Summary

The vapor phase heats of hydrobromination of cyclopropane and propylene have been measured at 94°. A numerical value for the heat of formation of cyclopropane has been calculated by applying these data, the known heat of formation of propylene, and an estimate of the heat of isomerization of *n*-propyl bromide to isopropyl bromide.

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[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

Magnetic Susceptibilities of the Halogen Derivatives of Methane[1]

BY J. R. LACHER,* R. E. SCRUBY AND J. D. PARK

Introduction.—In conjunction with the calorimetric work being carried on in this Laboratory, a systematic research is being carried out on the magnetic susceptibilities of the simpler organic halogen compounds. In addition to shedding further light on the magnetic properties of these compounds, it is hoped that as the work progresses a correlation between the change of susceptibility and the heat of a reaction will become apparent. It is the intention of this paper to present the experimental data for six mixed halogenomethanes and to summarize and present a correlation of the magnetic susceptibilities of the seventy halogenated derivatives of methane.

Experimental.—Magnetic susceptibilities of the following compounds have been measured: $CClBrH_2$, $CHBrCl_2$, $CHClBr_2$, $CBrCl_3$, CBr_2Cl_2 and $CClF_3$. The five chlorobromomethanes were distilled in an efficient column packed with glass helices in order to remove any trace of paramagnetic impurities. Freezing points and an estimation of purity of the compounds were obtained from the time–temperature freezing curves using an apparatus similar to that of the National Bureau of Standards.[2] The curves were analyzed according to their procedure. Refractive indices at 20 and 25° were also measured.

The magnetic susceptibilities of the chlorobromomethanes were measured by means of the Quincke method.[3] A field strength maximum of about 20,000 oersteds was used. This produced a depression in liquid level in the Quincke tube of about one millimeter. Carefully purified benzene (χ = 0.702)[4] was used as standard for these measurements. The susceptibility of $CClF_3$ was measured by means of a modification of the Quincke method using a high pressure container.[5] Unfortunately at room temperature the liquid is only a few degrees below its critical temperature. Considerable difficulty was encountered in observing the meniscus. For this reason the value of susceptibility obtained for this compound is subject to considerable uncertainty. The experimental results are given in Table I. With these results and values of susceptibility from other sources, experimental data are now available for fourteen of the fifteen possible chlorobromo derivatives of methane, for all but five of the fluoro-chloro derivatives and for all the iodo derivatives.

TABLE I

MAGNETIC SUSCEPTIBILITIES OF SOME HALOGENATED METHANES

Compound	χ_M expt.	$n^{20}D$	$n^{25}D$	t_{f_0}, °C.	Purity, mole %
C_6H_6[a]		1.5007	1.4975	5.5	99.65
$CClBrH_2$	55.0 ± 0.6	1.4842	1.4811	−90	97.9
$CHBrCl_2$	66.3 ± 0.3	1.4979	1.4951	−57.1	97.9
$CHClBr_2$	75.1 ± 0.4	1.5478	1.5449	−30.0	98.4
$CBrCl_3$	73.1 ± 0.7	1.5063	1.5034	− 5.6	98.9
CBr_2Cl_2	81.1 ± 0.4		1.5499	22.7	98.9
$CClF_3$	45.3 ± 1.5				

[a] Used as standard (χ = 0.702).

Correlation of Data.—With the aid of these data various correlations have been examined in an effort to determine what factors must be considered to reproduce the experimental results in a satisfactory manner. The first correlation considered is one of atomic increments only. Values of the increments for this correlation were calculated from the experimental data by the method of least squares in order to give the best possible fit to the data. However, the average deviation was then considerably larger than the maximum probable error of the experimental values. Other methods of correlation are those of Pascal,[6] Gray and Cruickshank[7] and Anantakrishnan.[8] Although these correlations contain terms in addition to atomic increments, they may be reduced for all practical purposes to an atomic

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* Harvard University Ph.D. 1936.

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[2] A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, R. P. 1676 (1945).

[3] G. Quincke, *Ann. Physik*, **24**, 347 (1885); **34**, 401 (1888).

[4] The factor -1×10^{-6} is to be understood with all values of magnetic susceptibility and increments of susceptibility given in this paper.

[5] J. R. Lacher, R. E. Scruby and J. D. Park, THIS JOURNAL, **71**, 1797 (1949).

[6] P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., 1943, p. 51.

[7] F. W. Gray and J. H. Cruickshank, *Trans. Faraday Soc.*, **31** 1491 (1935).

[8] S. V. Anantakrishnan, *Proc. Ind. Acad. Sci.*, **21A**, 114 (1945).

increment correlation by suitable manipulation of the additional factors. This statement applies only to the methane derivatives considered here. Since it was shown that the best possible correlation that could be produced by atomic increments only was not satisfactory, additional factors must be considered.

The additional factor which must be considered has been indicated by Pascal[9] and Lacher.[10] It is the interaction between adjacent non-bonded atoms. For this correlation two types of increments are used, atomic increments and interaction increments. For example, the increments making up the susceptibility of $CHBrCl_2$ are C, H, Br, 2Cl, 2(H–Cl), 2(Br–Cl), (H–Br), and (Cl–Cl); where the atomic symbols represent atomic increments and the terms in parentheses represent interaction increments. Thus the molar susceptibility for $CHBrCl_2$ may be written

$$\chi_M = C + H + Br + 2Cl + 2(H\text{–}Cl) + 2(Br\text{–}Cl) + (H\text{–}Br) + (Cl\text{–}Cl) \quad (1)$$

The series of chlorobromomethanes provides six linearly independent relations with which to calculate ten different increments. It is, therefore, necessary to group the increments into six groups if the factors are to be uniquely determined. For the methane derivatives, the most convenient grouping is illustrated by the above example, the molar susceptibility being written as

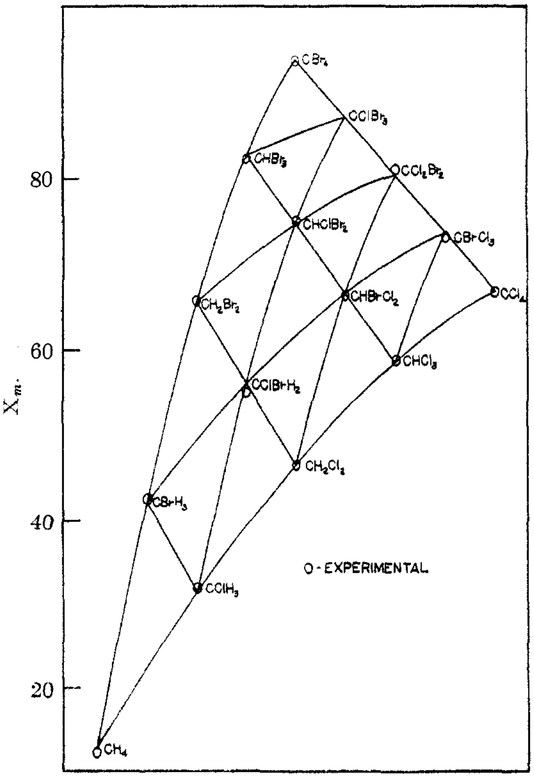

Fig. 1.—Magnetic susceptibilities of the chlorobromomethanes.

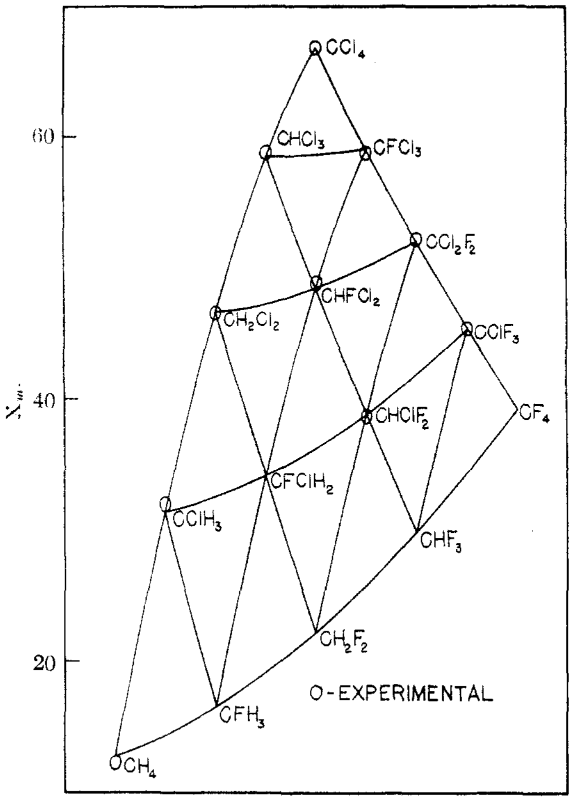

Fig. 2.—Magnetic susceptibilities of the fluorochloromethanes.

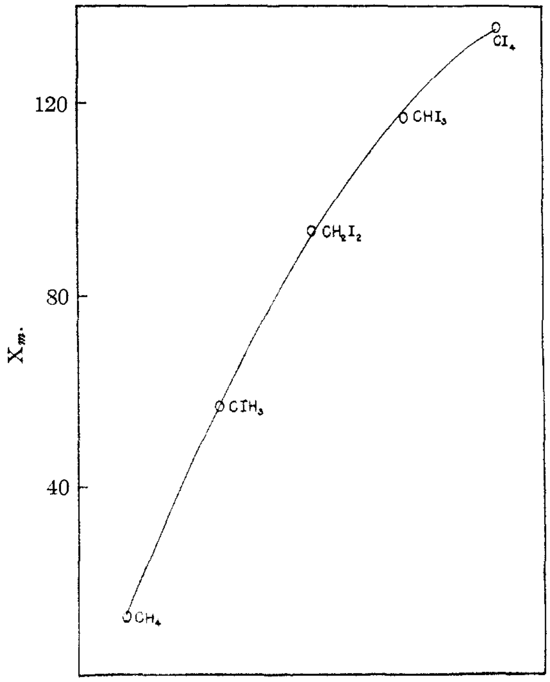

Fig. 3.—Magnetic susceptibilities of the iodomethanes: O, experimental.

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[9] P. Pascal, *Compt. rend.*, **217**, 657 (1943).

[10] J. R. Lacher, This Journal, **69**, 2067 (1947).

$$\chi_M = [1/4\text{C} + \text{Br} + 3/2(\text{Br–Br})] + [1/4\text{C} + \text{H} + 3/2(\text{H–H})] + 2[1/4\text{C} + \text{Cl} + 3/2(\text{Cl–Cl})] + 2[(\text{H–Cl}) - 1/2(\text{H–H}) - 1/2(\text{Cl–Cl})] + 2[(\text{Br–Cl}) - 1/2(\text{Br–Br}) - 1/2(\text{Cl–Cl})] + [(\text{H–Br}) - 1/2(\text{H–H}) - 1/2(\text{Br–Br})] \tag{2}$$

It is apparent that there are two classes of groups —the first of the type [1/4C + X + 3/2 (X–X)] involving atomic increments and interaction between like atoms, and the second of the type [(X–Y) – 1/2(X–X) – 1/2(Y–Y)], the leading term of which is a mixed interaction. The example given above has utilized all of the six groups necessary to correlate the entire series of chlorobromomethanes.

These six groups have been calculated from the fourteen experimental values for the chlorobromomethanes by the method of least squares. The correlation obtained is excellent, the average deviation being only 0.5 which is within the experimental error. Utilizing three of the terms calculated from the chlorobromomethanes and four of the five experimental values of susceptibility for the fluorochloromethanes, the three additional terms necessary to correlate the entire series of fluorochloromethanes have been calculated. The experimental value for $CClF_3$ was not used in this calculation due to the uncertainty in this value as noted above. The two additional groups necessary for the iodomethanes were calculated from the four iodo compounds.

The eleven groups whose calculation has been discussed above are given in Table II together with four groups whose values have been assumed. The experimental and calculated values of susceptibility of the chlorobromo-, fluorochloro- and iodomethanes are presented graphically in Figs. 1, 2 and 3, respectively. The lines in these figures intersect at the calculated values of susceptibility and the circles represent the experimental values. Utilizing the fifteen groups listed in Table II, the susceptibilities of the seventy halogen derivatives of methane have been calculated. These values are given in Table III together with the experimental values where available.

TABLE II

GROUP AND INTERACTION SUSCEPTIBILITIES

1/4C + H + 3/2(H–H)	3.17
1/4C + F + 3/2(F–F)	9.79
1/4C + Cl + 3/2(Cl–Cl)	16.69
1/4C + Br + 3/2(Br–Br)	23.42
1/4C + I + 3/2(I–I)	33.78
(H–F) – 1/2(H–H) – 1/2(F–F)	–0.93
(H–Cl) – 1/2(H–H) – 1/2(Cl–Cl)	1.74
(H–Br) – 1/2(H–H) – 1/2(Br–Br)	3.09
(H–I) – 1/2(H–H) – 1/2(I–I)	4.65
(F–Cl) – 1/2(F–F) – 1/2(Cl–Cl)	–0.25
(F–Br) – 1/2(F–F) – 1/2(Br–Br)	0 (assumed)
(F–I) – 1/2(F–F) – 1/2(I–I)	0 (assumed)
(Cl–Br) – 1/2(Cl–Cl) – 1/2(Br–Br)	0.05
(Cl–I) – 1/2(Cl–Cl) – 1/2(I–I)	0 (assumed)
(Br–I) – 1/2(Br–Br) – 1/2(I–I)	0 (assumed)

TABLE III

EXPERIMENTAL AND CALCULATED VALUES OF MAGNETIC SUSCEPTIBILITY OF THE HALOGEN METHANES

Compound	χ_M, calcd.	χ_M, expt.	Ref.	Compound	χ_M calcd.
CX_4 Class					
CH_4	12.7	12.2	a	CF_4	39.2
CCl_4	66.8	66.8	e		
CBr_4	93.7	93.7	e		
CI_4	135.1	135.6	b		
CXY_3 Class					
$CHCl_3$	58.5	58.8	d	CHF_3	29.8
$CHBr_3$	82.7	82.2	e	CFH_3	16.5
CHI_3	118.5	117.1	e	$CFBr_3$	80.0
$CFCl_3$	59.1	58.7	f	CFI_3	111.1
$CClH_3$	31.4	32.0	b	$CClBr_3$	87.1
$CClF_3$	45.3	45.3	c	$CClI_3$	118.0
$CBrH_3$	42.2	42.8	b	$CBrF_3$	52.8
$CBrCl_3$	73.6	73.1	c	$CBrI_3$	124.8
CIH_3	57.2	57.2	b	CIF_3	63.2
				$CICl_3$	83.8
				$CIBr_3$	104.0
CX_2Y_2 Class					
CH_2Cl_2	46.7	46.6	b	CH_2F_2	22.2
CH_2Br_2	65.5	65.9	b	CF_2Br_2	66.4
CH_2I_2	92.5	93.5	b	CF_2I_2	87.1
CF_2Cl_2	52.0	52.2	f	CCl_2I_2	100.9
CCl_2Br_2	80.4	81.1	c	CBr_2I_2	114.4
$CXYZ_2$ Class					
$CHFCl_2$	48.4	48.8	f	$CHFBr_2$	65.0
$CHClF_2$	38.8	38.6	f	$CHFI_2$	55.1
$CHClBr_2$	74.7	75.1	c	$CHClI_2$	98.5
$CHBrCl_2$	66.6	66.3	c	$CHBrF_2$	47.4
$CClBrH_2$	56.2	55.0	c	$CHBrI_2$	106.5
$CHIF_2$	59.3			$CFICl_2$	76.4
$CHICl_2$	78.5			$CFIBr_2$	90.4
$CHIBr_2$	94.6			$CClBrF_2$	59.2
$CFClH_2$	34.2			$CClBrI_2$	107.7
$CFClBr_2$	73.2			$CClIH_2$	69.6
$CFClI_2$	93.8			$CClIF_2$	69.6
$CFBrH_2$	43.9			$CClIBr_2$	97.4
$CFBrCl_2$	65.2			$CBrIH_2$	79.0
$CFBrI_2$	100.8			$CBrIF_2$	76.8
$CFIH_2$	57.4			$CBrICl_2$	90.7
CWXYZ Class					
CHFClBr	56.8			CHClBrI	86.6
CHFClI	68.6			CFClBrI	83.5
CHFBrI	77.0				

[a] F. Bitter, *Phys. Rev.*, (2) **33**, 389 (1927). [b] Value from Pascal as given in reference *e*. [c] Value from this paper. [d] Value from Trew as given in reference *e*. [e] C. M. French and V. C. G. Trew, *Trans. Faraday Soc.*, **41**, 439 (1945). [f] J. R. Lacher, R. E. Scruby and J. D. Park, THIS JOURNAL, **71**, 1797 (1949).

Although the data given in Table II are all that is necessary for the calculation of the magnetic susceptibility of any of the halogen methanes, the extension of this work to more complex compounds requires a further insight into these groups. It is particularly desirable that the individual increments be known. This problem has been approached from the standpoint of Gray and Cruickshank[7] and Anantakrishnan,[8] except that interaction terms are included. In this analysis the atomic increments for atoms bonded to carbon are broken down into two terms. The first is the atomic susceptibility as calculated from Slater's[11] set of shielding constants and quantum numbers, and the second is a term called bond depression which is associated with the second term in the Van Vleck equation[12] for molecular susceptibility, *i. e.*, the paramagnetic term.

We have calculated the susceptibility for the free carbon atom. Those for hydrogen and the halogen atoms are corrected for bond depressions and ionic strength of the C–X bond. The results are given in Table IV.

TABLE IV

CALCULATED ATOMIC SUSCEPTIBILITIES

Element	χ_A	Element	χ_A
C	10.0	Cl	19.3
H	1.0	Br	30.5
F	8.5	I	45.3

Using this information, the absolute value of the interaction increments may be calculated from the data in Table II and the results are shown in Table V.

TABLE V

INTERACTION INCREMENTS

(H–H)	−0.2	(H–F)	−1.4	(F–Br)	−3.6
(F–F)	−0.8	(H–Cl)	−0.1	(F–I)	−5.1
(Cl–Cl)	−3.4	(H–Br)	−0.2	(Cl–Br)	−4.9
(Br–Br)	−6.4	(H–I)	−0.2	(Cl–I)	−6.4
(I–I)	−9.4	(F–Cl)	−2.4	(Br–I)	−7.9

Discussion of Results.—The interaction increments listed in Table V all make a temperature independent paramagnetic contribution to the molar susceptibility. The magnitude of the interaction between like atoms indicates that the size of the atoms is of primary significance as has been indicated by Pascal.[9] This is shown strikingly in the first column of figures in Table V and the fact that the hydrogen–halogen interactions are small, except for fluorine. The (F–Cl) and (Cl–Br) interactions are approximately the arithmetic means of the interactions between the same atoms. For this reason we assumed the same to be true of other mixed halogens in Table II. When the atoms bonded to carbon in methane derivatives are large, their electron clouds are sufficiently modified to make an appreciable effect on the molar susceptibility. The drop in susceptibility is simply related to the geometry of a tetrahedron. The (H–F) interaction increment is quite large, −1.4, even though both atoms involved are small. We believe the effect is real as it also appears in Table II where the (H–F) interaction is greater than one-half the sums of the (H–H) and (F–F) interactions. This may possibly be associated with the relatively large unscreened nuclear charge carried by the fluorine atom.

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Summary

Magnetic susceptibilities of the following compounds have been measured: $CClBrH_2$, $CHBrCl_2$, $CHClBr_2$, $CBrCl_3$, CCl_2Br_2 and $CClF_3$. The various methods of correlation of magnetic susceptibilities have been examined. It is shown that the experimental values of susceptibility of the halogen methanes may be correlated in a satisfactory manner only when tetrahedral interactions are considered. Using this type correlation, values of magnetic susceptibility have been calculated for all halogen derivatives of methane. An estimate of the magnitude of the contribution of the tetrahedral interactions to the magnetic susceptibilities has been made for each type of interaction occurring in the above compounds.

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[11] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

[12] J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, Oxford, 1932, p. 275.