[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity of Methane and its Halogen Derivatives from Spectroscopic Data

BY ROBERT D. VOLD

Introduction

There has been considerable discussion in the literature concerning the use of the rigid rotator-harmonic oscillator assumption in the calculation of thermodynamic properties of polyatomic molecules from spectroscopic data. There is a double problem involved, one concerning the completeness with which the spectrum is known, and the other the validity of certain simplifying assumptions made in the calculation. In the case of entropy Mayer, Brunauer and Mayer[1] believe that the approximate method is correct to 0.5 E. U. even for complicated molecules such as ethane and acetylene.

The enormous amount of work on Raman spectra has provided a wealth of data without much present prospect of the more detailed knowledge of the spectrum necessary for precise calculations. Consequently it seems useful to investigate to what extent methods actually applicable to the available data can be made to give correct results. This is all the more desirable since most of the present thermal and equilibrium data are very unreliable. As a step toward the solution of this problem the molecular heat capacities of methane, methyl chloride, methylene chloride, chloroform and carbon tetrachloride have been calculated over the temperature range 0 to 500° from their Raman spectra.

Calculation of Results

The heat capacity of a polyatomic gas is given by the well-known equation[2]

$$C^\circ = 3/2\ R\ (\text{translation}) + 3/2\ R\ (\text{rotation}) + R\ (\text{for } C_p - C_v) + R \sum_n \left(\frac{h\nu_n}{kT}\right)^2 \frac{e^{h\nu_n/kT}}{(e^{h\nu/kT} - 1)^2}$$

That it is very nearly correct to use the classical value for the rotational heat capacity at room temperatures or above has been demonstrated by many investigators.[3]

The vibrational frequencies used were selected only after a thorough consideration of the literature.[4] In cases of disagreement most weight was given to the results of Langseth[4i] and of Cabannes and Rousset.[4j] The values are all Raman frequencies determined by use of the compounds in the liquid state with the exception of methane and methyl chloride. The methane frequencies 2915 and 3022 are from Raman spectra but 1520 and 1304 are from theoretical considerations and infra-red spectra, respectively. The methyl chloride frequencies are all from the infra-red absorption spectrum of the gas. The reason for this choice is that some of these frequencies are entirely absent in the Raman spectrum and those which do appear are in real disagreement with the infra-red values. The difference probably cannot be simply attributed to the fact that the Raman spectrum was determined with the liquid and the infra-red spectrum with the gas since sometimes the one and sometimes the other have the higher value of the frequency. In accord with a suggestion of Adel and Barker[5] the frequencies 2967 and 2880 in the methyl chloride spectrum were regarded as a case of resonance degeneracy and 2924 taken as the value of the unperturbed frequency. Whether or not this procedure is rigorously correct is unimportant in the present instance, since at 100° this frequency contributes only 0.003 cal. per deg. per mole to the heat capacity. The frequencies for methylene chloride, chloroform and carbon tetrachloride have been determined many times and are all quite accurately known.

Raman frequencies of the liquid are generally somewhat lower than those of the gas. The use of such frequencies in the equation for heat capacity consequently leads to values for the vibrational contribution which are somewhat too high. However, the difference probably is not very great with the molecules under consideration here. In the case of methane the difference in frequen-

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(1) Mayer, Brunauer and Mayer, THIS JOURNAL, **55**, 37 (1933).

(2) The values of the fundamental constants were taken from the "International Critical Tables."

(3) (a) Gordon and Barnes, *J. Phys. Chem.*, **36**, 2601 (1932); (b) Deitz and Andrews, *J. Chem. Phys.*, **1**, 62 (1933); (c) Villars, *Phys. Rev.*, **38**, 1552 (1931); (d) MacDougall, *ibid.*, **38**, 2074 (1931); (e) MacDougall, *ibid.*, **38**, 2296 (1931).

(4) (a) Kohlrausch, "Der Smekal-Raman Effekt," 1931; (b) Mecke, *Z. physik. Chem.*, **B17**, 1 (1932); (c) Pai, *Indian J. Physics*, **7**, 285 (1932); (d) Urey and Bradley, *Phys. Rev.*, **38**, 1969 (1931); (e) Dickinson, Dillon and Rasetti, *ibid.*, **34**, 582 (1929); (f) Bennett and Meyer, *ibid.*, **32**, 888 (1928); (g) Dennison, *Astrophys. J.*, **62**, 84 (1925); (h) Trumpy, *Z. Physik*, **88**, 226 (1934); (i) Langseth, *ibid.*, **72**, 350 (1931); (j) Cabannes and Rousset, *Ann. phys.*, [10] **19**, 229 (1933).

(5) Adel and Barker, *J. Chem. Phys.*, **2**, 627 (1934).

cies is only 6 cm.$^{-1}$ in 2900.[4a] With more polar substances the difference is greater, reaching 3.7% for hydrogen chloride, which has a dipole moment of 1.03×10^{-18} e. s. u. The error that such differences cause in the heat capacity varies from molecule to molecule, depending on the absolute value of the vibration frequency, and will be further discussed later. For purposes of comparison the dipole moments, dielectric constants, and some other data to be used presently, are shown in Table I.

TABLE I[6]

PHYSICAL CONSTANTS OF HALOGENATED METHANES

	CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
$\mu \times 10^{18}$	0	1.73	1.59	1.10	0
ϵ	...	12.61	9.14	4.84	2.24
Crit. temp., °C.	−82.85	143.2	245.1	262.9	283.15
Crit. press., atm.	45.60	65.85	60.9	53.8	44.98

TABLE II

FREQUENCIES AND MULTIPLICITIES

ν cm.$^{-1}$	p	ν cm.$^{-1}$	p	ν cm.$^{-1}$	p
CCl_4		$CHCl_3$		CH_2Cl_2	
217.9	2	260.8	2	284	1
314.0	3	365.9	1	700	1
458.9	1	760.4	2	735	1
776.3	3	667.1	1	898	1
CH_3Cl		1215.6	2	1060	1
733	1	3018.7	1	1150	1
1020	2	CH_4		1419	1
1355	1	1304	3	2984	1
1460	2	1520	2	3044	1
2924	1	2915	1		
3047	2	3022	3		

The frequency assignment and multiplicities finally adopted as being in accord with all the experimental facts of intensity and polarization are those of Cabannes and Rousset[4j] confirmed by the work of Trumpy[4h] and Langseth.[4i]

In order to facilitate calculation of mean heat capacities the energy contents of the gases were also calculated, and are given in Table IV. These values were obtained by the equation

$$E^\circ - E^\circ_0 = 3RT + \sum_n \frac{N\epsilon_n}{e^{\epsilon_n/kT} - 1}$$

The molal heat capacities at constant pressure calculated from these data by the methods described above are given in Table III. These values are for the respective gases in their standard state, *i. e.*, unit fugacity and zero pressure. In order to use them for determination of the heat capacity at any given pressure, correction must be made for the change of specific heat of a real gas with pressure. Thermodynamically

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

which becomes $+(81RT_c^3/32P_cT^3)P$ if Berthelot's equation of state is used and one limit of integration taken as zero pressure. On the other hand, van der Waals' equation gives zero correction. A modified Callendar equation, much used by Eucken,[7] gives $-T(\partial^2 B/\partial T^2)P$ for the correction where B is defined by $PV = RT + BP$.

It is evident that a certain degree of arbitrariness is unavoidable in making this correction. The uncertainty is increased by the fact that the Berthelot equation is known not to hold very well for saturated vapors and still this is just the state of some of the substances under investigation in

TABLE III

MOLAL HEAT CAPACITIES OF THE HALOGENATED METHANES

Temp.,	CH_4		CH_3Cl		CH_2Cl_2		$CHCl_3$		CCl_4	
°C.	$C_{\text{vib.}}$	C_{P_0}	$C_{\text{vib.}}$	C_{P_0}	$C_{\text{vib.}}$	C_{P_0}	$C_{\text{vib.}}$	C_{P_0}	$C_{\text{vib.}}$	C_{P_0}
0	0.39	8.33	1.40	9.34	3.92	11.86	7.16	15.11	11.35	19.30
10	.47	8.41	1.56	9.50	4.15	12.09	7.42	15.36	11.63	19.57
20	.55	8.49	1.72	9.66	4.38	12.32	7.67	15.62	11.89	19.84
25	.59	8.54	1.80	9.75	4.49	12.44	7.79	15.73	12.02	19.96
30	.64	8.59	1.89	9.83	4.60	12.55	7.91	15.85	12.14	20.09
40	.74	8.68	2.05	10.00	4.83	12.78	8.14	16.09	12.38	20.33
50	.84	8.78	2.23	10.17	5.05	13.00	8.37	16.32	12.60	20.55
60	.95	8.89	2.40	10.35	5.28	13.22	8.59	16.54	12.82	20.76
80	1.18	9.13	2.75	10.70	5.71	13.65	9.01	16.96	13.21	21.16
100	1.43	9.37	3.11	11.05	6.12	14.07	9.41	17.36	13.57	21.52
200	2.81	10.75	4.83	12.77	7.94	15.89	11.05	19.00	14.90	22.84
300	4.23	12.18	6.36	14.30	9.37	17.31	12.24	20.19	15.72	23.67
400	5.59	13.54	7.69	15.63	10.50	18.44	13.13	21.08	16.26	24.20
500	6.85	14.79	8.84	16.79	11.42	19.37	13.82	21.77	16.62	24.56

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[6] Data mostly from "I. C. T.," Vol. VI, pp. 82 ff., and Landolt-Börnstein, Vol. I, pp. 253 (1923). Also Morgan and Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

[7] Eucken and Lüde, *Z. physik. Chem.*, **B5**, 413 (1929).

TABLE IV

INTERNAL ENERGY OF HALOGENATED METHANES

Temp., °C.	$E^\circ - E^\circ_0$, cal. per mole				
	CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
0	1643	1709	2006	2468	3095
25	1804	1898	2261	2804	3536
100	2325	2528	3107	3899	4947
200	3132	3523	4410	5523	6972
300	4081	4680	5875	7287	9103
400	5169	5980	7466	9154	11,300
500	6388	7404	9160	11,100	13,542

this study. The use of the Callendar equation is limited by the fact that unless the data of state are determined over a wide temperature range, there is much latitude in the choice of x in the equation $B = b + (aP/T^x)$. Consequently, although the equation chosen may represent the values of B very closely, it may well be useless for calculation of the second derivative. Under these circumstances it seems best to use the Berthelot equation, despite its limitations, especially since Giauque and Wiebe[8] found it gave reasonably satisfactory results.

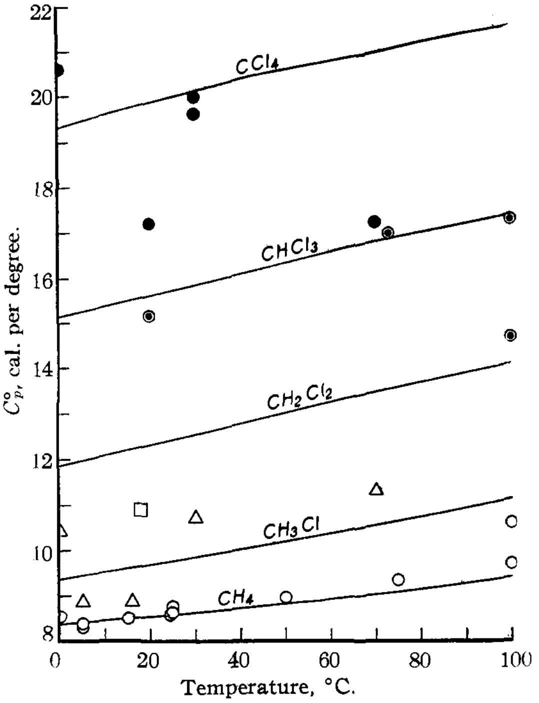

Fig. 1.—Calculated molal heat capacity of halogenated methanes. Experimental values: CCl_4, ●; $CHCl_3$, ◉; CH_2Cl_2, □; CH_3Cl, △; CH_4, ○.

Discussion

The comparison of the calculated with the experimental values is given in Fig. 1. The experimental values shown there, mostly obtained from the "I. C. T." and Landolt-Börnstein, have been corrected to zero pressure by use of the Berthelot equation. The absolute magnitude of these corrections varies from 0.02 cal. per deg. per mole per atmosphere for methane at 100° to 0.95 cal. per deg. per mole per atmosphere for carbon tetrachloride at 0°. The values of the critical temperatures and pressures used have already been given in Table II and are all experimental values except the critical pressure of methylene chloride. This value was obtained as the average of extrapolations from the critical pressures of molecules on either side of it in the series CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, the extrapolations being made proportional to the ratio of the differences between the various dipole moments. The plot is extended only to 100°, since there are practically no experimental values above that temperature for most of the molecules.

Unfortunately, as is evident from the figure, the experimental values are so poor that they cannot be used as a criterion of the accuracy of the calculated results. There is a tendency, most marked with chloroform, for the experimental values to scatter on either side of the calculated curves. However, the discordance of the measured values is so great, and their number so few, that no definite conclusions can be drawn. All that can be done is to specify the probable limit of error of the calculated values.

The most serious source of error is the frequency uncertainty due to the use of liquids in the determination of the Raman spectra. Despite their considerable polarity, however, there are several indications that the frequencies of the gas for these molecules are not far different from those of the liquid. The difference in molal heat capacity of methyl chloride at 30° calculated from infra-red frequencies of the gas and Raman frequencies of the liquid is only 0.1 cal. per deg. It seems probable that in even the worst cases (CH_3Cl and CH_2Cl_2) the difference between the frequencies of the gas and the liquid is not greater than 3%. Over the range of temperatures and frequencies considered the error in heat capacity due to a frequency uncertainty of 3% is not greater than 2%.

Gordon and Barnes[9] have shown that the error due to the assumption that molecules behave as rigid rotators and harmonic oscillators is small. In the present case a liberal outside limit for this

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(8) Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

(9) (a) Gordon and Barnes, *J. Chem. Phys.*, **1**, 692 (1933); (b) Gordon, *ibid.*, **2**, 65 (1934).

error is 0.1 cal. per deg. per mole. It is reasonable to conclude that the values of C_{P_0} in Table III are correct to within 3% with perhaps a small systematic positive error due to the use of vibration frequencies determined with liquids. When these values are calculated to various finite pressures by use of the Berthelot equation in the thermodynamic expression, further error is introduced. It seems probable that no greater accuracy than 5% can be claimed at the present time for such values. Such accuracy, however, far exceeds that of most of the experimental determinations at present available.

The author wishes to express his appreciation to Professor W. F. Giauque for many helpful conversations during the course of this investigation.

Summary

1. The molal heat capacity over the temperature range 0 to 500° has been calculated for methane, methyl chloride, methylene chloride, chloroform and carbon tetrachloride from spectroscopic data.

2. It has been shown that the values obtained are probably good to 3% and are far more reliable than the fragmentary experimental thermal data.

BERKELEY, CALIF. RECEIVED APRIL 12, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 49]

Reactions of Zirconium Tetrabromide and Thorium Tetrabromide with Potassium and with Potassium Amide in Liquid Ammonia

BY RALPH C. YOUNG

Zirconium tetrabromide was found to be soluble in liquid ammonia, at least to the extent of 2 g. per 10 cc. of ammonia at −33.5°. It thus differs from zirconium tetraiodide[1] which is insoluble in this solvent, and from titanium tetrabromide[2] which ammonolyzes to give an insoluble product. Thorium tetrabromide,[3] as has been previously described, gives an insoluble ammine in liquid ammonia.

The procedure for carrying out reactions in ammonia as to the drying of the solvent, the introduction of the salt and the potassium, preparation of potassium amide, and the washing of the reaction product was in general that described in the numerous papers of Kraus and co-workers and of Franklin and co-workers on this subject.

The apparatus in which the reactions were carried out was constructed to allow a solution of potassium, or potassium amide, to be poured from one leg of 100 cc. capacity through a connecting tube packed with glass wool into another leg of the same volume. Both legs were provided with short tubes which were connected by pressure tubing to separate mercury manometers with mercury reservoirs by means of which the pressure in the apparatus could be regulated. Sealed also to each leg were tubes with ground glass joints which afforded a means of introducing the reactants and through which a solution could be decanted. A tube also extended to the bottom of each leg and these allowed the introduction of ammonia and afforded a method of stirring the contents with ammonia gas. The legs of the apparatus rested in separate Dewar tubes containing ammonia.

When into a solution of 2 g. (0.005 mole) of zirconium bromide in 10 cc. of ammonia there was poured 75 cc. of an ammonia solution containing 2 g. (0.05 mole) of potassium, there was formed a black precipitate and a red solution, neither of which was permanent. Secondary reactions began immediately which resulted in the precipitate becoming white, the solution slightly yellow, probably due to potassium amide, and an evolution of hydrogen gas. Burgess and Smoker[4] have reported observations somewhat similar to these for the reaction between manganese iodide and sodium in liquid ammonia. The anions of some metal compounds[5] are highly colored in this solvent, as are the solutions of certain salts.[6] Black precipitates are formed by finely divided metals, and may be formed by nitrides and ammonobasic salts.

After the solution was decanted and the precipitate washed with ammonia, the potassium bromide recovered was found to be equivalent to the zirconium bromide used. Since the white product was very reactive, and oxidized rapidly in the air, it was necessary, before analysis, to introduce it, in an atmosphere of ammonia, into an apparatus similar to that described by Franklin.[7] This afforded a means of obtaining the weight after all adsorbed ammonia had been pumped off, and allowed the product to be attacked by water vapor in the absence of air, after which it was readily analyzed.

Anal. Calcd. for $Zr(NK)_2 \cdot NH_3$: Zr, 42.54; K, 36.47; N, 19.58. Found: Zr, 41.22, 41.75; K, 36.45, 36.30; N, 18.14, 18.85.

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[1] Shähler and Denk, *Ber.*, **38**, 2615 (1905).

[2] Ruff and Eisner, *ibid.*, **41**, 2260 (1908).

[3] Moissan and Martinsen, *Compt. rend.*, **140**, 1514 (1905).

[4] Burgess and Smoker, *Chem. Reviews*, **8**, 269 (1931).

[5] Kraus and Kurtz, THIS JOURNAL, **47**, 43 (1925).

[6] Bergstrom, *ibid.*, **47**, 2317 (1925).

[7] Franklin, *J. Phys. Chem.*, **15**, 516 (1911).