

PRESSURE-BROADENING EFFECTS IN MIXTURES OF METHYL CHLORIDE AND NON-POLAR GASES AT MICROWAVE FREQUENCIES

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Summary

Absorption measurements using 3 cm microwave resonant-cavity techniques have been performed on binary mixtures of methyl chloride and five non-polar gases (CO_2 , Ar, N_2 , He, H_2) at pressures up to 4 atm. The results have been analysed in terms of the pressure-broadening theory of Van Vleck and Weisskopf, modified to include the effects of many-body collisions and a distribution of line widths.

Microwave collision diameters have been calculated for the various gases. Agreement is found with other workers in that the values for hydrogen and helium are less than the kinetic values. It has been established that measured collision diameters do not vary systematically with the mix-ratio of the polar and non-polar constituents of the mixture as reported in the literature.

I. INTRODUCTION

Measurements in this laboratory of the self-broadening of the inversion spectrum of methyl chloride at pressures up to 2 atm have been reported previously (Burton *et al.* 1964, hereafter referred to as Paper I). This work has now been extended to a study of binary mixtures of methyl chloride with five non-polar gases at pressures up to 4 atm. A transmission resonant-cavity technique was again used, and the absorption of microwaves of frequency 10 Gc/s was measured as a function of gas pressure. The data were analysed in terms of the theory of Van Vleck and Weisskopf (1945), but with modifications following the variation suggested by Bleaney and Loubser (1950) to account for the effect of many-body collisions and including the variation proposed by Birnbaum (1957) to allow for a distribution of line widths among the various rotational states of the methyl chloride molecule. For the pressures used in this work, none of the non-polar gases shows measurable absorption at 10 Gc/s, so the effect of diluting the methyl chloride with one of them is merely to increase the collision frequency and hence, for a given partial pressure of methyl chloride, to broaden the inversion line.

The pressure broadening of the inversion spectrum of methyl chloride by various foreign gases has previously been investigated by Birnbaum and Maryott (1964). However, their analysis of the experimental data was performed solely in terms of a distribution of line widths, and no allowance was made for the effect of many-body collisions. In Paper I, it was shown that the Van Vleck-Weisskopf expression, modified only to include the effects of many-body collisions, gave good

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agreement with the experimental data for pure methyl chloride, and that this interpretation led to an estimate of the collision diameter for self-broadening that was 16% higher than that deduced by Birnbaum. This point is of particular interest in considering the collision diameters for the broadening of the methyl chloride inversion by hydrogen and helium; in these cases, Birnbaum and Maryott found values approximately 40% lower than the kinetic collision diameters, as deduced from transport phenomena, although for 10 other gases, values at least 10% higher than the kinetic values were reported. These conclusions, which refer to broadening of the methyl chloride spectrum, show the same trend as the reported values for the broadening of the $J = 3$, $K = 3$ line in the inversion spectrum of ammonia (Bleaney and Penrose 1948; Smith and Howard 1950; Legan *et al.* 1965). However, Weber (1951) obtained an ammonia-hydrogen collision diameter greater than the kinetic value, while Potter, Buschkovitch, and Rouse (1951) reported that the collision diameters for broadening of the ammonia inversion lines by foreign-gas molecules in various mixtures appeared to decrease by as much as 10% as the proportion of foreign gas in the mixture was increased from 40% to 70%. This surprising result does not appear to have been substantiated by other workers.

It should be pointed out that the experimental techniques for studying the ammonia inversion have differed considerably from those employed for methyl chloride. For ammonia, most measurements were made at low pressures, ranging from a few microns up to a few mmHg, and at microwave frequencies close to the natural frequency of the inversion transition. At pressures above 10 cmHg, the 29 closely spaced lines of the inversion spectrum, corresponding to different rotational states of the ammonia molecule, broaden to the extent of overlapping. With increase in pressure, the resonance frequency, where maximum absorption occurs, shifts rapidly towards lower values and at 2 atm is almost zero. When methyl chloride is being studied, even at pressures less than 1 mmHg, the inversion frequency is very close to zero. Since the measured absorption at the centre of the line depends on the square of the line frequency and is almost independent of the pressure, it is necessary to use higher pressures ranging from a few cmHg to several atmospheres; this gives a large line width so that absorption measurements in the wing of the line can then be made at microwave frequencies. Recent work by Parsons and Roberts (1965) shows that microwave collision diameters deduced from low pressure measurements may be underestimated if, as has so far been the case, the Doppler contribution to the line width is ignored; in particular, they found that the error in the cross section for the broadening of the ammonia lines by hydrogen could be as much as 8%, although less than this for other gases.

II. THEORETICAL CONSIDERATIONS

In the work to be described, the attenuation produced by a gas mixture in a resonant cavity is measured as a function of the total pressure for a given mix-ratio M , the latter being defined as the ratio of the number N_2 of foreign gas molecules per unit volume to the corresponding number N_1 of methyl chloride molecules. From the measured attenuation, the power absorption coefficient a due to the presence of the gas can be deduced. According to the Van Vleck-Weisskopf theory,

this is related to N_1 , to the wave number $\bar{\nu}$ of the incident microwaves, and to the line width $\Delta\bar{\nu}$ by

$$\alpha = \frac{A\bar{\nu}^2 N_1 \Delta\bar{\nu}}{\bar{\nu}^2 + (\Delta\bar{\nu})^2}, \quad (1)$$

where A is a constant that can be evaluated from a knowledge of the temperature and the dipole moment of the methyl chloride molecule, and $\Delta\bar{\nu}$ is given in terms of the mean interval τ between line-broadening collisions by

$$\Delta\bar{\nu} = \frac{1}{2\pi c\tau}, \quad (2)$$

where c is the velocity of light *in vacuo*. It is here assumed that there is no dependence of τ , and hence of $\Delta\bar{\nu}$, on the rotational state of the emitting or absorbing molecule; this will be considered later.

If τ_1 and τ_2 are the mean intervals between collisions of a methyl chloride molecule with a like molecule and with a foreign-gas molecule respectively, then

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2},$$

providing only binary collisions occur. This equation merely states that the total collision frequency is the sum of the partial frequencies; it can be expressed in terms of the collision diameters b_1 and b_2 , for self- and foreign-gas-broadening collisions respectively, and the mean relative speeds u_1 and u_2 of the interacting molecules to give

$$\frac{1}{\tau} = \pi b_1^2 u_1 N_1 + \pi b_2^2 u_2 N_2, \quad (3)$$

and substitution in (2) gives

$$\Delta\bar{\nu} = BN_1, \quad (4)$$

where

$$B = \frac{(b_1^2 u_1 + Mb_2^2 u_2)}{2c} = B_1 + MB_2. \quad (5)$$

Hence, from (1),

$$\frac{N_1^2}{\alpha} = \frac{\bar{\nu}^2}{AB} + N_1^2 \frac{B}{A}. \quad (6)$$

This is similar in form to the corresponding equation for pure methyl chloride (equation (7) of Paper I), and it predicts that, for a given mixture, a plot of N_1^2/α versus N_1^2 should be linear. However, as can be seen from Figure 1, this is not in agreement with the experimental results, so that modifications to the theory are required. Two such modifications are considered in the following paragraphs; the first is an extension of equation (4) to account for the possible effects of other than binary collisions, while the second involves a modification of equation (1) to allow for a possible dependence of the line width $\Delta\bar{\nu}$ on the rotational state of the emitting or absorbing molecule.

(a) *Many-body Collision Theory*

If, while a molecule is emitting a photon, it is struck by a second molecule, the emission is interrupted and the length of the wave train is, therefore, reduced; the shorter the wave train, the greater will be the range of frequencies necessary to synthesize, it and hence the greater will be the line width. However, if other

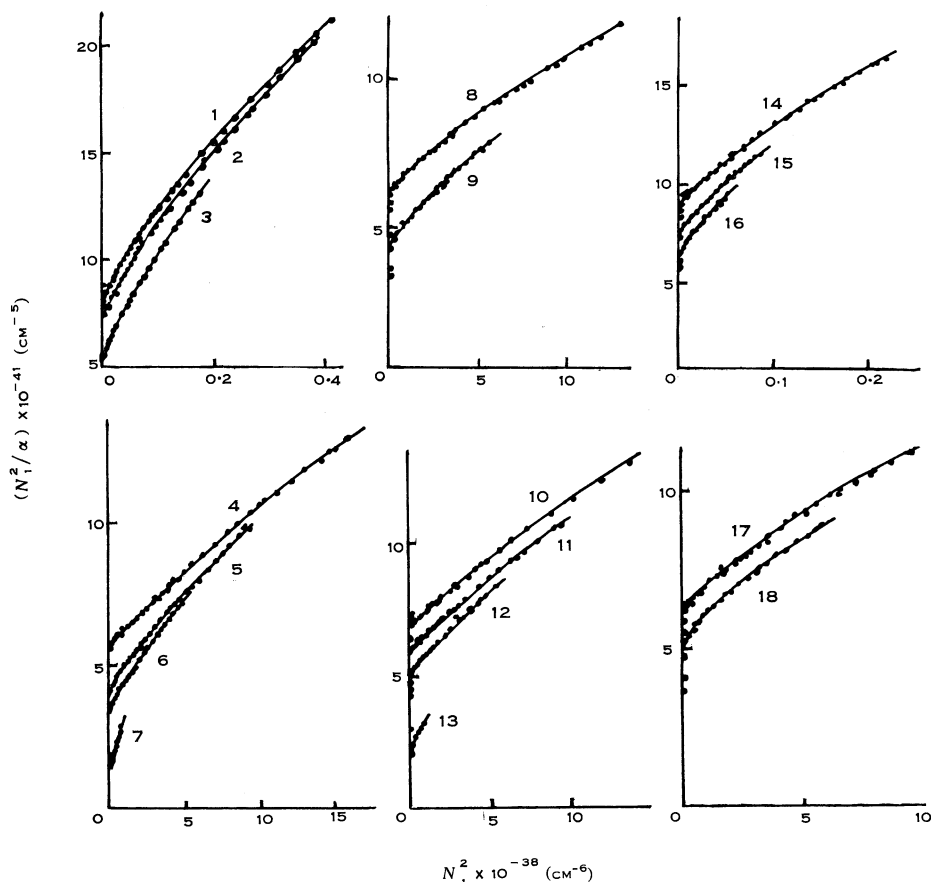


Fig. 1.— N_1^2/α plotted (●) against N_1^2 for various mixtures of methyl chloride and foreign gases and for different mix-ratios. — predictions of multiple-collision theory.

Curves 1, 2, 3: $\text{CO}_2/\text{CH}_3\text{Cl}$ mixtures with $M = 0.389, 0.576, 1.29$.

Curves 4, 5, 6, 7: $\text{CO}_2/\text{CH}_3\text{Cl}$ mixtures with $M = 1.29, 2.24, 3.20, 9.75$.

Curves 8, 9: $\text{N}_2/\text{CH}_3\text{Cl}$ mixtures with $M = 1.52, 2.94$.

Curves 10, 11, 12, 13: $\text{Ar}/\text{CH}_3\text{Cl}$ mixtures with $M = 1.48, 2.07, 2.90, 9.51$.

Curves 14, 15, 16: $\text{He}/\text{CH}_3\text{Cl}$ mixtures with $M = 0.862, 1.93, 3.01$.

Curves 17, 18: $\text{H}_2/\text{CH}_3\text{Cl}$ mixtures with $M = 1.88, 2.71$.

molecules collide with the first while it is already interacting with the second, they make no further contribution to the termination of the emission and hence do not contribute to the line broadening. It follows that, if many-body collisions occur, the effective collision frequency will not be the sum of the individual binary collision

frequencies, as expressed by equation (3), but will rise less rapidly with N_1 and N_2 than is predicted by this equation. An approximate relation between $\Delta\nu$, N_1 , and N_2 may be derived as follows.

Consider a volume V of gas that contains many molecules, that is, N_1V and N_2V are both much greater than unity. Suppose that v_1 represents the volume of the region of influence for the interaction between two methyl chloride molecules and that v_2 is the corresponding volume for the methyl chloride-foreign-gas interaction. These regions will not be spherical, since the interactions are presumably of the dipole-dipole, which includes dipole-induced-dipole, type or may involve higher multipoles, and these fields are not spherically symmetrical. The probability P that a particular methyl chloride molecule will not be in a state of collision at a given instant is

$$P = \left(1 - \frac{v_1}{V}\right)^{N_1V} \left(1 - \frac{v_2}{V}\right)^{N_2V},$$

and hence the probability that it is in a state of collision is

$$1 - P = N_1 v_1 - \frac{1}{2} N_1^2 v_1^2 + N_2 v_2 - \frac{1}{2} N_2^2 v_2^2 - N_1 v_1 N_2 v_2, \quad (7)$$

where terms of higher order have been neglected; this a valid approximation for the pressures used in the present work.

The first two terms in this expression give the probability that the methyl chloride molecule will be interacting with one or two other molecules of the same type, irrespective of whether it is also interacting with a foreign molecule; such collisions will be referred to as types AA and AAA respectively. If the mean duration of such collisions is T_1 , it follows that the frequency Γ_1 of these collisions is given by

$$\Gamma_1 = \frac{N_1 v_1 (1 - \frac{1}{2} N_1 v_1)}{T_1}.$$

Similarly, the frequency Γ_2 of collisions between a methyl chloride molecule and one or two foreign molecules (types AB and ABB), irrespective of whether it is simultaneously interacting with another methyl chloride molecule as well, is, from the third and fourth terms of (7),

$$\Gamma_2 = \frac{N_2 v_2 (1 - \frac{1}{2} N_2 v_2)}{T_2},$$

where T_2 is the mean duration of these collisions.

The remaining term in (7) corresponds to collisions involving two methyl chloride molecules and one of the foreign gas (type AAB), and the frequency of these is more difficult to estimate. If it is assumed that there is an equal probability that such collisions will have a duration of T_1 or T_2 , then the frequency is

$$\Gamma_3 = \frac{1}{2} N_1 v_1 N_2 v_2 \left(\frac{1}{T_1} + \frac{1}{T_2} \right).$$

This is, at best, a very rough approximation, but since Γ_3 contains no first-order

terms as compared with Γ_1 and Γ_2 , a rough approximation may suffice. The total collision frequency is then

$$\Gamma = \frac{1}{\tau} = \Gamma_1 + \Gamma_2 - \Gamma_3,$$

where the negative sign before Γ_3 is consistent with (7) and expresses the fact that type AAB collisions must not be counted twice, once in the expression for Γ_1 and again in Γ_2 . It follows that

$$\frac{1}{\tau} = \left(\frac{N_1 v_1}{T_1} + \frac{N_2 v_2}{T_2} \right) \left(1 - \frac{N_1 v_1}{2} - \frac{N_2 v_2}{2} \right),$$

and substitution in (2) gives

$$\Delta\bar{\nu} = BN_1(1 - \tfrac{1}{2}N_1 v), \quad (8)$$

where

$$B = \frac{v_1}{2\pi c T_1} + \frac{M v_2}{2\pi c T_2}$$

and

$$v = v_1 + M v_2.$$

Equation (8) has the same form as equation (8) of Paper I, which refers to pure methyl chloride. It gives the width of the inversion line observed in a binary mixture with mix-ratio M and predicts that the total line-broadening coefficient B and the volume parameter v should vary linearly with mix-ratio, provided the collision diameters or the volumes of the regions of influence do not themselves vary with M as found by Potter, Buschkovitch, and Rouse (1951). This can be tested experimentally.

(b) *Distributed Line Width Theory*

An alternative reason why the experimental data are not well described by equation (6) may be that equation (1) is incorrect; this would be the case if the collision diameter, and hence the value $\Delta\bar{\nu}$, varied with the rotational quantum numbers J , K of the interacting molecules. In the absence of any detailed knowledge of such a variation, Birnbaum (1957) assumed that equation (1) should be replaced by the semi-empirical expression of Cole and Cole (1941), which may be written

$$\alpha = \frac{0.5A\bar{\nu}N_1 \cos \tfrac{1}{2}C\pi}{\cosh\{(1-C)\ln(\bar{\nu}/\Delta\bar{\nu})\} + \sin \tfrac{1}{2}C\pi}, \quad (9)$$

where $\Delta\bar{\nu}$ is a weighted mean of the line widths averaged over the rotational states, and C is the Cole-Cole parameter; the latter is a measure of the dispersion of line widths, and if it is zero, corresponding to no dispersion, equation (9) reduces to (1).

Birnbaum did not consider the effect of many-body collisions and assumed that the molecular density was directly proportional to the pressure, as for an ideal gas, so that $\Delta\bar{\nu}$ in the above expression is related to N_1 by equation (4). Equation (9) can be fitted to the experimental data by suitable choice of the two quantities B and C , since A is a constant that can be evaluated in terms of quantities already

known, and it should again be possible to determine whether B does vary linearly with M and, if so, to deduce the collision diameters b_1 and b_2 .

TABLE 1
TOTAL LINE-BROADENING AND VOLUME PARAMETERS B AND v CHARACTERIZING
THE ABSORPTION IN METHYL CHLORIDE/FOREIGN GAS MIXTURES
Values derived from the many-body theory

Foreign Gas	$B \times 10^{21}$ (cm ²)	$v \times 10^{21}$ (cm ³)	Mix-ratio M	Number of Observations
CO ₂	7.2	30.3	0.389	48
	8.3	35.1	0.576	41
	9.7	45.1	0.892	53
	10.3	33.5	1.292	30
	10.8	41.1	1.293	51
	14.3	52.0	2.24	49
	17.0	61.1	3.20	56
	37.3	111.9	9.75	37
N ₂	8.5	23.1	1.52	53
	11.9	30.9	2.94	42
	11.5	25.8	2.94	23
Ar	8.3	31.5	1.48	43
	9.3	30.2	2.08	47
	10.7	31.9	2.90	47
	22.2	36.1	9.51	32
H ₂	8.6	31.4	1.88	49
	10.0	34.6	2.71	45
He	5.9 ₇	19.5	0.792	48
	6.1 ₆	21.7	0.862	48
	7.1 ₃	23.7	1.93	45
	8.0 ₈	24.5	3.01	47

III. EXPERIMENTAL DETAILS

Absorption measurements were carried out, using the technique described in Paper I, on binary mixtures of methyl chloride with five non-polar gases, namely, H₂, He, Ar, N₂, and CO₂, at total pressures up to 4 atm. For each of the foreign gases a number of mixtures was prepared, and for each of them the absorption coefficient was determined as a function of pressure at a temperature of 33.7°C. The mix-ratios M and the number of experimental observations made on each mixture are listed in Table I.

The gases were mixed and stored in an 8.5 l. stainless steel cylinder. Lengths of $\frac{1}{4}$ in. diameter copper tubing connecting the cylinder to the various valves and to the mercury manometer were kept as short as possible, since in these sections mixing of the gases by diffusion would be very protracted. In preparing a mixture, the non-polar gas was always injected at a pressure at least 4 atm above the pressure of the methyl chloride already present in the mixing cylinder. The mixtures were

always prepared several hours before measurements were made. The mix-ratio M was calculated from pressure measurements, corrections being made according to the data of Condon and Odishaw (1958) for departures from the ideal-gas law.

IV. RESULTS

The experimentally determined absorption coefficients represent microwave absorption due both to inversion transitions and to transitions between low-lying rotational states. Since no information is available on the foreign-gas broadening of these rotational lines, this broadening was neglected and the data were merely

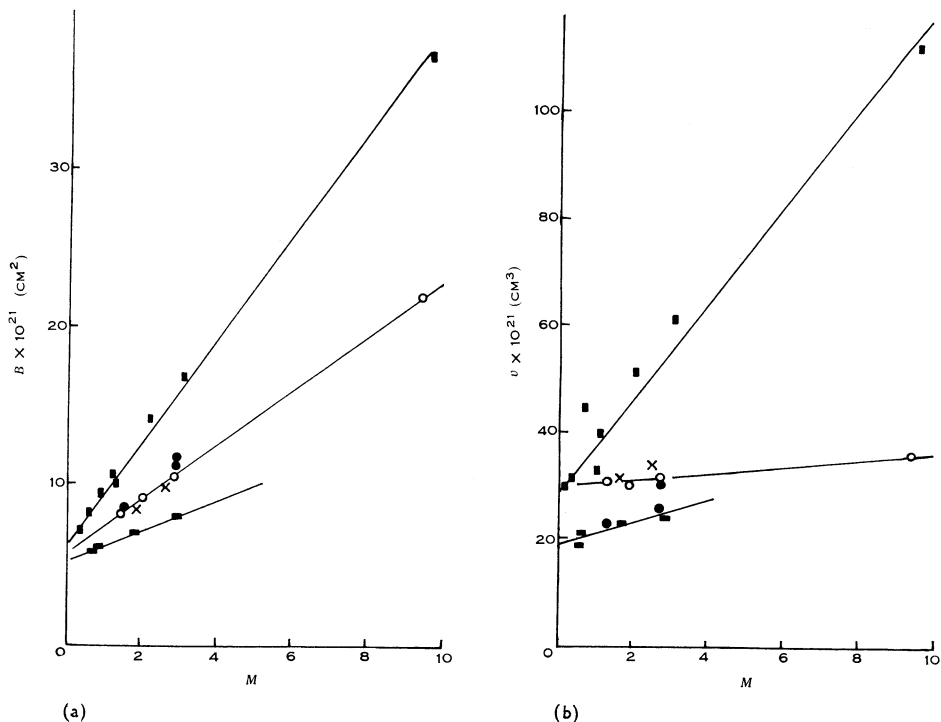


Fig. 2.—(a) Line-broadening parameter B , (b) volume parameter v , derived on the basis of the multiple-collision theory, plotted against mix-ratio M . ■ CO_2 ; ● N_2 ; ○ Ar ; × H_2 ; ■ He .

corrected for the self-broadening of the rotational lines in the manner described in Paper I. Order-of-magnitude calculations indicated that, at worst, neglect of the foreign-gas broadening of the rotational lines may introduce an error of up to 3%, as in the case of a methyl chloride/carbon dioxide mixture at 4 atm, but for all other cases the error should be considerably lower.

(a) *Many-body Analysis*

Graphs of N_1^2/a versus N_1^2 are shown in Figure 1. The solid curves are calculated from the many-body theory. The parameters B and v that gave the best fit to the data are listed in Table 1.

In Figure 2, B and v are plotted against M , and within the experimental error these graphs appear to be linear and so do not support the finding of Potter, Buschkovitch, and Rouse that collision diameters vary with mix-ratio. The values of v show considerably more scatter than do those of B , but this is not surprising since v appears in the equations, such as equation (8), as a second-order term compared with B . From the slopes and intercepts of these graphs, values of B_1 , B_2 , v_1 , and v_2

TABLE 2

INDIVIDUAL LINE-BROADENING AND VOLUME PARAMETERS B AND v AND COLLISION DIAMETERS b
Values derived from the multiple-collision theory

Foreign Gas	$B_1 \times 10^{21}$ (cm ²)	$v_1 \times 10^{21}$ (cm ²)	$B_2 \times 10^{21}$ (cm ²)	$v_2 \times 10^{21}$ (cm ²)	$b_2(B_2)$ (Å)	$b_2(v_2)$ (Å)	b_{kin} (Å)	$(K_e/u) \times 10^{30}$ (cm ² sec)
CO ₂	6.59	30.5	3.17	8.47	6.0	12.7	4.04	55.4
N ₂	5.13	17.5	2.25	3.72	4.7	9.6	3.88	29.0
Ar	5.72	29.8	1.74	0.67	4.4	5.4	3.75	30.4
H ₂	5.25	24.2	1.77	3.81	2.4	9.6	3.50	4.35
He	5.32	19.3	0.92	1.90	2.0	7.7	3.33	1.59

TABLE 3

COMPUTED COLLISION DIAMETERS FOR METHYL CHLORIDE-FOREIGN GAS INTER-ACTIONS* COMPARED WITH THOSE OBTAINED BY BIRNBAUM AND MARYOTT (1964) AND WITH THE KINETIC-THEORY VALUES CALCULATED FROM THE DATA OF HIRSCHFELDER, CURTISS, AND BIRD (1954)

Foreign Gas	b_2 (Å)			
	Multiple-collision	Distributed Line Width	Birnbaum and Maryott	Kinetic
CO ₂	6.0	5.7	5.74	4.04
N ₂	4.7	4.5	4.22	3.88
Ar	4.4	4.3	4.22	3.75
H ₂	2.4	2.2	2.03	3.50
He	2.0	2.0	1.94	3.33

* Derived from individual line-broadening coefficients on the basis of the multiple-collision and distributed line width theories.

were calculated; these quantities, together with the corresponding collision diameters b_2 , are listed in Table 2. Values of b_2 deduced from B_2 are designated $b_2(B_2)$, while those deduced from v_2 are designated $b_2(v_2)$. Although the individual values of B_1 and v_1 show considerable scatter, their average values agree reasonably well with those found for these parameters for pure methyl chloride as reported in Paper I.

All collision diameters b_2 deduced from the line-broadening parameter B_2 are larger than the kinetic values except in the case of hydrogen and helium. Values

of b_2 derived from v_2 are also given in Table 2, but these show no systematic relationship to the kinetic values and are more than double the latter values in the cases of hydrogen and helium. However, in this method of estimating a "diameter" b_2 , it is assumed that the volume v_2 is spherical, and, as already pointed out, this is certainly not the case for the multipole interactions involved.

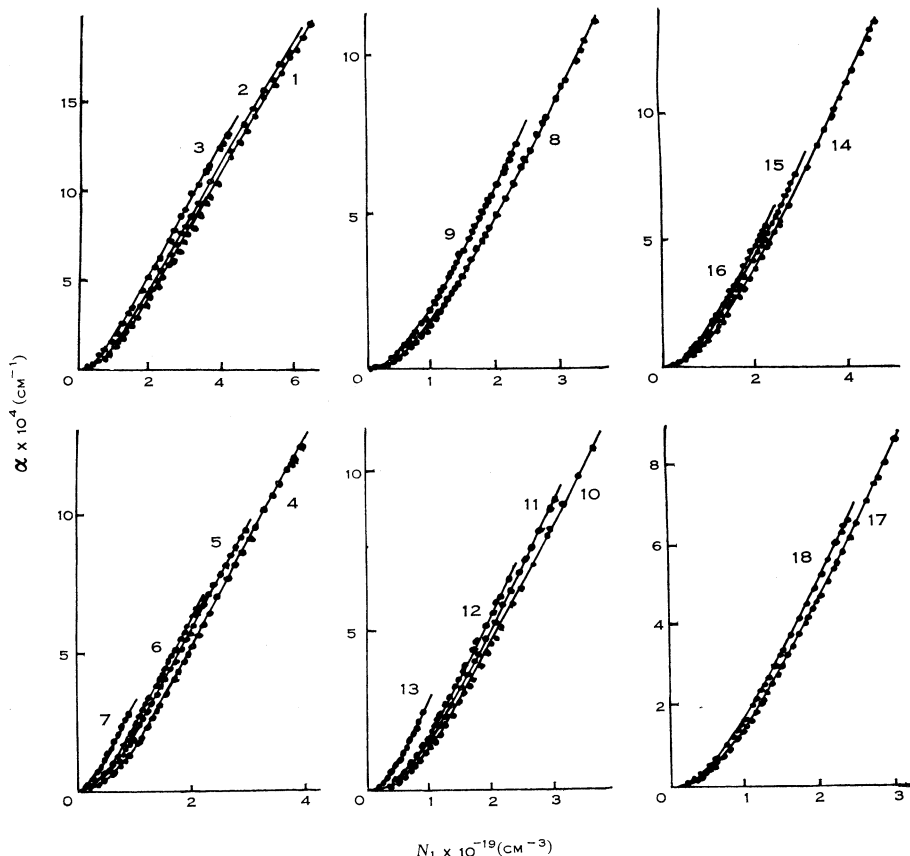


Fig. 3.— α plotted (●) against N_1 for various mixtures of methyl chloride and foreign gases and for different mix-ratios. — predictions of distributed line width theory.

Curves 1, 2, 3: $\text{CO}_2/\text{CH}_3\text{Cl}$ mixtures with $M = 0.389, 0.576, 1.29$.

Curves 4, 5, 6, 7: $\text{CO}_2/\text{CH}_3\text{Cl}$ mixtures with $M = 1.29, 2.24, 3.20, 9.75$.

Curves 8, 9: $\text{N}_2/\text{CH}_3\text{Cl}$ mixtures with $M = 1.52, 2.94$.

Curves 10, 11, 12, 13: $\text{Ar}/\text{CH}_3\text{Cl}$ mixtures with $M = 1.48, 2.07, 2.90, 9.51$.

Curves 14, 15, 16: $\text{He}/\text{CH}_3\text{Cl}$ mixtures with $M = 0.862, 1.93, 3.01$.

Curves 17, 18: $\text{H}_2/\text{CH}_3\text{Cl}$ mixtures with $M = 1.88, 2.71$.

Birnbaum and Maryott suggested, using a simple dimensional argument, that the collision diameters b_2 should be related to the polarizability K_e of the foreign molecule and its mean speed u relative to the methyl chloride molecules. As can be seen from Table 2, values of b_2 derived from B_2 do vary systematically with K_e/u , but those deduced from v_2 do not.

(b) *Distributed Line Width Analysis*

The experimental data were also analysed in terms of the distributed line width theory discussed in Section II. Best-fit values of the parameters B and C were found with the aid of a computer. The collision diameters deduced from the values of B are listed in Table 3 and are compared with the values found previously by Birnbaum and Maryott. The agreement is reasonably good, in spite of differences in experimental technique and in the method of analysing the data. However, the value of the parameter C was found from the present work to be 0.074, while

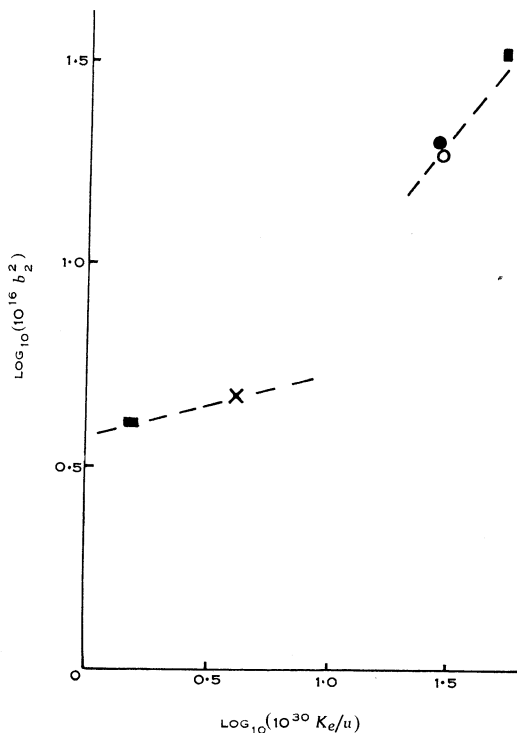


Fig. 4.—Log b_2^2 plotted against $\log(K_e/u)$ for five non-polar gases used in binary mixtures with methyl chloride. ■ CO₂; ● N₂; ○ Ar; × H₂; ■ He.

Birnbaum, in his work on pure methyl chloride, found a value of 0.051. A value of 0.074 implies, according to the theory of Fuoss and Kirkwood (1941), who considered the relation between the Cole-Cole and Van Vleck-Weisskopf expressions, that 90% of the individual line widths $\Delta\bar{\nu}'$ lie in the range $0.5 \leq (\Delta\bar{\nu}'/\Delta\bar{\nu}) \leq 2$, where $\Delta\bar{\nu}$ is the average line width.

As shown in Figure 3, where α is plotted against N_1 , the experimental points are well represented by the predictions of the distributed line width theory. The parameter B also varies linearly with M , in agreement with equation (5).

A graph of $\log b_2^2$ versus $\log(K_e/u)$ is shown in Figure 4. The existence of a linear relationship between these quantities was deduced by Birnbaum and Maryott,

and, according to the theory of Anderson (1949), the slope of the line should vary from 0.33 for interactions of the dipole-induced dipole-quadrupole type to 0.4 for dipole-induced dipole interactions. The slope of the lines through the experimental points representing hydrogen and helium is less than that in the case of nitrogen, argon, and carbon dioxide, indicating that different types of interaction are involved. However, the experimental values of 0.2 and 0.6 for the two different slopes are in only rough agreement with the above theoretical values.

V. DISCUSSION

The investigations have shown that the experimental data may be well represented by either the many-body or the distributed line width theory. In both cases, however, the line-broadening parameter B varies linearly with mix-ratio M , and so the present work does not support the finding of Potter, Buschkovitch, and Rouse that in the case of ammonia the collision diameter decreases with increasing mix-ratio.

The collision diameters for line broadening by hydrogen and helium are found to be significantly smaller than their kinetic values, and this is in agreement with the trend shown in similar work with ammonia if the results of Weber (1951) are discounted.

There seems to be no way of determining from the present data which, if either, of the two modifications of the Van Vleck-Weisskopf theory is correct. However, the distributed line width theory leads to values of the collision diameter approximately 5% lower than the many-body analysis, and, since many-body collisions become more prevalent as the pressure is increased, investigations at higher pressures should allow a more stringent test of theoretical predictions. Such measurements, made in this laboratory with two foreign gases, hydrogen and argon, at pressures of the order of 100 atm will be reported in a later paper.

VI. ACKNOWLEDGMENTS

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