

which represents the liquid-vapor equilibrium of alcohol-hydrocarbon systems quite accurately. Constants in this equation are presented for etha-

nol-toluene solutions and a number of systems previously investigated.

PEORIA 5, ILLINOIS

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[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

Diamagnetic Susceptibilities of Some Chloro and Fluoro Derivatives of Methane and Ethylene¹

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

In this Laboratory direct measurements of reaction heats of simple organic fluorine compounds are being made.² The results obtained to date show that the addition of chlorine to fluorinated olefins gives heats which deviate strongly from an additivity rule. For example, the vapor phase heat of chlorination of tetrafluoroethylene is -57.3 kcal./mole. When one fluorine atom is replaced by chlorine in this olefin to give trifluoro-chloroethylene, the heat of chlorination drops by 8.5 kcal./mole. On the other hand, if a fluorine atom is replaced by a trifluoromethyl group to give hexafluoropropene, the reaction heat falls off 10.1 kcal./mole. Hexafluorocyclobutene in the same reaction liberates only 37.3 kcal./mole.

These large variations in reaction heats are probably to be correlated with the fact that a C-Cl bond distance will undergo a shrinkage depending on whether or not one or two fluorine atoms are attached to the same carbon atom as is the chlorine.³ Further, the C=C bond distance is shorter in tetrafluoroethylene than it is in ethylene. If the bond distances change, so will the bonding energies, as will also the densities of the electron cloud associated with these bonds.

It is well known⁴ that molar diamagnetism is, to a first approximation, a measure of the sum of the mean cross sectional areas of the electron orbits present in a molecule. One might expect, therefore, to be able to correlate the strongly exothermic character of the reaction heat which results when chlorine adds to tetrafluoroethylene with a general shrinkage in the electron orbits as measured by the change in susceptibility associated with the reaction. On the other hand, since the reaction of chlorine with hexafluorocyclobutene is considerably less exothermic, one might expect in this case either no change or perhaps an expansion of the electron clouds. In order to test these ideas it is necessary to measure first the susceptibilities of the organic fluorine compounds involved. The present paper reports measurements

on some chloro and fluoro derivatives of methane and ethylene.

Very little experimental information is available concerning the molar susceptibilities of the simpler organic halogen compounds, particularly those containing fluorine. Recently, French and Trew⁵ have summarized the molar susceptibilities of some polyhalogen derivatives of methane. All of these compounds show strong deviations from Pascal's additivity rule. Pascal⁶ interprets the anomalous diamagnetism of organic polyhalogen compounds as being due to the mutual deformation of the electronic orbitals of the halogen atoms in contact. This effect is a maximum for iodine and is small for fluorine. The observed molar susceptibilities of the chlorine, bromine and iodine derivatives of methane can be interpreted empirically by assuming that they are the sum of atomic susceptibilities and six interaction terms directed along the edges of a tetrahedron.⁷

Experimental

The Quincke method,⁴ which is well suited for measurements on liquids, was used. The measurements were relative ones and the displacement of the meniscus of a given liquid was compared with that produced by a standard liquid in the same field strength and in an identical tube. For liquids boiling above room temperature, the tubes were made from 50-ml. distilling flasks using 3.0-mm. precision bore tubing. Since several of the compounds studied are gases at ordinary conditions, special tubes were constructed which would hold liquids under moderate pressures. One is shown diagrammatically in Fig. 1. The reservoir was constructed of brass and had an internal diameter of 4.3 cm. The movement of the meniscus was observed in a thick-walled glass precision bore capillary. "Teflon" gaskets were used to ensure a tight seal. With this arrangement, the susceptibility of the vapor above the meniscus is not negligible. However, if one assumes that the mass susceptibility of the vapor is identical to that of the liquid (which is undoubtedly true for the non-associated compounds used here), one can readily show that the change in height of the meniscus is independent of the vapor density. The reason is that the net magnetic force operating will then be directly proportional to the difference in density of the vapor and liquid. This is also true of the opposing force due to the hydrostatic head developed.

The electromagnet⁸ used operated on 21 to 25 amperes at 120 volts and gave fields around 18,000 gauss. Changes in liquid level were measured by means of a traveling microscope to an accuracy of ± 0.004 mm. Displacements be-

(1) Presented before the Division of Inorganic and Physical Chemistry, 114th Meeting of the American Chemical Society, Portland, Oregon, September 13-17, 1948. This work was supported by Contract N6onr-231, Task Order 6, with the Office of Naval Research, United States Navy.

(2) J. R. Lacher, J. D. Park, *et al.*, submitted to THIS JOURNAL.

(3) S. H. Bauer, MDDC-1494, U. S. A. E. C.

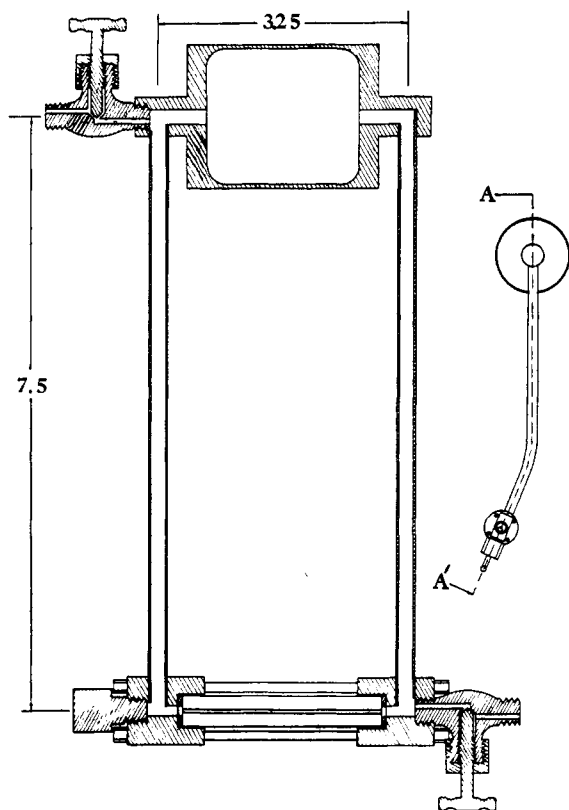
(4) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943.

(5) French and Trew, *Trans. Faraday Soc.*, **41**, 439 (1945).

(6) P. Pascal, *Compt. rend.*, **217**, 657 (1943).

(7) J. R. Lacher, THIS JOURNAL, **69**, 2067 (1947).

(8) H. C. Staehle, Ph.D. Thesis, University of Colorado, 1933.



Section A-A'

Fig. 1.

tween 0.6 and 1.2 mm. were obtained. Dried, distilled, thiophene-free benzene was used as the standard liquid. It had been previously compared with redistilled water as a primary standard using the accepted value for water of -0.720×10^{-6} . Our observed value for benzene, relative to water, was 0.702×10^{-6} which is in agreement with that given by French and Trew.⁵

The compounds^{9,10} used in this research were dried and then distilled in efficient vacuum-jacketed columns packed with glass helices. The indices of refraction of the liquids boiling above room temperature are given in Table I.

TABLE I
INDICES OF REFRACTION

Compound	Observed		Literature		Ref.
	n_D	$t, ^\circ\text{C.}$	n_D	$t, ^\circ\text{C.}$	
C_6H_6	1.5007	20.0	1.5012	20.0	a
CCl_4	1.4602	20.0	1.4603	20.0	a
$\text{CCl}_2=\text{CCl}_2$	1.5054	20.0	1.5055	20.0	b
$\text{CCl}_2=\text{CHCl}$	1.4774	20.0	1.4777	19.8	b
$\text{CCl}_2=\text{CH}_2$	1.4218	25.0	1.4249	20.0	c
$\text{CHCl}=\text{CHCl-cis}$	1.4490	20.0	1.4519	15.0	d
$\text{CCl}_2=\text{CClF}$	1.4349	20.0	1.4360	20.0	e

^a R. M. Davies, *Phil. Mag.*, 21, 1008 (1936). ^b Bruhl, *Ann.*, 200, 173 (1880). ^c R. C. Reinhardt, *Ind. Eng. Chem.*, 35, 422 (1943). ^d Chavanne, *Compt. rend.*, 154, 776 (1912). ^e A. L. Henne, *THIS JOURNAL*, 56, 1726 (1934).

(9) Research samples of *cis*- and *trans*-dichloroethylene were kindly furnished to us by Mr. W. B. Rose, Westvaco Chlorine Products Corp., South Charleston, West Virginia.

(10) Samples of CCl_2F , CCl_2F_2 , CHCl_2F , CHClF_2 , $\text{CCl}_2=\text{CF}_2$, and $\text{CClF}=\text{CF}_2$ were kindly furnished to us by The Jackson Laboratory, du Pont Company.

TABLE II
DIAMAGNETIC SUSCEPTIBILITIES

Compound	$-x \times 10^6$	$-x_M \times 10^6$	$-\chi_M \times 10^6$, Pascal
C_6H_6	0.702	54.8	55.0
CCl_4	.434	66.8	86.4
CCl_2F	.427	58.7	77.8
CCl_2F_2	.432	52.2	69.2
CHFC_2	.474	48.8	60.6
CHClF_2	.446	38.6	52.0
$\text{CCl}_2=\text{CCl}_2$.492	81.6	86.9
$\text{CCl}_2=\text{CHCl}$.501	65.8	69.7
$\text{CCl}_2=\text{CH}_2$.508	49.2	52.6
$\text{CHCl}=\text{CHCl-cis}$.526	51.0	52.6
$\text{CHCl}=\text{CHCl-trans}$.504	48.9	52.6
$\text{CHCl}=\text{CH}_2$.574	35.9	35.4
$\text{CCl}_2=\text{CClF}$.485	72.5	78.3
$\text{CCl}_2=\text{CF}_2$.451	60.0	69.7
$\text{CClF}=\text{CF}_2$.422	49.1	61.1

The experimental results obtained are given in Table II. The second and third columns give the mass and molar susceptibilities, respectively, and the last column the susceptibility obtained by summing Pascal's atomic susceptibilities.⁴ The susceptibilities for benzene and carbon tetrachloride determined in this research are in excellent agreement with those obtained by French and Trew.⁵ However, our value of 0.492 for tetrachloroethylene is somewhat lower than the value of 0.508 reported by Pascal.¹¹ It is estimated that the maximum probable error in the measurements is 1.5% except possibly for $\text{CCl}_2=\text{CFCl}$ where difficulty was encountered in preparing a sufficiently large sample.

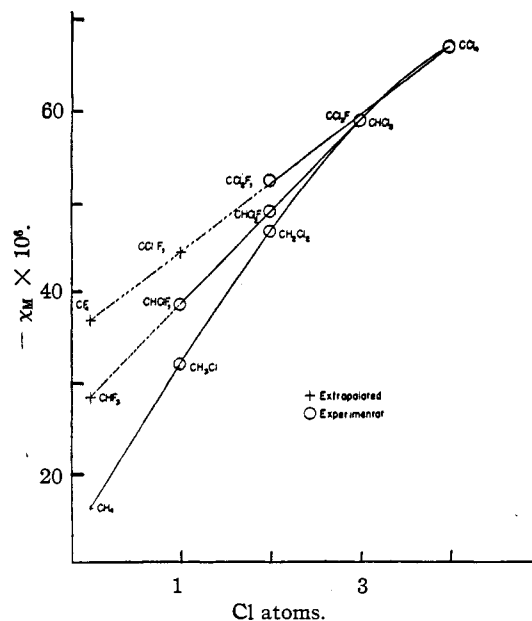


Fig. 2.—Diamagnetic susceptibilities of some fluoro and chloro derivatives of methane.

The data on the methane derivatives are illustrated in Fig. 2, where the molar susceptibility is given as a function of the number of chlorine atoms in the molecule. The data of French and Trew⁵ on the series methane-carbon tetrachloride are also included. In this case the suscepti-

(11) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., Vol. 6, 1929, p. 361.

bility is not a linear function of the number of chlorine atoms present, and therefore a strictly additive rule will not apply. The carbon tetrafluoride-carbon tetrachloride and trifluoromethane-chloroform series give curves which are nearly linear. The slopes, however, are different. If a chlorine atom in carbon tetrachloride or fluorotrichloromethane is replaced by fluorine, the susceptibility drops about 7.3 units; whereas in chloroform and fluorodichloromethane the drop is 10.1 units. According to Pascal's constants, the susceptibility should decrease by 8.6 units. Unfortunately, we were unable to measure the susceptibilities of carbon tetrafluoride, fluorotrichloromethane, and trifluoromethane in our apparatus since their vapor pressures at room temperature are quite high. If one extrapolates the curves as straight lines, one obtains -36.8×10^{-6} , -44.2×10^{-6} and -28.3×10^{-6} as the molar susceptibilities for these compounds, respectively.

The data on the ethylenic derivatives are illustrated in Fig. 3. The molar susceptibilities are practically a linear function of the number of chlorine atoms present in the molecule. However, *trans*-chloroethylene and vinylidene chloride have measurably lower susceptibilities than the *cis*-isomer. The decrease in susceptibility which results when a chlorine atom is replaced by fluorine in a chloro-fluoro ethylene is 11.0 units. In the ethylene-perchloroethylene series the decrease is 15.3 units when chlorine is replaced by hydrogen. Pascal's constants give 17.2 for the latter. A linear extrapolation of the curves in Fig. 3 gives -38.2×10^{-6} and -20.6×10^{-6} for the molar susceptibilities for tetrafluoroethylene and ethylene, respectively. The latter figure agrees well with -18.22×10^{-6} which can be calculated from Pascal's constants but deviates widely from the values of -44.8×10^{-6} given in the "International Critical Tables."¹¹

Acknowledgment.—We wish to thank Mr. P. W. Trott for preparing samples of $\text{CCl}_2=\text{CH}_2$ and $\text{CCl}_2=\text{CFCl}$. Dr. M. L. Sharrah carried out the measurements on the *cis*- and *trans*-dichloroethylenes.

Summary

An apparatus is described for measuring the susceptibilities of liquids under pressure. Diamagnetic susceptibilities of the following compounds were determined: CCl_3F , CCl_2F_2 , CHCl_2F ,

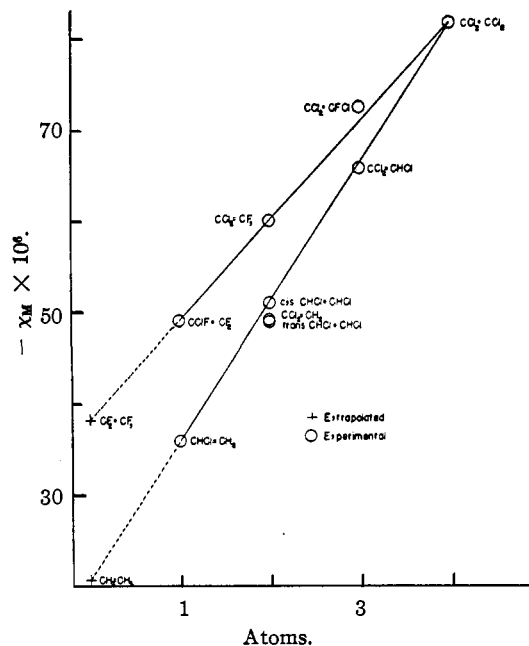


Fig. 3.—Diamagnetic susceptibilities of some fluoro and chloro derivatives of ethylene.

CHClF_2 , $\text{CCl}_2=\text{CCl}_2$, $\text{CCl}_2=\text{CHCl}$, $\text{CCl}_2=\text{CH}_2$, $\text{CHCl}=\text{CHCl}$ *cis* and *trans*, $\text{CHCl}=\text{CH}_2$, $\text{CCl}_2=\text{CClF}$, $\text{CCl}_2=\text{CF}_2$, and $\text{CClF}=\text{CF}_2$. The data give, by extrapolation, an estimate of the susceptibilities of the following compounds: CClF_3 , CF_4 , CHF_3 , C_2H_4 , and C_2F_4 . The relationship of the data obtained to Pascal's constants is discussed. It was found that *trans*-dichloroethylene and vinylidene chloride have measurably lower susceptibilities than the corresponding *cis*-isomer.

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Ethylgermanium Isocyanates

BY HERBERT H. ANDERSON

Six binary volatile inorganic isocyanates resulted from previous investigations: silicon tetra-isocyanate,¹ believed to be the first volatile inorganic isocyanate ever prepared; phosphorus tri-isocyanate¹; thiophosphoryl triisocyanate²; phosphoryl triisocyanate³; arsenic triisocyanate³; germanium tetrakisocyanate, isolated both by the author (in June, 1942),² and by Laubengayer and Reggel⁴ at Cornell University.

However, not all ternary derivatives containing isocyanate were capable of isolation. Germanium chloroisocyanates⁵—as well as germanium chloro-

bromides⁶—could not be purified by distillation, whereas methylsilicon isocyanates,⁷ silicon chloroisocyanates,⁸ phosphorus fluoroisocyanates⁹ and numerous other such compounds could be distilled.

This paper in turn reports all three possible ethylgermanium isocyanates.

Preparation of Ethylgermanium Isocyanates.—Professor Eugene G. Rochow, of Harvard University, kindly furnished pure samples of ethyltrichlorogermane and diethylchlorogermane, boiling at 140.0 and 172.8°, respectively, under 763 mm. pressure. Germanium tetrachloride, prepared and previously studied by the present author at Harvard University^{2,5,6} was made available as a starting material.

(7) to (9) Forbes and Anderson, *ibid.*, **70**, 1222 (1948); Anderson, *ibid.*, **66**, 934 (1944); **69**, 2495 (1947). Also other publications by the same authors.

(1) to (3) Forbes and Anderson, *THIS JOURNAL*, **62**, 761 (1940); **65**, 2271 (1943); Anderson, *ibid.*, **64**, 1757 (1942).

(4) Laubengayer and Reggel, *ibid.*, **65**, 1783 (1943).

(5), (6) Forbes and Anderson, *ibid.*, **67**, 1911, 1703 (1945); **66**, 931 (1944).