[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLORADO SCHOOL OF MINES]

Diffusion as an Aid in the Analysis of Gaseous Paraffin Hydrocarbon Mixtures

BY ROBERT A. BAXTER AND LELAND J. BECKHAM

The purpose of the present investigation is the development of a supplementary procedure to be used in conjunction with the usual combustion analysis on paraffin hydrocarbon gases in order to increase the information attainable. It is a well-known fact that lighter gases will diffuse more rapidly than heavy ones. Thus if a mixture of several gases be allowed to undergo partial diffusion, the residue remaining after part of the gases have diffused away will have a composition which is richer in the heavier constituents. This change in composition can be calculated by means of the kinetic theory.

The present paper describes an apparatus suitable for this determination, together with charts for its application to ordinary analytical practice.

The apparatus (Fig. 3), later described in detail, is operated as follows. The hydrocarbon mixture is introduced into the apparatus, the orifice opened and the gases allowed to diffuse into the air for a certain period of time; the stopper is then replaced, and a sample withdrawn for the usual combustion analysis. From the results of this combustion analysis and from one on the original mixture before diffusion, and by the use of proper equations or charts, considerably more information concerning the nature of the gas sample can be obtained, as is described in this paper.

In the calculation of the composition of gaseous paraffin hydrocarbon mixtures from the results of combustion and absorption data, assumptions are usually made as to the "two most prevalent hydrocarbons" and the analysis is reported in terms of the quantity of these in the mixture.[1] This practice has led to much confusion, particularly when a natural gas is reported as a mixture of ethane and propane before stripping gasoline out of it, and as another mixture of these same two gases after the stripping. The heating value, the air required for combustion, the theoretical flame temperature and the composition of the stack gases resulting from the combustion of any such mixture can be calculated from the analysis reported in this manner. The same results could be obtained from the calculation to any other assumed mixture of paraffin hydrocarbon gases, one of which is lighter, and the other one heavier than the average of the gases actually present. Although several measurable quantities result from the combustion of the gas and the subsequent absorption of the carbon dioxide which is formed, there are only two independent equations, and

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(1) "Methods of the Chemists of the U. S. Steel Co. for the Sampling and Analysis of Gases," Carnegie Steel Co., Pittsburgh, 1927, p. 88. Also see Burrell, Seibert and Jones, *Bur. Mines Bull.*, **197**, 96 (1926).

consequently only two hydrocarbons can be calculated. Earnshaw[2] developed the equations by means of which the total volume of paraffin hydrocarbons and the average number of carbon atoms per paraffin molecule may be calculated. Similar equations for various combustible gases were set up by de Voldere and de Smet[3] and condensed by Anderson.[4] A further correlation of these equations was made by Baxter.[5] The evidence in these references is very conclusive as to the superiority of reporting these analyses in terms of the amount of paraffin hydrocarbons of a stated average number of carbon atoms per molecule.

The difference in the diffusion characteristics of gases will produce a measurable difference in the value of n (the average number of carbon atoms per molecule of hydrocarbons in the gas) determined before and after diffusion. From the value of Δn (the increase in n which results from the greater rate of diffusion of the smaller molecules) and the value of n in the original mixture, a new equation is obtained by which the calculation may be extended to three hydrocarbons.

However, the use of this equation for the calculation of three component mixtures requires considerable time and effort for solution; therefore, diagrams of the relationship between n and Δn have been prepared for the two ternary mixtures: methane–ethane–propane (Fig. 1) and methane–ethane–butane (Fig. 2). It is obvious that the sides of these diagrams give the five binary relationships.

If a set of charts is determined for any given apparatus these charts can be used completely in place of numerical calculation and the application of the method is extremely simple and rapid. There are three distinct methods whereby any one wishing to use this procedure could obtain charts for an apparatus which he might construct.

1. The charts might be constructed from the fundamental equations given later in the paper. (The charts shown in this paper were obtained in this manner.)

2. One could so choose the length of time of the run that the same total amount of diffusion would take place as in the apparatus which we used. Then the charts in this paper would be applicable. This could be easily calibrated by determining the proper time so that 80% of a sample of pure methane would diffuse out, as our charts were constructed for this amount of diffusion.

3. A sufficient number of experimental determinations upon known mixtures could be run so that the charts could be plotted entirely from experimental data without resorting to the kinetic equations.

The value of n is obtained by the equation: $n = 3y/(2x - y)$, in which

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(2) Earnshaw, *J. Franklin Inst.*, **146**, 161–176 (1898).

(3) De Voldere and de Smet, *Z. anal. Chem.*, **49**, 661–688 (1910).

(4) R. P. Anderson, see Dennis and Nichols, "Gas Analysis," The Macmillan Co., New York, 1929, Chapt. XII.

(5) Robert A. Baxter, *Color. School Mines Mag.*, **20**, No. 1, 13–16 (1930).

x is volume contraction resulting from combustion and y is volume of carbon dioxide formed by combustion.

For purposes of illustration we will confine our attention to mixtures in which the average value of n as obtained from combustion analysis is 1.60.

The ordinary method of reporting this gas would be as methane and ethane in the ratio of four to six parts by volume in the combustible hydrocarbon mixture. If this happens to be 50% of the original gas sample, the analysis will usually be given as 20% methane and 30% ethane. As pointed out by one of us in an earlier paper to which reference was made above, better information can be obtained by reporting this mixture as 50% total paraffin hydrocarbons of an average value of $n = 1.60$. The volume of the total paraffin in the sample burned is obtained by the equation: $V = (2x - y)/3$. x and y have the meanings given above. This avoids any unwarranted assumptions.

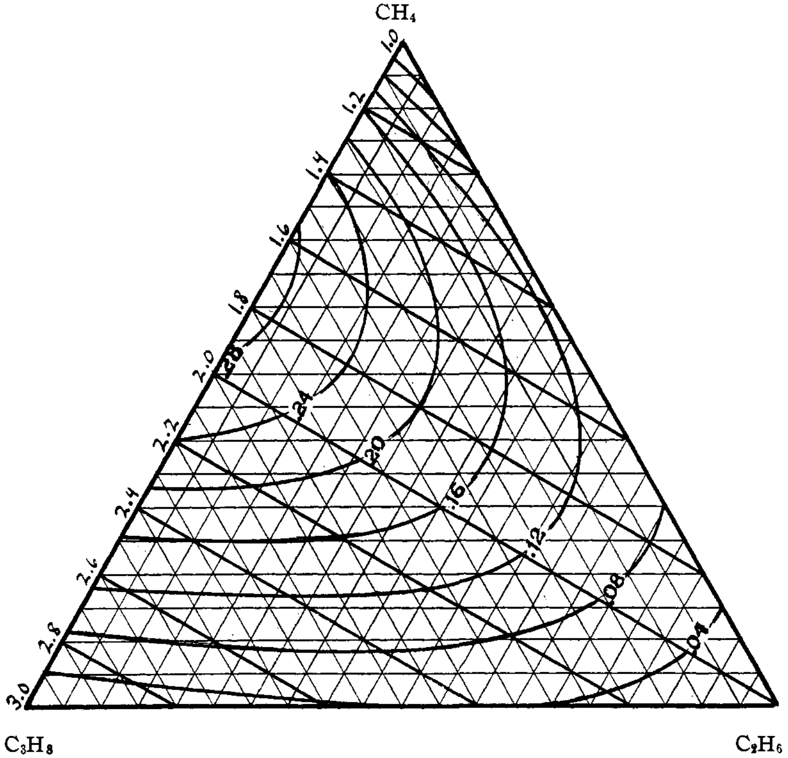

Fig. 1.—Methane–ethane–propane diagram: curved lines are values of Δn.

A glance at the chart or a brief calculation will indicate that one might assume 70% methane and 30% propane, 80% methane and 20% butane, or some corresponding higher ratio of methane to pentane or other hydrocarbons instead of the assumed value of 40% methane and 60% ethane.

In addition, the mixture might be one of methane with two or more higher hydrocarbons. There is just one point which is clear, namely, that in a mixture of paraffin hydrocarbons in which $n = 1.60$, the methane is not less than 40%.

Two gaseous mixtures will be considered. Each has $n = 1.60$. One gives $\Delta n = 0.12$ while the other gives $\Delta n = 0.36$. The intersection of the $\Delta n = 0.12$ curve with the line $n = 1.60$ will first be considered. If the system present is methane–ethane–propane, the propane will be 4% of the entire mixture. If the system present is methane–ethane–butane, the butane will be 2% of the entire mixture. Since still less of any higher paraffin hydrocarbon will be required to have the same effect as the 4% of propane or the 2% of butane, the limits of not less than 96% total methane and ethane mixture, not more than 2% butane, and less than 2% of any higher hydrocarbons are definitely established. The mixture which gives $\Delta n = 0.36$ will now be considered. Since this value is greater than any which appear on the chart for the system methane–ethane–propane, the one first dependable conclusion is that there must be some butane or higher hydrocarbon present. The intersection of the two appropriate

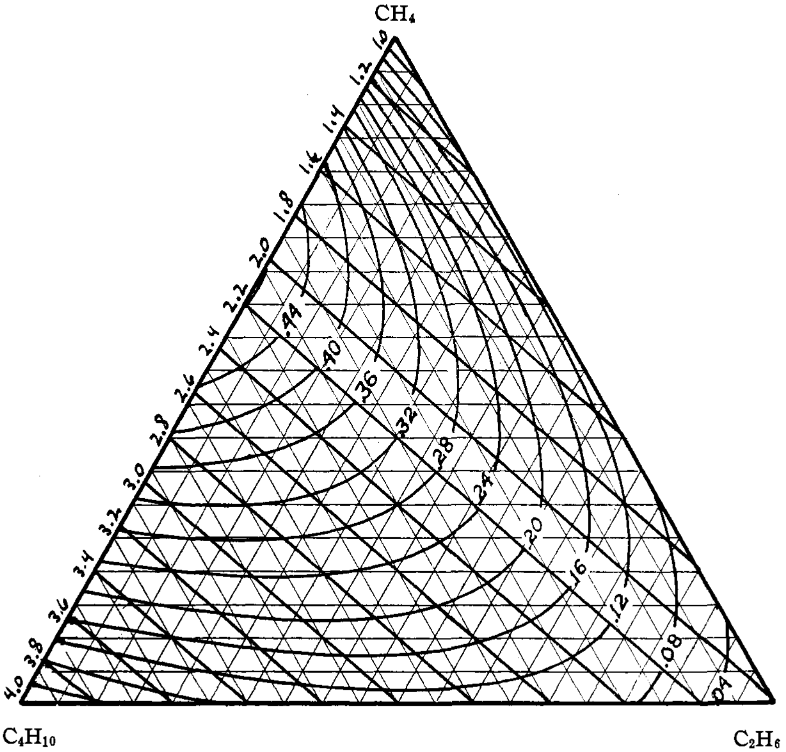

Fig. 2.—Methane–ethane–butane diagram: curved lines are values of Δn.

curves on the methane–ethane–butane diagram indicates that if the system actually happens to consist of these three constituents, the butane must be 17% of the mixture. This is the maximum limit for the butane or heavier hydrocarbons. In case higher ones are present, their amount will be relatively less and the fraction of lighter hydrocarbons relatively more. The minimum amount of methane and ethane cannot be read directly from the methane–ethane–propane diagram as in the former case for the value of Δn does not fall on the chart. However, the minimum can be obtained in this case from a chart constructed for methane–propane–butane. We have constructed only the two charts shown. Similar charts could be constructed for any three assumed hydrocarbons (including hydrogen as a paraffin hydrocarbon in which $n = 0.00$).

The triangular diagrams indicate very definitely the difference between the two gases which would be reported as identical by the conventional method. The gas with $\Delta n = 0.12$ is sufficiently evaluated for most purposes by the diffusion method. The necessity for further work in order to get an accurate evaluation of the one in which $\Delta n = 0.36$ is shown. In general, when the value of Δn is small the analysis as obtained by the combination of diffusion with the combustion and absorption procedures will meet the ordinary analytical requirements, but when the value of Δn is large the presence of higher hydrocarbons is definitely shown. In the latter case the nature of the constituents as well as their concentration is obscure. When Δn is large some type of low-temperature fractional distillation device[6] would probably be the most satisfactory for the separation and identification of the higher boiling constituents. However, this equipment is expensive and more or less complicated, and it requires liquid air or similar material for cooling.

The diffusion method will minimize guessing in the analysis of gaseous mixtures, will itself give sufficient results in many instances, and in the remainder it will give definite indications as to the necessity for using the more complex and expensive methods.

Experimental

Preparation of Materials.—The hydrocarbons used, methane, ethane, propane and butane, were prepared from the corresponding halides by means of the Grignard reaction. The gases were washed with concentrated sulfuric acid and stored over water.

Combustion Analyses.—The combustion and absorption analyses were performed with the laboratory apparatus of the U. S. Steel Corporation[7] using mercury as the confining agent. All samples of gas were analyzed two to eight times, and the average of these values was recorded as the true composition of the gas. The average variation from the mean on the values of n obtained from calculation from the observed data was 0.015.

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(6) Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931).

(7) "Methods of the Chemists of the U. S. Steel Co. for the Sampling and Analysis of Gases," Fig. 2, p. 8.

Description of Diffusion Apparatus.—The device which was used is shown in Fig. 3. It consists of a Shaw filter flask, into which a metal orifice cup has been fitted and held in place by rubber. This is in turn closed by a rubber stopper which fits into the wide opening of the orifice cup, of which the orifice plate is the bottom. The side neck serves as the filling and flushing connection and the bottom serves for the connection to the leveling bottle containing the confining liquid. The stopcock in the bottom is very convenient in handling the device. The diameter of the orifice is 2.44 mm. in a plate 2.15 mm. thick. It is essential that there be no narrow tube leading to or from it, since this sets up extra resistance by providing a region on either side of the orifice in which an appreciable gradient is maintained so that diffusion is hindered.

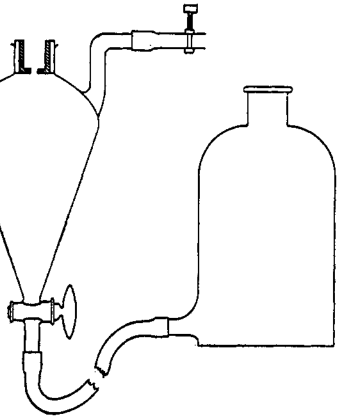

Fig. 3.—Diffusion apparatus.

Operation of Diffusion Equipment.—The diffusion apparatus was operated as follows. The confining liquid used was water. This was saturated with the gas to be used by allowing the apparatus to stand for several hours filled with a sample of the gas. Occasional shaking was employed. A fresh sample of the gas was then placed in the apparatus and the device set in a thermostat at 25° for the duration of the run. The orifice was opened, the gases allowed to diffuse for 195 minutes, the orifice closed and the sample withdrawn for combustion analysis. The volume of sample used was 250 cc. The time of 195 minutes was chosen because in that time approximately 80% of the methane will have diffused. The figure of 80% is a compromise between errors caused by general difficulties in securing complete combustion on small residues from more complete diffusion and normal experimental errors in Δn which have a greater relative value as the magnitude of Δn is decreased. As both the gas inside and the air outside were essentially saturated with water vapor, no correction for humidity was made. Barometric fluctuations were disregarded; the average barometric pressure was 620 mm.

Experimental Data.—Table I shows the experimental data and the data calculated from the diffusion equations for the different mixtures of gases which were employed.

The difference between the calculated and observed values are all within the probable limits of experimental error. A brief comparison of Table I

TABLE I

Composition of the gas							
CH_4	C_2H_6	C_3H_8	C_4H_{10}	n_0	n	Δn Obs.	Δn Calcd.
100	..	..	..	1.00	1.00	0.00	0.000
90	10	..	..	1.10	1.14	.04	.056
90	..	10	..	1.20	1.34	.14	.156
80	10	10	..	1.30	1.48	.18	.170
90	..	..	10	1.30	1.55	.25	.264
40	60	..	..	1.60	1.69	.09	.100
60	20	20	..	1.60	1.84	.24	.223
80	..	..	20	1.60	2.03	.43	.407
..	100	..	..	2.00	2.00	.00	.000

with the charts will show the degree of accuracy of the analyses based upon diffusion much better than any written explanation. Only samples were employed in which the average value of n is less than two for two reasons: first, most samples of natural gas fall in this region; and second, the experimental error is higher for values of n appreciably over two because of the form of the equations for the determination of n.

The equations and diagrams are based on the assumption of a pure paraffin hydrocarbon mixture. Small amounts of other gases will not have any great effect on the value of Δn. In order to minimize the effects of interference of different types of molecules, any gas which does not consist mainly of paraffin hydrocarbons should be treated to remove these other constituents before placing it in the diffusion apparatus. Impurities which consist of air or nitrogen need not be removed. Calculations show that since these gases are already considered in the diffusion equations, even large quantities of them in the original mixture will change the value of Δn by an amount considerably less than the average experimental error.

Theoretical Considerations of the Diffusion Equations and Charts

Derivation of an Equation for the Diffusion Coefficient.—For the coefficient of diffusion D_{12} for two gases diffusing into each other, Maxwell[8] modified the Meyer diffusion formula

$$D_{12} = \frac{1}{3(\nu_1 + \nu_2)} [\bar{C}_1\lambda_1\nu_2 + \bar{C}_2\lambda_2\nu_1] \tag{1}$$

λ_1 and λ_2 are the expressions for the mean free paths of the two species of molecules from which the terms involving collisions between the same species of molecules are neglected because such collisions should not affect diffusion, as the total forward momentum is not changed. $\bar{C}_1$ and $\bar{C}_2$ are the average velocities of the molecules, and ν_1 and ν_2 their respective molecular concentrations. Substituting the values for the mean free path, Maxwell obtained

$$D_{12} = \frac{1}{3\nu_0\pi}\left[\frac{\bar{C}_1}{S_{12}^2\sqrt{1 + M_1/M_2}} + \frac{\bar{C}_2}{S_{12}^2\sqrt{1 + M_2/M_1}}\right] \tag{2}$$

M_1 = mol. wt. of gas 1; M_2 = mol. wt. of gas 2
S_{12} = sum of radii of molecules of gas 1 and 2

We have generalized the above formula to apply to a mixture of s gases, $s - 1$ of which are diffusing in one direction while the other gas is diffusing in the opposite direction.

$$D_{mk} = \frac{1}{3\nu_0\pi}\left[\frac{\bar{C}_m}{\Sigma_1^{s-1}\,\alpha_s S_{ms}^2\sqrt{1 + M_m/M_s} + \alpha_k S_{mk}^2\sqrt{1 + M_m/M_k}} + \frac{\bar{C}_k}{\Sigma_1^{s-1}\,\beta_s S_{ks}^2\sqrt{1 + M_k/M_s} + \beta_m S_{km}^2\sqrt{1 + M_k/M_m}}\right] \quad S \neq M \tag{3}$$

The subscript s represents the general gas diffusing in one direction
The subscript k represents the gas diffusing in the opposite direction

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[8] Maxwell, "Coll. Scientific Papers," Vol. I, p. 392, and Vol. II, pp. 57 and 345; see also Jeans, "Dynamical Theory of Gases," Cambridge University Press, Cambridge, 1921, p. 315.

The subscript m represents the particular one of the s gases for which the diffusion coefficient is to be calculated.

α_s = mole fraction of gas s, calculated by omitting gas m
β_s = mole fraction of gas s, calculated by omitting gas k
α_k = mole fraction of gas k, calculated by omitting gas m
β_m = mole fraction of gas m, calculated by omitting gas k

These mole fractions are the average mole fractions taken over the whole diffusion column.

This equation is obtained by integrating the simultaneous partial second order differential equations as obtained from Meyer's theory[9] of gas diffusion using assumptions similar to those Maxwell used in his equation and also with the additional assumption that there is no net motion of translation of any constituent except the two for which the diffusion constant is to be determined.[10]

M. J. Stefan[11] has developed a theory covering the diffusion of any number of constituents; but it is based on the hydrodynamical rather than the kinetic hypothesis.

Rigorous mathematical analyses for the determination of diffusion coefficients are given by Chapman[12] and by Enskog.[13] They involve the assumption of a definite molecular model (elastic spheres, point centers of force repelling according to an inverse power law, or others). Their formulas are very laborious for numerical computation.

The Diffusion Equation.—The form for the coefficient given in equation (3) is for steady flow. As the apparatus does not employ steady flow, the logarithmic mean of the initial and final concentrations of each constituent is used as the proper concentration for the calculation of the mole fraction. The ordinary diffusion equation

$$\partial A/\partial t = D\partial^2 A/\partial x^2 \tag{4}$$

upon integration gives

$$A = A_0 e^{-Dt} \tag{5}$$

provided we assume that the concentration inside the apparatus remains essentially uniform and that the size of the orifice is large in comparison to the mean free path. The second of these statements tends to invalidate the first, but the actual results obtained indicate that the concentration gradient in the body of the diffusion apparatus is small enough to be neglected, since the cross sectional area is large as compared to that of the orifice.

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(9) Jeans, "Dynamical Theory of Gases," pp. 307 and 312.

(10) It is realized that this equation is complicated for calculation but such simple relations as that of Graham, that rates of diffusion are inversely proportional to the square root of the densities, do not even approximately apply to the interdiffusion of gases; for instance two gases of the same density, ethylene and nitrogen, have coefficients of diffusion into hydrogen of 0.486 and 0.674, respectively. See "Int. Crit. Tables," Vol. V, p. 62. By Graham's law of diffusion these gases would diffuse at the same rate.

(11) Stefan, *Sitzb. Akad. Wiss. Wien, Math-naturw. Klasse*, **63**, 63–124 (1871).

(12) Chapman, *Trans. Roy. Soc.* (London), **A217**, 166 (1917).

(13) Enskog, Inaug. Dissertation, Upsala, 1917, see Jeans, "Dynamical Theory of Gases," p. 319.

Derivation of an Expression for Δn.—The average number of carbon atoms per molecule is

$$n = An_a/V + Bn_b/V + Cn_c/V + \ldots \tag{6}$$

A, B, C, etc., represent the concentrations of the various hydrocarbons, V being the sum of the concentrations of all the hydrocarbons and n_a, n_b, etc., the average number of carbon atoms per molecule of the corresponding hydrocarbons. We shall hereafter consider constituent A to be methane, B to be ethane, C propane, D n-butane, etc., for the normal paraffin hydrocarbons. We shall indicate initial concentrations and conditions by a subscript 0.

$$n_0 = A_0 + 2B_0 + 3C_0 + \ldots/V_0 \tag{7}$$

and n at any time t

$$n = A + 2B + 3C + \ldots/V \tag{8}$$

Then $\Delta n = n - n_0$, the increase in the average value of n during diffusion is given by the difference of equations (8) and (7). From a knowledge of the initial concentrations and the numerical values for the diffusion coefficients, the value of Δn may be calculated. The triangular diagrams are plotted from data of this type.

Numerical Illustration.—A numerical illustration of the calculation is given to make the method entirely clear. For purposes of numerical calculation equation (3) may be rewritten in the form

$$D_{mk} = \frac{\overline{C}}{\sum_1^{s-1}\alpha_s\varphi_{ms} + \alpha_k\varphi_{mk}} + \frac{\overline{C}_k}{\sum_1^{s-1}\beta_s\varphi_{ks} + \beta_m\varphi_{km}} \tag{9}$$

The numerical values of the terms together with their equivalents in eqn. (3) are given in Table II. The numerical values for $\overline{C}_m$ and $\overline{C}_k$ include the constant factors, those from the equation, those depending on the size of the apparatus, and those depending on the units used. The time of the runs (195) minutes is considered as the unit of time, $t = 1$.

A pure hydrocarbon gas composed of 60% methane, 20% ethane and 20% propane will be considered.

To calculate D_{ak} the appropriate values are substituted in equation (9). All the quantities are given in Table II except the values of the coefficients representing mole fractions. From similar runs we know that only approximately 0.25 of the methane, 0.36 of the ethane and 0.45 of the propane are left at the end of the run. Initial and final concentrations together with the log mean of the concentrations of the gases are as follows.

	Methane	Ethane	Propane
Initial	60.0	20.0	20.0
Final	15.0	7.2	9.0
Log mean	32.3	12.5	13.8

For the calculation of the diffusion coefficient D_{ak} eqn. (9) is used replacing m by a (a represents methane).

$\alpha_b = 12.5/126.3$ $\alpha_0 = 13.8/126.3$ $\alpha_k = 100.0/126.3$
$\beta_a = 32.3/58.6$ $\beta_b = 12.5/58.6$ $\beta_c = 13.8/58.6$

The quantities $e^{-D_{ak}t}$, $e^{-D_{bk}t}$, and $e^{-D_{ck}t}$ are found to be 0.252, 0.396 and 0.467, respectively. This means that 25.2% of the methane, 39.6% of the ethane and 46.7% of the propane remain. Now in order to obtain greater accuracy we recalculate the values for the diffusion coefficient using the 25.2, 39.6 and 46.7% instead of the 25, 36 and 45% figures previously used. This gives $D_{ak} = 1.374$. Similarly D_{bk} and D_{ck} are found to be 0.924 and 0.753, respectively. Substitution in equation (7) gives

TABLE II

$\varphi_{AK} = 18.6 = S_{ak}^2 \sqrt{1 + M_a/M_k}$

$\varphi_{AB} = 25.7 = S_{ab}^2 \sqrt{1 + M_a/M_b}$

$\varphi_{AC} = 29.5 = S_{ac}^2 \sqrt{1 + M_a/M_c}$

$\varphi_{AD} = 33.1 = S_{ad}^2 \sqrt{1 + M_a/M_d}$

$\varphi_{BK} = 28.0 = S_{bk}^2 \sqrt{1 + M_b/M_k}$

$\varphi_{BA} = 35.2 = S_{ba}^2 \sqrt{1 + M_b/M_a}$

$\varphi_{BC} = 40.5 = S_{bc}^2 \sqrt{1 + M_b/M_c}$

$\varphi_{BD} = 44.0 = S_{bd}^2 \sqrt{1 + M_b/M_d}$

$\varphi_{CK} = 37.9 = S_{ck}^2 \sqrt{1 + M_c/M_k}$

$\varphi_{CA} = 48.9 = S_{ca}^2 \sqrt{1 + M_c/M_a}$

$\varphi_{CB} = 48.8 = S_{cb}^2 \sqrt{1 + M_c/M_b}$

$\varphi_{CD} = 55.2 = S_{cd}^2 \sqrt{1 + M_c/M_d}$

$\varphi_{DK} = 48.3 = S_{dk}^2 \sqrt{1 + M_d/M_k}$

$\varphi_{DA} = 63.0 = S_{da}^2 \sqrt{1 + M_d/M_a}$

$\varphi_{DB} = 61.3 = S_{db}^2 \sqrt{1 + M_d/M_b}$

$\varphi_{DC} = 63.2 = S_{dc}^2 \sqrt{1 + M_d/M_c}$

$\varphi_{KA} = 25.2 = S_{ka}^2 \sqrt{1 + M_k/M_a}$

$\varphi_{KB} = 27.5 = S_{kb}^2 \sqrt{1 + M_k/M_b}$

$\varphi_{KC} = 30.7 = S_{kc}^2 \sqrt{1 + M_k/M_c}$

$\varphi_{KD} = 34.3 = S_{kd}^2 \sqrt{1 + M_k/M_d}$

$\bar{C}_a = 18.0$

$\bar{C}_b = 13.2$

$\bar{C}_c = 10.9$

$\bar{C}_d = 9.5$

$\bar{C}_k = 13.4$

The molecular radii used in the above calculations are: air, 1.87×10^{-8}, CH_4, 2.00×10^{-8}; C_2H_6, 2.56×10^{-8}; C_3H_8, 3.02×10^{-8}; and C_4H_{10}, 3.42×10^{-8} cm. The value for air was taken from Jeans, "Dynamical Theory of Gases," p. 327. We calculated the others from Trautz's viscosity data [Max Trautz, *Ann. Physik*, [5] **10**, 81-96 (1931)]. Those for methane and ethane agree very closely with diameters calculated from diffusion coefficients for different pairs of gases taken from "Int. Critical Tables," and calculated by means of the Stefan–Maxwell equation (equation (2)).

$$n_0 = (60 \times 1 + 20 \times 2 + 20 \times 3)/100 = 1.6 \qquad (10)$$

and in equation (8)

$$n = \frac{A + 2B + 3C}{V} = \frac{A_0e^{-D_{ak}t} + 2B_0e^{-D_{bk}t} + 3C_0e^{D_{ck}t}}{A_0e^{-D_{ak}t} + B_0e^{-D_{bk}t} + C_0e^{-D_{ck}t}} = 1.823 \qquad (11)$$

$$\text{Therefore: } An = n - n_0 = 0.223 \qquad (12)$$

Summary

1. An extension of the Maxwell diffusion equation has been made to apply to a mixture of gases diffusing out through an orifice, which is large in comparison to the mean free path, against air diffusing in at barometric pressure and constant temperature.
2. An inexpensive device which is simple to operate has been developed.
3. The apparatus and equations have been checked by application to known mixtures of paraffin hydrocarbons.
4. Charts have been developed for the use of this information in gas analysis, whereby a much closer approximation to the actual paraffin hydrocarbons can be obtained by a combination of the diffusion apparatus

with the absorption and slow combustion equipment than can be obtained without the diffusion apparatus.

Golden, Colorado

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[Contribution from the Chemical Laboratories of Duke University and Randolph Macon Woman's College]

Dipole Moment and Group Rotation. I. The Moments of the Chloro- and Nitrobenzyl Chlorides and the Effect of Group Separation[1]

By J. M. A. de Bruyne, Rose M. Davis and Paul M. Gross

Discussion of the effect of rotation of component dipoles within molecules on their dipole moments has been confined largely to substituted straight chain hydrocarbons with two identical polar groups at each end. Ethylene chloride is the simplest case. By increasing the length of the hydrocarbon chain, it has been sought to separate the like polar groups at its ends and so study their interactions as a function of the distance separating them.[2]

Unless an extended zigzag chain is assumed with the polar groups rotating about its ends, the number of possible configurations such a molecule can assume by rotation about the various bonds is very great, so that conclusions concerning the interaction of the polar groups as affected by their separation must be drawn with considerable reservation.

The substituted benzyl halides are compounds in which this uncertainty is eliminated, since the benzene ring fixes the position of the second polar group and defines its separation from the rotating halide group in the side chain. This paper gives the results of the determination of the dipole moments of the ortho, meta, and para chlorobenzyl chlorides and the ortho and meta nitrobenzyl chlorides in different solvents. These are the first of a series of measurements designed to extend broadly the experimental background of this field by measuring the dipole moments of molecules containing varying types of rotating groups located at different distances apart in the molecule.

Method.—The dielectric constant ϵ, density d, and refractive index for the sodium D line n_D were determined for dilute solutions of these compounds at 30 ± 0.01°. The molar polarization P_2 of the solute at each concentration was calculated from the equation of Debye[3] in the form

$$P_2 = \frac{\epsilon - 1}{\epsilon + 2}\frac{M_2}{d}\frac{w_1 + w_2}{w_2} - \frac{w_1}{w_2}\frac{M_2}{M_1}P_1 \qquad (1)$$

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[1] Part of a thesis submitted by J. M. A. de Bruyne in partial fulfilment of the requirements for the Ph.D. degree in Chemistry at Duke University, in June, 1932.

[2] Compare Smyth and Walls, This Journal, **54**, 2261 (1932).

[3] Debye, "Polar Molecules," Chemical Catalog Co., New York, 1929, p. 45.