By graphical treatment of the "constants" of Table III relative to the temperature the following equation of state for "infinite" temperatures was deduced.

$$p = \frac{5.1173\ T}{v - 3.64\ e^{-2.25/v}} - \frac{9370}{(v + 0.42)^2} \qquad (1)$$

The equation of state obtainable by neglecting the curvature of the isometrics is as follows.

$$p = \frac{5.1173\ T}{v - 3.96\ e^{-2.857/v}} - \frac{10151.4}{(v + 0.536)^2} \qquad (2)$$

Equation 2 represents the pressures at 40 cc. per g. to about 0.1 to 0.2%. At 10 cc. per g., however, Equation 2 gives pressures 1% too high at zero, and 0.2% at 200°.

The difference between the pressures given by Equation 1 and the observed pressures should, by the hypothesis of molecular aggregation, be capable of correlation as a function of the temperature and volume by means of a formula resembling presumably more or less closely the equation commonly used to represent the equilibrium constant of a true chemical association (for example, $NO_2 = 1/2\ N_2O_4$). The latter type of equation, when double aggregates alone are considered, is as follows, where differences in the heat capacities of the two molecular species are neglected, y is the fraction associated and g a constant.

$$K_y = \frac{y}{(1 - y)^2} = g\ e^{2\Delta U/RT}\ \frac{1}{v} \qquad (3)$$

In Equation 3 ΔU refers to the heat of association or aggregation due to one mole of the simpler species. Of course it is by no means clear that

the aggregation effect, which is not generally a chemical reaction of the type exemplified in the reaction $NO_2 = {}^1/_2\, N_2O_4$, follows the mass law assumed in Equation 3. However, the investigation of the validity of the aggregation hypothesis is in its initial stage only and definite conclusions of value can be drawn by applying Equation 3, not omitting to keep clearly in mind that the use of the latter may be only a provisional expedient.

The remark is apropos also that p, v, T measurements alone are neither entirely adequate to decide finally the question of whether aggregation or molecular clustering is actually present in a gas, nor by what laws its extent is related to temperature and pressure. Other properties of gases, however, will serve to provide data by which definite progress in the desired direction can be secured. The properties referred to are viscosities over a range of temperatures preferably at constant volume, and similarly dielectric constants and refractive indices.

The interpretation of the differences between the observed pressures and Equation 1 depends on whether it is assumed that one or more of the constants A, β, α and l are affected by the aggregation. In the present treatment it was assumed that the cohesive-pressure constant A per mole for the aggregated species (double molecules) was twice the magnitude of the unaggregated species. Unpublished data for mixtures indicate that the square roots of the A constants for separate species vary as the amounts of material in the mixture, that is, $(\Sigma \sqrt{A_1} n_1)^2 = A_{\text{mix.}}$.

Applying this rule of combining the A constants gives, where y is the fraction associated, for A in the equation of state for methane, $A = (1 - 0.586\, y)$, neglecting y^2. The equation of state for methane containing a small aggregated fraction thus becomes

$$p = \frac{5.1173\, T\, (1 - y/2)}{v - 3.64\, e^{-2.25/v}} - \frac{A\, (1 - 0.586\, y)}{(v + 0.42)^2} \tag{4}$$

or $\quad p = \dfrac{5.1173\, T}{v - \delta} - \dfrac{9370}{(v + 0.42)^2} - y\left[\dfrac{5.1173\, T}{2(v - \delta)} - 0.586\, \dfrac{9370}{(v + 0.42)^2}\right] \tag{4'}$

The differences between $p_{\text{obs.}}$ and p by Equation 1 would, on this basis, be given by $y(\psi T/2) - 0.586\, \phi$, where ψ is written for $R/(v - \phi)$ and ϕ for $A/(v + 0.42)^2$. The values of y obtained in this way were found to be fairly well represented by the following equation, resembling Equation 3 in form.

$$\log_{10}(v - \delta)y/(1 - y)^2 = (527/T) - 1.25\,\log_{10} T + 0.813 \tag{5}$$

Equation 5 differs from 3 by the substitution of $(v - \delta)$ for v and the introduction of the term $1.25\,\log_{10} T$. These modifications appeared to improve slightly the correlation of the y data, although the only theoretical justification which can be advanced lies in the formal necessity of modifying Equation 3 in respect to its dependence on volume because of the failure of the perfect gas laws upon which 3 is based. The term

1.25 $\log_{10} T$ was assumed for the purpose of representing specific-heat differences between aggregated and unaggregated species. There are so many unsettled theoretical factors entering into the matter of aggregation that Equation 5 must be regarded as largely empirical.

Many users of the kind of data contained herein prefer to use the pv products expanded in series form. The following equations represent the data of Table I with considerable accuracy except those corresponding to 10 cc. per g.

$$(pv)_{0^\circ} = 1397.7 - 4485.3\,\frac{1}{v} + 7935.8\,\frac{1}{v^2} + 99998\,\frac{1}{v^3} - 5109961\,\frac{1}{v^4}$$

$$(pv)_{50^\circ} = 1653.5 - 3255.2\,\frac{1}{v} + 3554.3\,\frac{1}{v^2} + 172063\,\frac{1}{v^3} - 894859\,\frac{1}{v^4}$$

$$(pv)_{100^\circ} = 1909.4 - 2168.3\,\frac{1}{v} + 878.5\,\frac{1}{v^2} + 235365\,\frac{1}{v^3} - 1253210\,\frac{1}{v^4}$$

$$(pv)_{150^\circ} = 2165.3 - 1194.4\,\frac{1}{v} + 1130.1\,\frac{1}{v^2} + 243381\,\frac{1}{v^3} - 1276250\,\frac{1}{v^4}$$

$$(pv)_{200^\circ} = 2421.1 - 300.2\,\frac{1}{v} + 5690.7\,\frac{1}{v_2} + 160327\,\frac{1}{v^3} - 684619\,\frac{1}{v^4}$$

The coefficients of reciprocal v are given by $B = 14.8413\,T - 8207.9 + 1.74667 \times 10^6(1/T) - 8.006264 \times 10^8(1/T^2) + 8.16284 \times 10^{10}(1/T^3)$, and similar expansions will represent the remaining coefficients. Thus, by means of 25 constants, the measured data may be very accurately represented, except the 10cc. volumes. It is the opinion of the writers that the equation of state at the bottom of Table I is more to be relied upon for general computations involving derivatives.

Summary

1. New experimental pressure, volume and temperature data are given for pure methane. The volumes for which pressures and temperatures were measured are 40, 35, 30, 25, 20, 15, 12 and 10 cc. per g. The temperatures employed were 0, 50, 100, 150 and 200°.

2. The isometrics of pure methane show curvature which is slight at 40 cc. per g. and gradually increasing as small volumes are considered. The curvature for each volume measured decreased rapidly with rising temperature.

3. The constants of the equation of state for methane at high temperatures are derived by a "temperature extrapolation," wherein four sets of "constants" are determined for the experimental temperatures. The constants thus obtained are extrapolated to "infinite temperatures" by graphical means. The resulting equation is $p = 5.1173\,T/V - 3.64\,e^{-2.25/v} - 9370/(v + 0.42)^2$.

4. The curvature of the isometrics, as measured by the difference between the pressures given by the high-temperature equation of state for methane and the observed pressures is interpreted on the hypothesis of aggregation to double molecules.

In applying this hypothesis it was assumed that allowance was necessary for the influence of aggregation on the cohesive constant A of the equation of state. The assumption made was that A for the aggregated species was twice per mole the value of the unaggregated species. The aggregation equation was found to be, where y is the aggregated fraction, $\log_{10}(v - \delta)y/(1 - y)^2 = 527/T - 1.25 \log_{10}T + 0.813$. The pressures are accurately represented by the equation of state, wherein allowance has been made for aggregation.

5. The pressure-volume products, as functions of reciprocal volume, are given in series form for each of the five temperatures measured. The equation of state 4', however, represents the entire range of data with satisfactory exactness.

CAMBRIDGE, MASSACHUSETTS

A HITHERTO UNSUSPECTED SOURCE OF ARSENIC IN HUMAN ENVIRONMENT

BY ROE E. REMINGTON

The question as to whether or not arsenic is a constant constituent of the animal organism has been one of interest since the work of Gautier and of Bertrand. These workers maintained that it is always present, at least in man, one of them going so far as to assert that it exercises a normal and necessary function in the body. This position has been attacked by Ziemke and others, who maintain that arsenic is present only as an accidental contamination from many articles of food and drink, and may be, and oftentimes is entirely absent in the body. Before we can interpret the work of any investigator, however, we must scrutinize his methods and technique, and failure to find arsenic with certainty cannot in all cases justify the conclusion as to its absence.

The literature of this phase of the question has been fully summarized by Fordyce, Rosen and Myers,[1] and will not be recapitulated here. By far the most painstaking and delicate work of recent times has been that of Billeter and Marfurt,[2] who examined the organs and tissues of many bodies, from new-born infants to men of seventy years. They have so improved the Marsh method as to detect and estimate with certainty quantities of arsenic as small as one or two millionths of a milligram. Their conclusion is that arsenic is always present and progressively increases with age. They have established that in round numbers the body of an adult contains one ten-millionth of its weight in arsenic.

[1] Fordyce, Rosen and Myers, *Arch. Internal Med.*, **31**, 739 (1923).

[2] Billeter and Marfurt, *Helv. Chim. Acta*, **6**, 258, 771, 780 (1923).