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SPECTROSCOPY AND THERMODYNAMICS

I.
MOMENTS OF INERTIA OF METHYL BROMIDE

II.
EQUILIBRIUM CONSTANTS OF THE REACTION $CH_3Br + HCl \rightleftarrows CH_3Cl + HBr$

MOMENTS OF INERTIA OF METHYL BROMIDE

BY

B. BAK

KØBENHAVN
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I. MOMENTS OF INERTIA OF METHYL BROMIDE

I. Introduction.

In recent years, the application of quantum mechanics to chemical questions has proved especially fruitful in the treatment of problems which hitherto could only be dealt with correctly from a purely thermodynamical point of view, such as the determination of standard entropies, chemical affinities, etc. As quantum mechanics mainly work with symbols to be experimentally determined by means of spectroscopical methods, a near relationship between spectroscopy and thermodynamics has been established.

A survey of the work accomplished within this common field of spectroscopy and thermodynamics up to 1936 was given by Kassel.[1] It is a striking fact that most of the compounds investigated are simple inorganic molecules, and the development of the last ten years has hardly altered the situation. This is due partly to the restrictions laid upon the experimentator when working with unstable organic molecules, partly, as will be pointed out later, to theoretical difficulties arising when the more complex organic molecules are treated.

In the present paper the author attempts to combine the determination of the heat capacity of CH_3Br, carried out by Egan and Kemp,[2] with an analysis of the optical spectra of the same compound. In order to ascertain the correctness of the vibrational analysis, the Raman spectrum of CH_3Br was reinvestigated. Our result is in conformity with the results obtained earlier. The vibration frequencies, therefore, can only be unessentially changed by future work. As will be shown in the present paper, the combination of thermodynamical and spectroscopical data leads to definite values of the moments of inertia of CH_3Br.

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[1] Kassel, Chem. Rev. **18**, 277 (1936).

[2] Egan and Kemp, J. Am. Chem. Soc. **60**, 2097 (1938).

II. Entropy in Terms of Spectroscopically Determinable Quantities.

The fundamental equations were coherently published by Giauque.[1] The general expression for the absolute entropy of one mole of an *ideal gas*, S°, is:

$$S^\circ = S^\circ_{\text{trans}} + R\left(\ln Z + T\,\frac{d\ln Z}{dT}\right). \qquad (I)$$

Here, R is the gas constant, T the absolute temperature, and S°_{trans} the translational entropy.[2] Z is the so-called 'state sum'. For an ideal gas the individual molecule has a well-defined ground state, a first excited level, etc., unquantized translational energy being neglected. The separation of the translational energy from the quantized vibrational-rotational energy is correct for the ideal gas state because, in the field-free space, the part of the Schroedinger equation dealing with the translational movement of the molecule, factors out.[3] In Table I a survey of present circumstances is taken.

Table 1.

State	Energy minus translational energy	A priori probality of state	Number of molecules in state
Ground State	ε'	p_0	Ap_0
1. excited level...........	$\varepsilon'_0 + \varepsilon_1$	p_1	$Ap_1e^{\frac{-\varepsilon_1}{kT}}$
2. excited level...........	$\varepsilon'_0 + \varepsilon_2$	p_2	$Ap_2e^{\frac{-\varepsilon_2}{kT}}$
. . ..	.	.	.
i. excited level	$\varepsilon'_0 + \varepsilon_i$	p_i	$Ap_ie^{\frac{-\varepsilon_i}{kT}}$
. . ..	.	.	.

If the total number of molecules is denoted by N, we obtain:

$$N = A\left(p_0 + \sum_{i=1}^{\infty} p_i e^{\frac{-\varepsilon_i}{kT}}\right). \qquad Z = p_0 + \sum_{i=1}^{\infty} p_i e^{\frac{-\varepsilon_i}{kT}}.$$

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[1] Giauque, J. Am. Chem. Soc. **52**, 4808 (1930).

[2] The subscript zero applies to the ideal state throughout this and the following paper.

[3] Kassel, Chem. Rev. **18**, 279 (1936).

Within this field most rules are conveniently formulated by means of Z, as for example in (I). It should, however, be kept in mind that the state sum is sometimes defined as $Z = \sum_{i=0}^{\infty} p_i e^{\frac{-(\varepsilon_i + \varepsilon_0')}{kT}}$, where ε_0 is zero. This is done e. g. in the important paper by Gordon and Barnes.[1] As is seen from the papers cited,

$$Z\,(\text{Giauque}) = e^{\frac{\varepsilon_0'}{kT}}\,Z\,(\text{Gordon and Barnes}).$$

However, Giauque's definition seems to be more commonly used.

For the ideal gas state

$$S^\circ_{\text{trans}} = \frac{3}{2}\,R\ln M + \frac{5}{2}\,R\ln T - R\ln P + \frac{5}{2}\,R + C + R\ln R'.$$

Here, M is the molecular weight proportional to oxygen, P the pressure in atmospheres, R′ the gas constant in ccm atmospheres per degree and $C = R\ln \cdot \frac{(2\pi k)^{3/2}}{h^3 N^{5/2}}$, where k is Boltzmann's constant, h Planck's constant and N is Avogadro's number. Thus, for one mole of an ideal gas

$$\left.\begin{aligned} S^\circ = \frac{3}{2}\,R\ln M + \frac{5}{2}\,R\ln T - R\ln P + \frac{5}{2}\,R + C + R\ln R' + \\ + R\left(\ln Z + T\,\frac{d\ln Z}{dT}\right). \end{aligned}\right\} \quad \text{(II)}$$

Let us now try to find the special form for (II) in the case of CH_3Br by following the approximations step by step.

As a first approximation let us assume that no molecules are in a state of electronic excitation. This is practically true for most molecules up to ca. 1500°, because the available kinetic energy per degree of freedom at 0° C is $\sim 100\ \text{cm}^{-1}$ while the electronic excitation energy is 10000—$100000\ \text{cm}^{-1}$.

Furthermore, in the case of CH_3Br, p_0, the a priori probability of the electronic ground level, is 1. Hence

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[1] Gordon and Barnes, J. Chem. Phys. 1, 298 (1933).

$$Z = 1 + \sum_{i=1}^{\infty} p_i e^{\frac{-\varepsilon_i}{kT}},$$

where ε now simply means the height of one of the vibrational-rotational levels above the ground level. By defining $\varepsilon_0 = 0$ we may write:

$$Z = \sum_{i=0}^{\infty} p_i e^{\frac{-\varepsilon_i}{kT}},$$

where p_0 is equal to 1.

Generally, the vibrational and rotational energies of a molecule vary almost independently of each other. However, special interest will be paid to the case where they are completely independent. The correctness of this assumption will be discussed later. The assumption means that each ε_i can be written as $\varepsilon_n(\text{vib}) + \varepsilon_j(\text{rot})$, defining $\varepsilon_0(\text{vib}) = \varepsilon_0(\text{rot}) = 0$. To every fixed value of $\varepsilon_n(\text{vib})$ belongs the same series of rotational levels $\varepsilon_0(\text{rot}), \varepsilon_1(\text{rot}), \varepsilon_2(\text{rot}) \cdots$, superposed on the vibrational level. Simultaneously, p can be written as $p_n(\text{vib}) \cdot p_j(\text{rot})$, because of the independence of the a priori probabilities of the vibrational and the rotational states. As $p_0(\text{vib}) = p_0(\text{rot}) = 1$ we get:

$$Z = \sum_{i=0}^{\infty} p_i e^{\frac{-\varepsilon_i}{kT}} = \sum_{n=0}^{\infty} \sum_{j=0}^{\infty} p_n(\text{vib})\, p_j(\text{rot})\, e^{\frac{-\varepsilon_n(\text{vib}) - \varepsilon_j(\text{rot})}{kT}} =$$

$$= \sum_{n=0}^{\infty} p_n(\text{vib})\, e^{\frac{-\varepsilon_n(\text{vib})}{kT}} \sum_{j=0}^{\infty} p_j(\text{rot})\, e^{\frac{-\varepsilon_j(\text{rot})}{kT}} = Z_{\text{vib}} \cdot Z_{\text{rot}}.$$

The entropy expression (I), therefore, is changed into

$$S^\circ = S^\circ_{\text{trans}} + S^\circ_{\text{vib}} + S^\circ_{\text{rot}}. \tag{III}$$

a. Calculation of the vibrational entropy.

Here the simplifying assumption will be made that the molecules of the system perform **harmonic** vibrations. For a diatomic molecule, with only one vibration frequency, the vibrational energy diagram is considered to consist of a series of equidistant levels instead of the actually occurring converging ones.

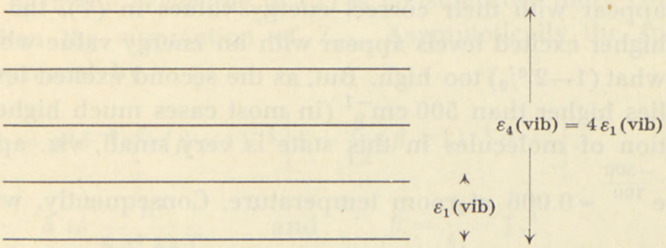

Fig. 1.

Fig. 1 is the energy diagram for a harmonic oscillator with one degree of freedom. $\varepsilon_i(\mathrm{vib}) = i \cdot \varepsilon_1(\mathrm{vib})$. The a priori probability of each level is 1. Therefore

$$Z\,(\text{vib., diatomic molecule}) = \sum_{i=0}^{\infty} e^{\frac{-\varepsilon_i(\mathrm{vib})}{kT}} = \frac{1}{1 - e^{\frac{-\varepsilon_1(\mathrm{vib})}{kT}}}.$$

If, moreover, we imagine a molecule with two vibrational degrees of freedom, an energy pattern like that shown in fig. 1 (but with a different distance between adjacent levels) must be superposed on each of the levels of fig. 1. Thus, when calculating Z_{vib}, the situation is completely analogous to that described earlier, which permitted the rotational state sum Z_{rot} to be factored out from the combined $Z_{\mathrm{rot+vib}}$: each vibrational level is superposed with the same series of other vibrational levels. Consequently, in the case of two vibrational degrees of freedom, Z_{vib} consists of two factors, each of the form stated for the diatomic molecule. Generally, for a molecule with n atoms, possessing $3n-6$ vibrational degrees of freedom, corresponding to $3n-6$ fundamental frequencies ν_f, where $h\nu_f = \varepsilon_f$, we get:

$$Z_{\mathrm{vib}} = \prod_{1}^{3n-6} \frac{1}{1 - e^{\frac{-\varepsilon_f}{kT}}} \qquad (1)$$

If ν_f is a double degenerate frequency, e. g. $\nu_f = \nu_{f+1}$, the same factor appears twice in (1); if ν_f is threefold degenerate, the same factor appears three times, etc.

The approximation made by assuming harmonic vibrations is mostly very good. The ground level and the first excited level appear with their correct energy values in (1), the second and higher excited levels appear with an energy value which is somewhat (1—2 $^0/_0$) too high. But, as the second excited level generally lies higher than 500 cm^{-1} (in most cases much higher), the fraction of molecules in this state is very small, viz. approximately $e^{\frac{-500}{100}} \sim 0.006$ at room temperature. Consequently, we may write

$$S^{\circ}_{\mathrm{vib}} = R \sum_{f=1}^{f=3n-6} \left(\frac{\frac{\varepsilon_f}{kT}}{e^{\frac{\varepsilon_f}{kT}} - 1} - \ln\left(1 - e^{\frac{-\varepsilon_f}{kT}}\right) \right).$$

$\dfrac{\frac{\varepsilon_f}{kT}}{e^{\frac{\varepsilon_f}{kT}} - 1} - \ln\left(1 - e^{-\frac{\varepsilon_f}{kT}}\right)$ is often abbreviated as $S_{\mathrm{Ein}}(\nu_f, T)$.

We then obtain:

$$S^{\circ}_{\mathrm{vib}} = R \sum_{f=1}^{f=3n-6} S_{\mathrm{Ein}}(\nu_f, T).$$

b. Calculation of the rotational entropy.

$$Z_{\mathrm{rot}} = \sum_{j=0}^{\infty} p_j(\mathrm{rot})\, e^{\frac{-\varepsilon_j(\mathrm{rot})}{kT}}$$

A common expression valid for all types of molecules; e. g. at room temperature, cannot be given. For small molecules a direct summation generally pays (H_2, HF). For larger molecules, such as CH_3Br, approximate formulas have been developed. CH_3Br has two different principal moments of inertia, A and C. If C be the moment of inertia around the C-Br axis,

$$\varepsilon_j(\mathrm{rot}) = \frac{h^2}{8\pi^2 A}\left[k(k+1) + n^2\left(\frac{A}{C} - 1\right)\right] \qquad |n| \leq k.$$

k and n are the integral quantum numbers. For a state with quantum numbers n, k the a priori weight is 2 k + 1. The summation to be made according to (2) is considerably more complicated than the summation of Z_{vib}. Asymptotically the sum can be expressed by

$$Z = \pi^{\frac{1}{2}} \delta^{-\frac{3}{2}} e^{\delta/4} (\beta + 1)^{-\frac{1}{2}} \left[1 + \frac{\beta}{12} (\beta + 1)^{-1} \delta \cdots \right],$$

where $\delta = \frac{h^2}{8\pi^2 AkT}$ and $\beta = \frac{A}{C} - 1$.[1]

In the case of CH_3Br the expression in the square brackets in good approximation is equal to 1. As $A \sim 10^{-38}$ gcm² we get $\delta \sim \frac{40 \cdot 10^{-54}}{8 \cdot 10 \cdot 10^{-38} \cdot 1.4 \cdot 10^{-16} \cdot T} \sim \frac{1}{2.8\,T}$. $A/C \sim 15$. Thus $\beta \sim 14$ and $\frac{\beta}{12}(\beta + 1)^{-1}\delta \sim \frac{1}{40\,T}$. At 100° K this is less than 0.001 and can safely be neglected.

$e^{\delta/4} \sim e^{\frac{1}{11T}}$. At 100° K this is approximately 0.001. Consequently, in good approximation we have

$$Z_{\text{rot}} = \pi^{\frac{1}{2}} \delta^{-\frac{3}{2}} (\beta + 1)^{-\frac{1}{2}} \quad \text{and} \quad S^{\circ}_{\text{rot}} = R\ln \cdot \left[\frac{8\pi^{\frac{7}{3}} A^{\frac{2}{3}} C^{\frac{1}{3}} kTe}{h^2} \right]^{\frac{3}{2}}.$$

Finally,

$$S^{\circ} = S^{\circ}_{\text{trans}} + S^{\circ}_{\text{vib}} + S^{\circ}_{\text{rot}} = R \left[\frac{3}{2} \ln M + \frac{5}{2} \ln T - \ln P + \frac{5}{2} + \right.$$

$$\left. + \frac{C}{R} + \ln R' + \sum_{f=1}^{3n-6} S_{\text{Ein}}(\nu_f, T) + \ln \left(\frac{8\pi^{\frac{7}{3}} A^{\frac{2}{3}} C^{\frac{1}{3}} kTe}{h^2} \right)^{\frac{3}{2}} \right].$$

Looking more closely into the matter and taking into consideration the possible presence of spin isomers, optical isomers, and a possible multiplicity of the electronic ground state differing from unity, we find:

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[1] Kassel, loc. cit.

$$\left.\begin{aligned} S^\circ = R\Big[&\frac{3}{2}\ln M + \frac{5}{2}\ln T - \ln P + \frac{5}{2} + \frac{C}{R} + \ln R' + \\ &+ \sum_{f=1}^{f=3n-6} S_{Ein}(\nu_f, T) + \ln\left(\frac{8\pi^{\frac{7}{3}}A^{\frac{2}{3}}C^{\frac{1}{3}}kTe}{h^2}\right)^{\frac{3}{2}}\frac{p_e p_n I}{\sigma}\Big]. \end{aligned}\right\} \quad (IV)$$

Here, p_e is the a priori probability of the electronic ground state (= 1 for CH_3Br), p_n is the number of nuclear spin isomers, I is the number of optical isomers (= 1 for CH_3Br), and σ is the 'symmetry number', equal to the number of permutations of identical atoms in a single molecule which could be carried out by rotating the molecule (= 3 for CH_3Br). The number p_n is unknown for the molecule in question, which means that the absolute entropy given by (IV) cannot be calculated. However, most entropy determinations are carried through at temperatures between a few degrees above the absolute zero and room temperature. As in all cases the calorimetric effect of the presence of spin isomers is detectable only in the immediate neighbourhood of 0° K, this means that such effects are not included in the experimentally determined entropy values. These experimental values may, therefore, be put equal to S, calculated from (IV), putting $p_n = 1$.

In this connexion it is worth mentioning that in the calculation of equilibrium constants for chemical reactions above 100° K all nuclear spin effects can be ignored[1].

Defining $A' = A \cdot 10^{38}$ and $C' = C \cdot 10^{38}$, and using the usual numerical values for the natural constants, we get the formula:

$$\left.\begin{aligned} S^\circ = R\Big[&2.307 + 4\ln T + \frac{3}{2}\ln M + 1/2\ln A'^2 C' + \\ &+ \ln\frac{p_e n_n I}{\sigma} + \sum_{f=1}^{f=3n-6} S_{Ein}(\nu_f, T)\Big], \end{aligned}\right\} \quad (V)$$

valid for the entropy of one mole in the ideal gas state at a pressure of one atmosphere.

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[1] Gibson and Heitler, Z. Phys. **49**, 465 (1928).

III. Moments of Inertia of Methyl Bromide.

a. Application of the calorimetric data of Egan and Kemp.

Egan and Kemp (loc. cit.) determined the entropy of CH_3Br-gas in the ideal state at 1 atm. and 276°.66 K (the boiling point) to 57.86 cal. $deg.^{-1}$ $mol.^{-1}$. They estimated the values of A' and C', using the data of Levy and Brockway[1] for the C-Br distance (1.91 ± 0.06 Å) and taking C-H equal to 1.09 Å and $<$ H-C-H $= 111°$. These values correspond to $A = 85.3\ 10^{-40}$ gcm^2 and $C = 5.36\ 10^{-40}$ gcm^2. Inserting A and C into (V) together with the known vibration frequencies, T, M, and σ ($= 3$), they calculated the entropy per mole CH_3Br in the ideal gas state at 276°.66 K to 57.99 cal. $deg.^{-1}$. Thus, good agreement between the calculated and the experimentally determined entropy was found.

In the present paper, however, we wish to reverse matters, e. g. exactly to determine the contribution of Egan and Kemp's calorimetric data to our knowledge of the dimensions of the CH_3Br-molecule. As is seen from (V), the calorimetric data determine the product $A'^2\,C'$. By combining the value found with spectroscopic results, the best possible values for the moments of inertia of CH_3Br are obtained. These figures will be applied in a paper to be published later.

From (V) we obtain:

$$1/2 \ln A'^2 C' = \frac{57.86}{R} + \ln 3 - \left(2.307 + 4 \ln T + \frac{3}{2} \ln M + \sum_{f=1}^{3n-6} S_{\mathrm{Ein}}(\nu_f, T) \right).$$

The uncertainty of the value 57.86 is ± 0.1, all other figures are known to be practically exact. This means that

$$A^2 \cdot C = 33400\ 10^{-120} g^3 cm^6 \pm 10\,\%. \qquad (V')$$

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[1] J. Am. Chem. Soc. **59**, 1662 (1937).

b. Application of the structure of infrared bands.

In 1928, Bennett and Mayer have studied the infrared absorption spectrum of gaseous CH_3Br.[1] Parallel bands ($\|$) were found at 610, 1305 and 2972 cm^{-1}, perpendicular bands ($\perp$) at 956.9, 1450.5 and 3061.5 cm^{-1}. A study of the structure of these bands gives us some information on the size of the molecule.

From the structure of the $\|$ bands the absorption maxima of the P- and R-branches could be determined. The distance between the absorption maxima of a single band is called the doublet separation and is denoted by $\delta\nu$. Gerhard and Dennison[2] have demonstrated that

$$\delta\nu = \frac{S}{\pi}\sqrt{\frac{kT}{A}} \qquad \log_{10} S = \frac{0.721}{\left(\frac{A}{C}+3\right)^{1.13}}. \qquad \text{(VI)}$$

$\delta\nu$ is ~ 25 cm^{-1} and could only be measured with an accuracy of ~ 2—3 cm^{-1}.

Therefore the average of the following results is taken.

Doublet separation cm^{-1}.

Bennet and Mayer[3]	25	23	23
Moorhead[4]	26	25	24
Sleator[5]		26	
Barker and Nielsen[6]		27.5	

As an average value is used $\delta\nu = 25.0\ cm^{-1} \pm 1.0$.

The $\perp$ bands show a rotational fine structure which was resolved by Bennett and Mayer (loc. cit.). The fine structure is found to be more complicated than usual since the $\perp$ vibrational levels are double-degenerate; this means that an interaction between rotational and vibrational movements takes place, disturb-

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[1] Phys. Rev. **32**, 888 (1928).

[2] Gerhard and Dennison, Phys. Rev. **43**, 197 (1933).

[3] Bennett and Meyer, loc. cit.

[4] Moorhead, Phys. Rev. **39**, 788 (1932).

[5] Sleator, Phys. Rev. **38**, 147 (1932).

[6] Barker and Nielsen, Phys. Rev. **46**, 970 (1934).

ing the usual regularity of the bands. However, Dennison and Johnston[1] assuming harmonic vibrations, showed that

$$\sum_{1}^{3} \Delta\nu = \frac{h}{4\pi^2}\left(\frac{3}{C} - \frac{7}{2A}\right), \qquad \text{(VII)}$$

where $\Delta\nu$ is the average line spacing within one of the $\perp$ bands, and $\sum_{1}^{3}\Delta\nu$ is the sum of the average values of all three $\perp$ bands. (VII) mainly determines C, because $A \sim 15\ C$. For a given A, Dennison and Johnston (loc. cit.) estimated that C may be found with an error of about 5 %.

c. Numerical calculations.

From (VII) it is seen that only a rough knowledge of A is necessary to obtain a good value of C. Using $A = 85 \cdot 10^{-40}$ gcm² in accordance with Egan and Kemp, we obtain

$$\underline{C = 5.42\ 10^{-40}\ \text{gcm}^2 \pm 5\ \%.}$$

An error of 10 % in the value assumed for A, only changes C by 1 %. The calculation is carried through on the basis of $\sum_{1}^{3}\Delta\nu = 28.32\ \text{cm}^{-1}$ from the paper of Bennett and Mayer (loc. cit.).

Now, by inserting $C = 5.42\ 10^{-40}$ in (V′) and (VI) we get two values of A. Substituting C in (V′) and allowing for an error of 5 % in C and 10 % in the calorimetric A^2C-value we find

$$\underline{A = 78 \cdot 10^{-40}\ \text{gcm}^2 \pm 8\ \%.}$$

Inserting $C = 5.42 \cdot 10^{-40}$ in (VI), it is seen at once that, as $A/C \sim 15$, $S \sim 1.065$. If C changes by 5 %, S becomes 1.070, *viz.* a change in C within the experimentally permissible limits is of negligible effect on S. Thus, the error of A simply is about twice the error of $\delta\nu$. Consequently we get:

$$\underline{A = 82 \cdot 10^{-40}\ \text{gcm}^2 \pm 10\ \%.}$$

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[1] Dennison and Johnston, Phys. Rev. **48**, 868 (1935).

According to the above-mentioned results the value of A, equally well consistent with calorimetric and with spectroscopic data, is then

$$\underline{A = 80 \cdot 10^{-40}\ \mathrm{gcm}^2 \pm 6\ {}^0/_0.}$$

In the calculation of $A = 82 \cdot 10^{-40}$ gcm^2 by means of (VI) and (VII) due regard was paid to the interdependence of rotational and vibrational energies. In using (VII) and (V′) which leads to $A = 78 \cdot 10^{-40}$ gcm^2, this interdependence is partly ignored. The fact that almost the same values of A are obtained supports the view that the approximation made in formulating (V) is rather good.

VI. Summary.

(1) The expression for the entropy of 1 mole of CH_3Br in the ideal gas state is considered and the derivation from more general expressions is discussed.

(2) The calorimetric data given by Egan and Kemp are applied to find the product A^2C. The infrared measurements of Bennett and Meyer are used to calculate the value of C. Combining calorimetric and spectroscopic data $A = 78 \cdot 10^{-40}$ gcm^2 (± 8 per cent) and $C = 5.42 \cdot 10^{-40}$ gcm^2 (± 5 per cent) is obtained.

Infrared measurements by Bennett and Meyer, Moorhead, Sleator, Barker and Nielsen permit the calculation of $A = 82 \cdot 10^{-40}$ gcm^2 (± 10 per cent) on a purely spectroscopical basis.

(3) A value for A, equally well consistent with spectroscopical and heat capacity measurements, is $80 \cdot 10^{-40}$ gcm^2.

Universitetets kemiske Laboratorium.
Copenhagen.

II. EQUILIBRIUM CONSTANTS OF THE REACTION $CH_3Br + HCl \rightleftarrows CH_3Cl + HBr$ MOMENTS OF INERTIA OF METHYL BROMIDE

I. Introduction.

In a previous paper by the present author[1] the formula

$$S^\circ = R\left[2.307 + 4\ln T + \frac{3}{2}\ln M + \frac{1}{2}\ln A'^2C' + \ln\frac{p_e p_n I}{\sigma} + \sum_{f=1}^{3n-6} S_{Ein}(\nu_f, T)\right] \qquad (I)$$

was shown to be valid in a large temperature interval (100°—1000° K) for the entropy of one mole of CH_3Br-gas in the ideal state at 1 atm. It was demonstrated how the measurements of heat capacity by Egan and Kemp[2] can be used for finding the product A'^2C'. In the present paper it is shown how A' can be determined by measuring another thermodynamical quantity, *viz.* the equilibrium constant of the reaction

$$CH_3Br + HCl \rightleftarrows CH_3Cl + HBr$$

at various temperatures, the final calculation of A' being based upon the equilibrium constants of the above reaction and spectroscopical data available in the literature.

For the most convenient formulation of the problem (I) is combined with the general thermodynamical relation

$$G = E - TS + pV, \qquad (1)$$

where the thermodynamical potential G, is defined as a function of the internal energy E, the absolute temperature T, the entropy

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[1] D. Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd. XXIV, 9. Here cited as (S-TI).

[2] J. Am. Chem. Soc. **60**, 2097 (1938).

S, the pressure p, and the volume V. As only ideal gases are considered $pV = RT$. Furthermore, $E^\circ = E_0^\circ + \frac{3}{2}RT + RT^2\frac{d\ln\cdot Z}{dT}$, where E_0° is the internal energy at the absolute zero, $\frac{3}{2}RT$ is the translational energy, and the last term is the energy due to all other degrees of freedom (electronic, vibrational, etc.). This equation is easy to derive by means of Table I, (S-TI). Substituting for E° in (1) we get

$$G^\circ = E_0^\circ + \frac{5}{2}RT - TS^\circ + RT^2\frac{d\ln Z}{dT}. \tag{2}$$

As already shown (S-TI), Z can be written as $Z_{vib}\cdot Z_{rot}$, which means that

$$\frac{d\ln Z}{dT} = \frac{d\ln Z_{vib}}{dT} + \frac{d\ln Z_{rot}}{dT}.$$

But

$$RT^2\frac{d\ln Z_{vib}}{dT} = RT\sum_{f=1}^{3n-6}\frac{\frac{\varepsilon_f}{kT}}{e^{\frac{\varepsilon_f}{kT}}-1} \quad \text{and} \quad RT^2\frac{d\ln Z_{rot}}{dT} = \frac{3}{2}RT.$$

Substituting for Z in (2) we get

$$\frac{G^\circ - E_0^\circ}{T} = R\left[4 - \frac{S^\circ}{R} + \sum_{f=1}^{3n-6}\frac{\frac{\varepsilon_f}{kT}}{e^{\frac{\varepsilon_f}{kT}}-1}\right]. \tag{3}$$

Introducing the value of S given by (I) we derive

$$\left.\begin{aligned}\frac{G^\circ - E_0^\circ}{T} = R\Bigg[\,&1.694 - 4\ln T - \frac{3}{2}\ln M - \frac{1}{2}\ln A'^2C' + \\ &+ \ln 3 + \sum_{f=1}^{3n-6}\ln\left(1 - e^{\frac{-\varepsilon_f}{kT}}\right)\Bigg].\end{aligned}\right\} \tag{4}$$

Now, we want to form $\Delta\frac{G^\circ - E_0^\circ}{T}$ for the reaction $CH_3Br + HCl = CH_3Cl + HBr$. The part of the function originating from the conversion of CH_3Br into CH_3Cl is easily seen to be

$$R\left[\frac{3}{2}\ln\frac{M(CH_3Br)}{M(CH_3Cl)}+\ln\frac{A'(CH_3Br)}{A'(CH_3Cl)}+\right. \qquad\qquad (5)$$
$$\left.+\sum_{f=1}^{3n-6}\ln\left(1-e^{\frac{-\varepsilon_f}{kT}}\right)_{(CH_3Cl)}-\sum_{f=1}^{3n-6}\ln\left(1-e^{\frac{-\varepsilon_f}{kT}}\right)_{(CH_3Br)}\right].$$

Here, $M(CH_3Y)$ is the molecular weight of the molecule CH_3Y, and $A'(CH_3Y)$ is $10^{38} \times$ the moment of inertia of the molecule with respect to an axis perpendicular to the C—Y bond through the centre of gravity. The term

$$\ln\cdot\frac{C'(CH_3Br)}{C'(CH_3Cl)}$$

has been put equal to zero. Experimentally $C'(CH_3Br)$ was found to be 0.0542, viz. the same as for CH_4.[1] Using the same experimental method, $C'(CH_3Cl)$ is found to be 0.0544. However, both values have an uncertainty of 5 per cent, but the deviations from $C'(CH_4)$ must have the same sign and be very nearly equal. Thus $C'(CH_3Br) = C'(CH_3Cl)$.

The part of the function $\Delta\frac{G^\circ-E_0^\circ}{T}$ originating from the conversion of HCl into HBr is found from tables available in the literature.[2] In Table I values of $-\frac{G^\circ-E_0^\circ}{T}$ for HBr and HCl are given.

Table I.

Values of $-\frac{G^\circ-E_0^\circ}{T}$ for HBr and HCl.
(cal. deg.$^{-1}$ mole^{-1})

Abs. temp....	250	300	400	500	600	700	800	900	1000
HBr	39.330	40.594	42.589	44.139	45.409	46.487	47.426	48.259	49.019
HCl.........	36.487	37.778	39.771	41.321	42.588	43.663	44.597	45.425	46.171
Difference ...	2.843	2.816	2.818	2.818	2.821	2.824	2.829	2.834	2.839

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[1] S-T I, p. 9—10.

[2] Gordon and Barnes, Journ. Chem. Phys..(1), 692 (1933); Giauque, J. Am. Chem. Soc. **54**, 1731 (1932).

The equilibrium in question was studied in the temperature interval 350° K—600° K. Table I shows that in this interval $\Delta \frac{G^\circ - E_0^\circ}{T}$ originating from HCl → HBr can with good approximation be put equal to -2.819 cal. deg.$^{-1}$ mole^{-1}.

Consequently we get for the reaction $CH_3Br + HCl \rightarrow CH_3Cl + HBr$

$$\left.\begin{aligned} \Delta \frac{G^\circ - E_0^\circ}{T} = R \Bigg[\frac{3}{2} \ln \frac{M(CH_3Br)}{M(CH_3Cl)} + \ln \frac{A'(CH_3Br)}{A'(CH_3Cl)} + \\ + \sum_{f=1}^{3n-6} \ln \left(1 - e^{\frac{-\varepsilon_f}{kT}}\right)_{(CH_3Cl)} - \sum_{f=1}^{3n-6} \ln \left(1 - e^{\frac{-\varepsilon_f}{kT}}\right)_{(CH_3Br)} - \frac{2.819}{R} \Bigg]. \end{aligned}\right\} \quad (6)$$

The general relation between the ΔG of a given reaction and the equilibrium constant for the corresponding equilibrium is

$$\Delta G = -RT \ln k,$$

where k or k (T), as it will often be written, is the thermodynamic equilibrium constant. Combining this relation with (6) we get

$$\left. k(T) = \left(\frac{M(CH_3Cl)}{M(CH_3Br)}\right)^{3/2} \frac{A'(CH_3Cl)}{A'(CH_3Br)} \frac{\prod\limits_{f=1}^{3n-6} \left(1 - e^{\frac{-\varepsilon_f}{kT}}\right)_{CH_3Br}}{\prod\limits_{f=1}^{3n-6} \left(1 - e^{\frac{-\varepsilon_f}{kT}}\right)_{CH_3Cl}} e^{\frac{2.819}{R} - \frac{\Delta E_0^\circ}{RT}}. \right\} \quad (7)$$

If the equilibrium constants at two different temperatures are known, the knowledge of the quantity ΔE_0° is unnecessary for our purpose (8):

$$\left.\begin{aligned} \frac{k(T_1)^{\frac{T_1}{T_1 - T_2}}}{k(T_2)^{\frac{T_2}{T_1 - T_2}}} = e^{\frac{2.819}{R}} \left(\frac{M(CH_3Cl)}{M(CH_3Br)}\right)^{3/2} \frac{A'(CH_3Cl)}{A'(CH_3Br)} \cdot \\ \cdot \left[\frac{\prod\limits_{f=1}^{3n-6} \left(1 - e^{\frac{-\varepsilon_f}{kT_1}}\right)_{CH_3Br}}{\prod\limits_{f=1}^{3n-6} \left(1 - e^{\frac{-\varepsilon_f}{kT_1}}\right)_{CH_3Cl}}\right]^{\frac{T_1}{T_1 - T_2}} \left[\frac{\prod\limits_{f=1}^{3n-6} \left(1 - e^{\frac{-\varepsilon_f}{kT_2}}\right)_{CH_3Cl}}{\prod\limits_{f=1}^{3n-6} \left(1 - e^{\frac{-\varepsilon_f}{kT_2}}\right)_{CH_3Br}}\right]^{\frac{T_2}{T_1 - T_2}} \end{aligned}\right\} \quad (8)$$

Thus, by means of equilibrium data and spectroscopical data the ratio

$$\frac{A'(CH_3Cl)}{A'(CH_3Br)}$$

can be calculated. From the fairly accurate value of $A'(CH_3Cl)$, known from work in the infrared by NIELSEN,[1] $A'(CH_3Br)$ can be calculated.[2]

II. Experimental Determination of the Equilibrium Constant at Different Temperatures.

a. Preparation of CH_3Br.

Commercial bromine was freed from chlorine by being kept 24 hours in contact with an aqueous solution of KBr under shaking at intervals. Subsequently the bromine was distilled off and reduced to HBr by means of SO_2 in the usual way, a constantly boiling hydrobromic acid being prepared. By heating the hydrobromic acid to 70° C and adding methyl alcohol a gentle evolution of gaseous CH_3Br is obtained. The gas is fractionated through a column, jacketed with water, at 5° C, led through 3 wash-bottles with water and 3 with concentrated sulphuric acid and is finally condensed. Its purity was checked by its Raman spectrum. Since the spectrum showed no lines originating from water, methyl alcohol, dimethyl ether, methyl chloride, or any other compound, the sample contains no water or methyl alcohol, such substances being very easily detectable in the Raman spectrum. Dimethyl ether and methyl chloride must be present in amounts of less than c. $\frac{1}{2}$ per cent and, actually, the way of preparing the sample makes it highly probable that it is even less. Unfortunately the constancy of the melting point and the course of the premelting curve could not be studied.

The CH_3Br was kept in a glass vessel, M (fig. 1), surrounded by ice. Prior to each experiment c. 1 g was distilled from M to T_1 (or T_2), which was placed in liquid air. Then a high vacuum was established and the CH_3Br was twice sublimated from T_1 to T_2, and vice-versa. At the end of each sublimation the last one-tenth was pumped off. This treatment ensures the presence

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[1] NIELSEN, Phys. Rev. **56**, 847 (1939).

[2] Compare, however, the note added in proof.

of an air-free sample, which was afterwards allowed to distil into that part of the apparatus (A), where the amount of CH_3Br was determined.

b. Preparation of HCl.

While a suitable amount of CH_3Br was prepared for a whole series of experiments, HCl was produced for each single determination of the equilibrium. Conc. hydrochloric acid (0.5—0.7 cc) was added to 400 cc conc. H_2SO_4[1] in a carfully evacuated flask through a separatory funnel, the tube of which was led to the bottom of the sulphuric acid (H, fig. 1). When the stopcock of the separatory funnel is cautiously opened the hydrochloric acid distils to the bottom of the conc. sulphuric acid, and a stream of dry HCl is obtained. The gas is condensed in T_1 or T_2. Before using it in the experiment it is subjected to the same treatment as CH_3Br (sublimation *in vacuo*). In this way an air- and water-free sample of HCl was prepared as will be seen from experiments referred to under d.

The pink, crystalline modification of HCl, noticed by GREY and BURT[2] and by GIAUQUE and WIEBE[3] was again observed.

c. Determination of the amount of CH_3Br used in the experiments.

From the evacuated tube T_1 (or T_2) CH_3Br was distilled into an evacuated 1 l-bulb A, placed in a thermostat. After 2 hours the pressure of the gas was read off by means of the mercury manometer P. A Dewar vessel with liquid air was put around the evacuated tube B until all CH_3Br was condensed. Now, in a series of preliminary experiments, the tube B was carefully sealed off, washed outside with ethyl alcohol and dried *in vacuo* over P_2O_5. The weight of the tube was determined on the analytical balance. Subsequently, the tube was broken by being scratched cautiously and heated in a little (2 mm) flame. In this way, a tube can be opened with practically no loss of solid material, as blanks have shown. The tube was again dried *in vacuo* and weighed. Its volume was determined by its water content being weighed.

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[1] This amount suffices for abt. 20 preparations of 0.01 mole dry HCl.

[2] Journ. Chem. Soc. Lond., 1669 (1909).

[3] Journ. Am. Chem. Soc. **50**, 101 (1928).

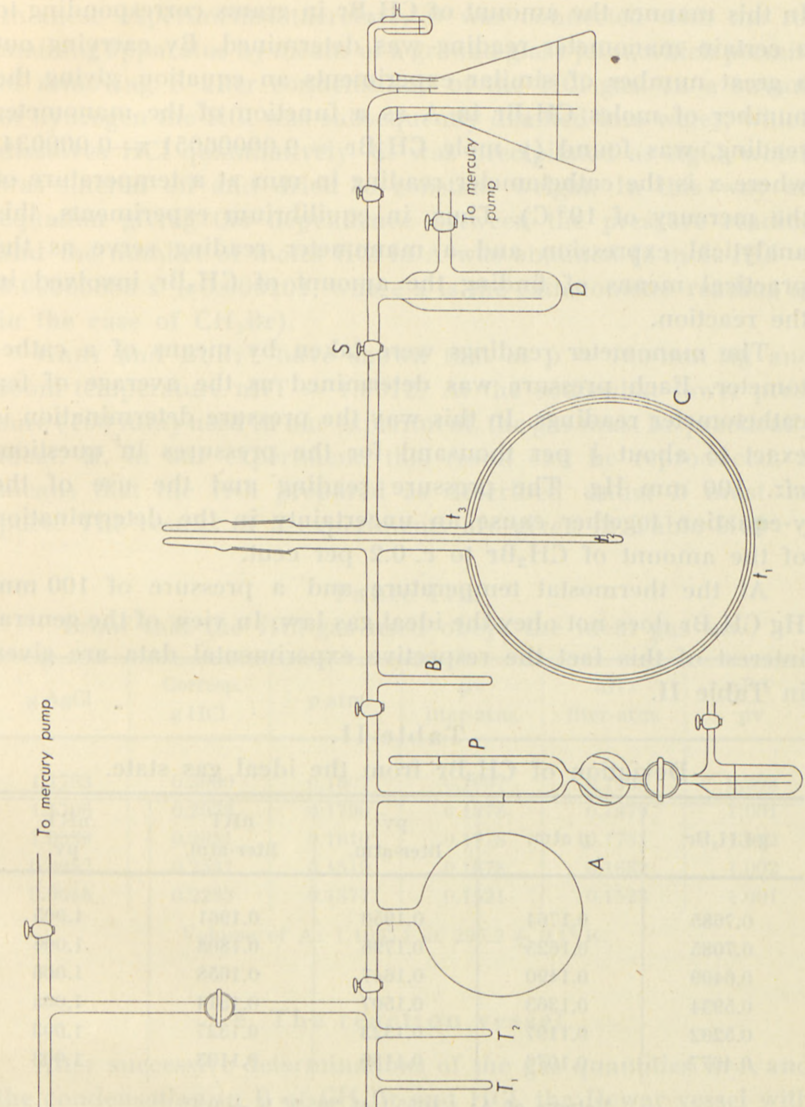

Fig. 1.

In this manner the amount of CH_3Br in grams corresponding to a certain manometer reading was determined. By carrying out a great number of similar experiments an equation, giving the number of moles CH_3Br in A as a function of the manometer reading, was found (y mole CH_3Br = 0.00006051 x—0.000034, where x is the cathetometer reading in mm at a temperature of the mercury of 19° C). Thus, in equilibrium experiments, this analytical expression and a manometer reading serve as the practical means of finding the amount of CH_3Br involved in the reaction.

The manometer readings were taken by means of a cathetometer. Each pressure was determined as the average of ten cathetometer readings. In this way the pressure determination is exact to about $\frac{1}{2}$ per thousand for the pressures in question, *viz.* 100 mm Hg. The pressure reading and the use of the y-equation together cause an uncertainty in the determination of the amount of CH_3Br to c. 0.2 per cent.

At the thermostat temperature and a pressure of 100 mm Hg CH_3Br does not obey the ideal gas law. In view of the general interest of this fact the respective experimental data are given in Table II.

Table II.
Deviation of CH_3Br from the ideal gas state.

g CH_3Br	p atm.	pv liter-atm.	nRT liter-atm.	$\frac{nRT}{pv}$
0.7685	0,1764	0.1950	0.1961	1.005
0.7085	0.1625	0.1796	0.1808	1.006
0.6499	0.1490	0.1647	0.1658	1.006
0.5934	0.1363	0.1507	0.1514	1.005
0.5202	0.1197	0.1323	0.1327	1.003
0.4677	0.1076	0.1189	0.1193	1.003

Volume of A: 1.1055 l at 295.2° K ± 0.1°.

d. Determination of the amount of HCl used in the experiments.

The amount of HCl present in A could not be determined in the same way as in the case of CH_3Br due to the high pressure developing in the ampulla when heated to room temperature.

In these experiments, therefore, B was connected with the remaining apparatus by means of a ground glass joint, which permits of removing B after condensation of the HCl gas. In a stream of hydrogen the HCl was subsequently distilled into water, which dissolves HCl quantitatively. Cl was precipitated as AgCl, which was filtered off and dried to constant weight. In this way an equation giving the dependence between the pressure reading and the number of moles HCl in A was obtained (z mole HCl $=$ $0.00005883\ x + 0.000101$, where x is the cathetometer reading as in the case of CH_3Br).

Grey and Burt[1] have shown that at $p = 180$ mm Hg and room temperature $nRT = 1.0012$. At the somewhat lower pressure (100 mm) used in our experiment, the gas must be practically ideal. If, in our experiment, this result can be reproduced, it means that the HCl prepared as described under b must be pure. The results of 5 experiments are given in Table III.

Table III.

Proof that the HCl-gas used obeys the ideal gas law.

g AgCl	Corresp. g HCl	p atm.	pv liter-atm.	nRT liter-atm.	$\frac{nRT}{pv}$
1.1793	0.3000	0.1807	0.1997	0.1993	0.998
1.1706	0.2978	0.1790	0.1978	0.1979	1.001
1.0539	0.2681	0.1610	0.1778	0.1781	1.002
0.9952	0.2531	0.1519	0.1678	0.1682	1.002
0.9015	0.2293	0.1377	0.1521	0.1523	1.001

Volume of A: 1.1055 l at 295.2 ± 0.1° K.

e. The reaction vessel.

After successive determinations of the gas quantities in A and the condensation in B of CH_3Br and HCl, the Dewar vessel with liquid air was removed from B, which results in the evaporation of the two gases into the reaction vessel C (fig. 1). The vessel was a 3 l-bulb of pyrex glass, surrounded by two tightly-fitting copper hemispheres. These hemispheres were surrounded by a layer of asbestos paper and asbestos wool together with an electrical heating wire. The whole arrangement was again surrounded by

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[1] Journ. Chem. Soc. Lond., 1669 (1909).

a big tin container, filled with kieselguhr. Copper-constantan thermocouples were placed at t_1, t_2, and t_3. In this way it was possible to maintain temperatures deviating less than 2°, t_2 generally being very nearly the mean of t_1 and t_3. No thermo-regulator was necessary for keeping the temperature constant within 1° during an experiment. By varying the heating current any desired temperature between 20° C and 450° C could be obtained.

The thermocouples were calibrated in the vapors of boiling benzene, water, toluene, bromobenzene, naphtalene, benzophenon and mercury. At 350° C the reading is accurate to 0.5°, at 100° C it is accurate to 0.2°.

f. Analytical determination of the position of the equilibrium.

After equilibrium had been established in C, the equilibrium mixture was frozen down into the carefully evacuated trap D, surrounded by liquid air. After 2 hours the stopcock S was closed. By means of a stream of hydrogen the reaction mixture was passed through 75 cc water in an 300 cc Erlenmeyer flask. HBr and HCl are dissolved quantitatively in water. Most of the CH_3Br and CH_3Cl is passing, as blanks have shown, the rest is removed by continued bubbling-through of hydrogen for 2 hours. In a special experiment it was shown, moreover, that neither CH_3Br nor CH_3Cl hydrolyse under the present circumstances.

The amount of acid was determined by titration with 0.5 n NaOH. Blank experiments with HCl alone prove that the quantity of acid found by means of this titration is in excellent agreement with the amount calculated by means of the equation mentioned under d.

Using the mass-law of action for the equilibrium we obtain:

	$CH_3Br\ +$	$HCl \rightleftarrows$	$CH_3Cl\ +$	HBr
Number of moles before reaction:	mc	c	o	o
Number of moles in the equilibrium:	$c(m-\alpha)$	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$k = \frac{\alpha^2}{(m-\alpha)(1-\alpha)}.$$

m is the known ratio between the number of moles CH_3Br and HCl before the reaction. If the ratio between HBr and HCl in the equilibrium is f, α is given by $f = \frac{1-\alpha}{\alpha}$. Consequently a determination of the ratio between $\overline{\mathrm{Br}}$ and $\overline{\mathrm{Cl}}$ in the aqueous solution of HBr + HCl must be made.

This special problem has been studied by several authors. (See e. g. Gmelin, Handb. der anorg. Chem.). I have checked a series of these methods. The method described by Lang[1] (oxidation of HBr by $KMnO_4$ in the presence of HCN and H_3PO_4, reduction of surplus $KMnO_4$ by $FeSO_4$, addition of KJ and titration with $Na_2S_2O_3$) was found to be of suitable accuracy and convenience. By this method the contents of $\overline{\mathrm{Br}}$ can be determined almost independently of the contents of $\overline{\mathrm{Cl}}$. In the present experiments we are interested in determining $\overline{\mathrm{Br}}$ in the presence of 3—5 times as much $\overline{\mathrm{Cl}}$. Table IV gives the results of using Lang's method on weighed quantities of KBr and KCl.

Table IV.

g KBr	Equiv. $\overline{\mathrm{Br}}$.	g KCl	Equiv. $\overline{\mathrm{Cl}}$.	$\frac{\overline{\mathrm{Br}}}{\overline{\mathrm{Cl}}}$	Equiv. $\overline{\mathrm{Br}}$. found.	Error
0.2029	0.001704	0.5025	0.006740	0.252	0.001721	1.0 %
0.1943	0.001632	0.5047	0.006769	0.241	0.001649	1.0 %
0.1460	0.001226	0.5103	0.006844	0.179	0.001239	1.1 %
0.1277	0.001073	0.4973	0.006670	0.161	0.001085	1.2 %

Lang's method thus gives reproduceable, although not quite correct values for the $\overline{\mathrm{Br}}$ contents. In practice, the thiosulphate solution used was adjusted to solutions of KBr + KCl, almost like those to be analyzed. In this way the amount of $\overline{\mathrm{Br}}$ can be found with an accuracy of about 0.3 per cent.

The inaccuracy in the determination of m and f is seen to cause an inaccuracy of k of about 1.5—2 per cent, as verified by equilibrium experiments.

g. The determination of the equilibrium constant at 606° K in the absence of a catalyst.

As seen from the preceding sections, the equilibrium was studied by mixing known amounts of CH_3Br and HCl in 'C' and

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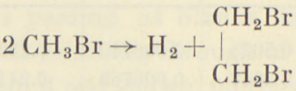
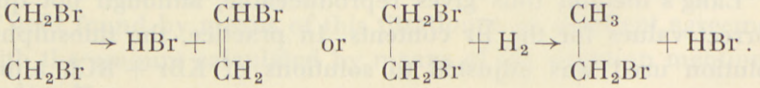
[1] Zeitsch. f. anorg. u. allg. Chemie **144**, 75 (1925).

heating the mixture. As preliminary experiments show, the exchange of Br and Cl starts at 250—300° C in the absence of a catalyst. At 330—340° C, equilibrium is established within 40—50 hours. Some experiments aiming at a faster establishment of the equilibrium were carried out at higher temperatures. At 390° C the following observations were made: After 40 hours the reaction mixture was led to the trap D. The condensation, being complete in corresponding experiments at 330° C, now was incomplete. At the same time the number of equivalents of acid, present in D after the reaction, exceeded the number present before the reaction. Thus, some 'side reaction' must take place, because all the reaction partners of the equilibrium $CH_3Br + HCl \rightleftarrows CH_3Cl + HBr$, are condensable and the number of equivalents of acid is constant. In fact, the only compound which could not be condensed in liquid air and which could be formed from the reaction partners, is hydrogen. When, in a following experiment, HCl was omitted, the contents of 'C' were likewise not completely condensable in D after 24 hours, a considerable amount of HBr (c. 0.1 mole per cent) being simultaneously formed. This indicates that the 'side reaction' probably is



$$2\,CH_3Br \rightarrow H_2 + \begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix}$$

HBr being produced by subsequent reactions such as



$$\begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix} \rightarrow HBr + \begin{matrix}CHBr\\ \|\\ CH_2\end{matrix} \quad \text{or} \quad \begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix} + H_2 \rightarrow \begin{matrix}CH_3\\ |\\ CH_2Br\end{matrix} + HBr.$$

At 330° C, however, the condensation in D was complete and no extra equivalents of acid were formed. To ensure that no secondary reactions take place in experiments at this temperature, an experiment with 0.01 mole CH_3Br alone was run for 10 days at 330° C. The subsequent condensation in D was complete and no HBr was formed. In a similar experiment with 0.05 mole CH_3Br the condensate in D was distilled into a Raman tube and the Raman spectrum was photographed. The spectrum showed no signs of other lines than those corresponding to CH_3Br. If e. g.

CH_2BrCH_2Br had been present it would have been particularly easy to detect because of the isolated Raman line of the C—C bond.

Consequently it was decided to carry out a series of determinations of the equilibrium constant at some temperature between 330 and 340° C. The results are given in table V.

Table V.

Equilibrium constant determinations at 606° K.

Exp. Nr.	Duration. (hours)	Equiv. CH_3Br. before exper.	Equiv. HCl before exper.	m	Equiv. HCl + HBr aft. exp.	Equiv. HBr after exper.	f	α	$\frac{\alpha^2}{(m-\alpha)(1-\alpha)}$
1	22 hours	0.007891	0.007986	0.9882	0.007996	0.001975	0.3280	0.2470	0.1093
2	46 —	0.007786	0.006162	1.2635	0.006162	0.001845	0.4274	0.2994	0.1327
3	64 —	0.007121	0.007146	0.9965	0.007131	0.001916	0.3674	0.2687	0.1356
4	93 —	0.007125	0.007381	0.9653	0.007377	0.001947	0.3586	0.2639	0.1349
5	112 —	0.007200	0.007007	1.0275	0.006982	0.001896	0.3728	0.2716	0.1340
6	141 —	0.006522	0.008077	0.8074	0.008087	0.001951	0.3180	0.2413	0.1355
7	72 —	0.007863	0.007767	1.0123	0.007767	0.002096	0.3696	0.2698	0.1342
8	72 —	0.007797	0.006774	1.1510	0.006781	0.001965	0.4080	0.2898	0.1373
9	67 —	0.006704	0.007587	0.8836	0.007578	0.001918	0.3389	0.2531	0.1360
10	63 —	0.007791	0.006341	1.2286	0.006334	0.001890	0.4253	0.2984	0.1364

Mean of experiments 2—10: 0.1352. Result: $0.1352 \pm 0.0008 = k$.

In connexion with Table V the use of the mass-law of action may be discussed. The law is only fulfilled for ideal gases. At higher temperatures and lower pressure, the actual gases can be considered ideal with better and better approximation. As HCl and HBr are already ideal at $p = 150$ mm Hg and room temperature they are even more so at the pressure of the experiment (50—100 mm Hg) and the temperatures 80°—340° C. Table II shows that at room temperature CH_3Br deviates a little from ideality. The same is probably the case with CH_3Cl. At the higher temperatures of the experiments the deviations from ideality are minor. Thus, the ratio between the activities of CH_3Br and CH_3Cl as a good approximation must be equal to the ratio between the concentrations. The application of the mass-law of action must be permissible.

h. Determinations of the equilibrium constant at 357° K in the presence of a catalyst.

For the determination of the equilibrium at a temperature as far as possible from 606° K a suitable catalyst was looked for. The first attempt with granulated active carbon turned out to be successful. The catalyst was suspended in a glass spiral in the centre of C (fig. 1). In the presence of this catalyst it is possible to study the equilibrium even at 80° C.

The first experiment with the catalyst was made at the same temperature as the experiments without a catalyst, 606° K. The experiment lasted for 24 hours. After that time the condensation in the trap D was incomplete and the number of equivalents of acid had increased. Thus, some side reaction is catalyzed, too. In the following experiment at the same temperature, which was interrupted after one hour, the condensation in D was nearly complete and the number of equivalents of acid had only increased by 0.5 per cent. When calculating the equilibrium constant on the assumption that no side reaction had taken place k was found to be 0.1300. Without a catalyst $k = 0.1352$. In broad outline these experiments indicate that active carbon is an excellent catalyst for the reaction we want to study. Since, however, also the side reactions are catalyzed it is impossible to study the equilibrium with and without a catalyst at the same temperature.

Next the highest possible temperature at which the side reactions are negligible was looked for. In experiments at 533° K and 497° K, excess equivalents of acid were formed in the course of 40 hours. At 458° K no excess equivalents of acid were produced during 40 hours. At 419° K the same result was found. Thus experiments with the catalyst at temperatures lower than about 450° K (177° C) can be performed without the complications originating from the side reactions.

Finally the lowest possible temperature at which the equilibrium can conveniently be studied was sought for. At 357° K (84° C) equilibrium is established in the course of 30—40 hours. As this is a suitable period, the experiments of Table VI were carried out at that temperature.

Table VI.

Determination of the equilibrium constant at 357°K.

Exp. no.	Duration. (hours)	Equiv. CH_3Br before exper.	Equiv. HCl before exper.	m	Equiv. HBr + HCl after exp.	Equiv. HBr after exp.	f	α	$\frac{\alpha^2}{(1-\alpha)(1-\alpha)}$
1	20	0.006335	0.006678	0.9486	0.006647	0.001003	0.1777	0.1509	0.03366
2	39	0.006730	0.006376	1.0555	0.006376	0.001027	0.1920	0.1611	0.03459
3	45	0.007021	0.006696	1.0485	0.006685	0.001070	0.1906	0.1601	0.03435
4	42	0.006264	0.007147	0.8888	0.007126	0.001035	0.1728	0.1473	0.03431
5	64	0.006270	0.006782	0.9245	0.006775	0.001021	0.1774	0.1507	0.34560
6	40	0.007167	0.006516	1.1000	0.006510	0.001070	0.1967	0.1644	0.03457
7	40	0.006724	0.007328	0.9230	0.007325	0.001101	0.1769	0.1503	0.03441
8	40	0.006247	0.006649	0.9395	0.006623	0.000998	0.1774	0.1507	0.03390
9	43	0.006635	0.007017	0.9455	0.007025	0.001063	0.1783	0.1513	0.03396

Mean number of experiments 2—9: 0.03433. Result: $k = 0.03433 \pm 0.00014$.

III. Calculation of Spectroscopically and Thermodynamically Important Quantities.

a. Calculation of the greatest moment of inertia of CH_3Br.

Formula (8) shows that sufficient data are now available to calculate A' (CH_3Br), the greatest moment of inertia of CH_3Br. Putting $T_1 = 606° K \pm 1.0°$, $T_2 = 357° K \pm 0.5°$ and A' (CH_3Cl) $= 0.579$[1] and using the vibration data of Bennett and Mayer[2] we obtain

$$A' (CH_3Br) = 0.782 \text{ gcm}^2 \pm 4 \text{ per cent.}$$

As $A' (CH_3Br) = A (CH_3Br) \cdot 10^{38}$, where $A (CH_3Br)$ is the true moment of inertia, we get

$$\underline{75 \cdot 10^{-40} \text{ gcm}^2 < A (CH_3Br) < 81 \cdot 10^{-40} \text{ gcm}^2.}$$

This value is in excellent agreement with values found by previous authors (S-TI, p. 13).

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[1] Nielsen, Phys. Rev. **56**, 847 (1939). Compare the note added in proof.

[2] Bennett and Mayer, Phys. Rev. **32**, 888 (1928)

The limits given for the value of A (CH_3Br) were calculated on the assumption that the sources of experimental error are exclusively to be found in the temperature measurements and the analytical determination of the equilibrium. To check the correctness of this we may determine the equilibrium at a third temperature, as different as possible from 357° K and 606° K. On page 28 it was mentioned that the equilibrium in question can be established at 458° K in the presence of the catalyst without side reactions. A temperature of 443° K (170° C) was chosen for the experiment. Two determinations were made.

Determination of the equilibrium at 443° K.

1. experiment. Duration 36 hours .... $k = 0.06610$
2. experiment. — 67 — .... $k = 0.06643$

Mean number: $k = 0.06636 \pm 0.00100$

Now, calculating A (CH_3Br) by means of the results at 606° K and 443° K we obtain

$$A\,(CH_3Br) = 70 \cdot 10^{-40}\,\mathrm{gcm}^2 \pm 8 \text{ per cent.}$$

The agreement between the two values found by the present 'equilibrium method' is not quite so satisfactory as was expected. This might mean that some systematic error was neglected. As no such error seems to have occurred in the experimental determination of the equilibrium constants it seems natural to reconsider the theoretical basis. In the derivation of equation (I) the simplifying, partly uncontrollable assumption was made that the interaction between the rotational and vibrational movements of the molecule can be neglected. For the methyl halides it is known with certainty that such interaction occurs. Unfortunately it is very difficult, if not impossible at present, to see to what extent such interaction will influence equations (I) and (8).

Paying due regard to both determinations of A (CH_3Br) made in this paper, we get:

$$\underline{A\,(CH_3Br) = 76.5 \cdot 10^{-40}\,\mathrm{gcm}^2 \pm 4 \text{ per cent.}}$$

Even if a systematic error of 5 per cent is taken into account the value found by the present 'equilibrium method' is of the same accuracy as the values hitherto determined by spectroscopical or physico-chemical methods.

Spectroscopical methods	$82 \cdot 10^{-40}$ gcm²	± 10 per cent.
Heat capacity measurements ...	$78 \cdot 10^{-40}$ —	± 8 —
'Equilibrium method'..........	$76.5 \cdot 10^{-40}$ —	± 4 —

The value, equally well conceivable with spectroscopical heat capacity and equilibrium measurements, is:

$$\underline{\underline{A\,(CH_3Br) = 77.5 \cdot 10^{-40} \pm 4 \text{ per cent.}}}$$

b. Calculation of $\varDelta E_0^\circ$ and the heat of reaction different temperatures.[1]

From (7) it follows that

$$\left. e^{\frac{\varDelta E_0^\circ}{RT}} = e^{\frac{2.819}{R}} \left(\frac{M\,(CH_3Cl)}{M\,(CH_3Br)}\right)^{3/2} \frac{A'\,(CH_3Cl)}{A'\,(CH_3Br)} \frac{\prod_{f=1}^{3n-6}\left(1 - e^{\frac{-\varepsilon_f}{kT}}\right)_{CH_3Br}}{\prod_{f=1}^{3n-6}\left(1 - e^{\frac{-\varepsilon_f}{kT}}\right)_{CH_3Cl}} k\,(T)^{-1}. \right\} \quad (9)$$

As all the quantities of the right-hand side are known, we can calculate:

$$\underline{\varDelta E_0^\circ = 2500 \text{ gcalmole}^{-1} \pm 75.}$$

The enthalpy H, the thermodynamical potential G, the entropy S, and the temperature T are connected by the relation:

$$H = G + TS.$$

Taking the value of G from (3) we get:

$$H^\circ = E_0^\circ + RT\left(4 + \sum_{f=1}^{3n-6} \frac{\frac{\varepsilon_f}{kT}}{e^{\frac{\varepsilon_f}{kT}} - 1}\right).$$

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[1] In the newest American literature $\varDelta H_0^\circ$ is were commonly used for $\varDelta E_0^\circ$.

We now want to calculate ΔH° for the reaction $CH_3Br + HCl \rightarrow CH_3Cl + HBr$. The fraction of ΔH° originating from $CH_3Br \rightarrow CH_3Cl$ is easily seen to be:

$$\Delta H^\circ (CH_3Br \rightarrow CH_3Cl) = \Delta E_0^\circ (CH_3Br \rightarrow CH_3Cl) +$$

$$+ RT \left(\sum_{f=1}^{3n-6} {}_{(CH_3Cl)} \frac{\frac{\varepsilon_f}{kT}}{e^{\frac{\varepsilon_f}{kT}} - 1} - \sum_{f=1}^{3n-6} {}_{(CH_3Br)} \frac{\frac{\varepsilon_f}{kT}}{e^{\frac{\varepsilon_f}{kT}} - 1} \right).$$

For the hydrogen halides tables of $\frac{G^\circ - E_0^\circ}{T}$ are available.[1] Denoting this function by B we can write $G = E_0 + BT$ and

$$H = E_0 + BT + TS.$$

Thus,

$$\Delta H^\circ (HCl \rightarrow HBr) = \Delta E_0^\circ (HCl \rightarrow HBr) + T \Delta B^\circ (HCl \rightarrow HBr) +$$
$$+ T \Delta S^\circ (HCl \rightarrow HBr)^2$$

and

$$\Delta H^\circ (CH_3Br + HCl \rightarrow CH_3Cl + HBr) = \Delta E_0^\circ (CH_3Br + HCl \rightarrow CH_3Br + HBr) +$$

$$+ RT \left(\sum_{f=1}^{3n-6} {}_{CH_3Cl} \frac{\frac{\varepsilon_f}{kT}}{e^{\frac{\varepsilon_f}{kT}} - 1} - \sum_{f=1}^{3n-6} {}_{CH_3Br} \frac{\frac{\varepsilon_f}{kT}}{e^{\frac{\varepsilon_f}{kT}} - 1} \right) +$$

$$+ T \Delta B^\circ (HCl \rightarrow HBr) + T \Delta S^\circ (HCl \rightarrow HBr).$$

By insertion of numerical values we get:

T°K	T°C	gcal mole^{-1}
0	−273	2500
298	25	2450
606	333	2340

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[1] Gordon and Barnes, Journ. Chem. Phys. (1), 692 (1933); Giauque, Journ. Am. Chem. Soc. **54**, 1731 (1932).

[2] Values of S for HCl and HBr in the papers of Gordon and Giauque.

The change in the evolution of heat at a change in temperature of about 300° is of the same order of magnitude as the experimental error.

The evolution of heat at the present reaction can be calculated in advance by using the data available from the literature.[1]

$$CH_3Br + HCl \rightarrow CH_3Cl + HBr$$

Heat of formation, kcal mole^{-1} 8.5 22.06 20.1 8.65

Consequently

$$\Delta Q^\circ = -\Delta H^\circ = (20.1 + 8.65) - (8.5 + 22.06) = -1.81 \text{ kcal.}$$

In this paper it is found that

$$\Delta Q^\circ = -2.45 \text{ kcal.}$$

The values of the heat of formation of HCl and HBr undoubtedly are correct, as they are based on consistent thermochemical and spectroscopical data. The data for the heat of formation of CH_3Br and CH_3Cl are mainly due to THOMSEN.[2] From Thomsen's book and from a paper by BERTHELOT[3] it is evident that the determination of the heat of combustion of the methyl halides meets with considerable difficulties. It seems safe to conclude that one or both of Thomsen's values of the heat of formation of CH_3Br and CH_3Cl are incorrect.

IV. Summary.

(1) A relation between the equilibrium constants at two different temperatures of the reaction $CH_3Br + HCl \rightleftarrows CH_3Cl + HBr$ and spectroscopically determinable quantities has been derived.

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[1] Revised and edited by BICHOWSKY and ROSSINI, Thermochemistry of Chemical Substances, New York 1936.

[2] THOMSEN, Thermochemische Untersuchungen IV, 86 and 116 (1886).

[3] BERTHELOT, Ann. de Chemie et de Physique (V), **23**, 214 (1881).

(2) An experimental determination of the equilibrium constants at various temperatures was carried through. The reaction vessel was a 3-l Pyrex bulb. At 606° K $k = 0.1352 \pm 0.0008$ was found in the absence of a catalyst. At 357° K $k = 0.03433 \pm 0.00014$ was found. At 443° K $k = 0.06636 \pm 0.00100$ was found. The two last-mentioned determinations were carried through in the presence of an active carbon catalyst.

(3) The results obtained permit of calculating the greatest moment of inertia of CH_3Br, $A(CH_3Br) = 76.5 \cdot 10^{-40}$ gcm^2 ± 4 per cent. The result is in good agreement with the values found by means of infrared spectroscopy ($82 \cdot 10^{-40}$ ± 10 per cent) and by heat capacity measurements ($78 \cdot 10^{-40}$ ± 8 per cent). At present $A(CH_3Br) = 77.5 \cdot 10^{-40}$ gcm^2 is considered the best value. It is accurate to 4 per cent.

(4) Furthermore, ΔE_0° for the reaction $CH_3Br + HCl \rightarrow CH_3Cl + HBr$ was found to be 2500 gcal mole^{-1} ± 75. The heat of the reaction at various temperatures was calculated. The value found is inconsistent with the value which can be calculated from existing thermochemical data. It is concluded that Thomsen's values for the heat of formation of CH_3Br and CH_3Cl must be incorrect.

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Note added in proof: In a 'letter' to Phys. Rev. 72, 344, (1947) Gordy, Simmons and Smith have reported the results of microwave experiments with CH_3Cl and CH_3Br. For CH_3Cl^{35} A is found to be $63.1 \cdot 10^{-40}$ gcm^2, for CH_3Cl^{37} $A = 64.0 \cdot 10^{-40}$ e. g. the 'weighed' average for ordinary methyl chloride is $63.4 \cdot 10^{-40}$. A serious discrepancy thus exists between this result and Nielsen's value $A = 57.9 \cdot 10^{-40}$ used in this work. The discrepancy is hardly explanable by experimental uncertainty. If the microwave results are confirmed by future experiments the results of the present paper are changed as follows:

pag. 29: $A(CH_3Br) = 85.6 \cdot 10^{-40}$ gcm^2 ± 4 per cent.

This is in fine agreement with the microwave result by Gordy et. al. who found $A(CH_3Br) = 87.5 \cdot 10^{-40}$ by direct measurement

pag. 31: $\Delta E_0^\circ = \Delta H_0^\circ = 2464$ gcal $\text{mol}^{-1} \pm 75$.
pag. 32: $\Delta H^\circ (298^\circ K) = 2414$ gcal mole^{-1}.
pag. 33: $\Delta Q^\circ (298^\circ K) = -24.1$ kcal mole^{-1}.

Universitetets kemiske Laboratorium.
Copenhagen.

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