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The Magnetic Susceptibility of Organic Compounds

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With the object to obtain new data for the statistical analysis of hydrocarbon mixtures, measurements on diamagnetic organic compounds at room temperature have been performed. The precision was of the order of 1 per mil (10^{-3}) of the diamagnetic effect. We checked the additivity rule and found it to be applicable within 5 per mil on the average. Mixtures were also investigated. A linear relation with the concentration was found to hold for hydrocarbon mixtures within the precision of measurement. For liquids containing electric dipole deviations up to 6 per mil were observed. We applied the results to the analysis of unknown mixtures.

I. EXPERIMENTAL RESULTS

IN this paper we shall deal with the susceptibilities of organic compounds. As the apparatus used is described elsewhere,¹ we shall, as far as concerns the measurements, restrict ourselves to some general remarks.

We applied two types of apparatus, *viz.*, a torsion balance (T.B.) and an inductance apparatus. (I.A.) This made it possible to avoid system errors which are often present, and indeed some were observed. In the author's thesis¹ more details about the work can be found.

The purity of the samples is of great importance. To avoid the effect of ferromagnetics we use a special filter, consisting of a funnel placed in a small magnet. If we pour the liquid through the funnel, on filling the cuvette it is found experimentally that most iron particles are withheld and that the measurement is not affected. A calculation shows that in the filter the magnetic forces exerted on the ferromagnetic particles are one thousand times larger than the forces of viscosity pushing them through the funnel. In the estimate we assume particles to be present, each producing one per mil of our diamagnetic effect. ($0.4 \cdot 10^{-8}$ g iron in 8 g of substance.)

The presence of paramagnetic oxygen is also of great interest. For water differences up to 3 per mil were found, after boiling for some time. Hydrocarbons never showed differences larger than our precision of measurement in this respect. However, measuring the effect of the cuvette filled with air, the barometric pressure has to be taken into account. A change of 15 mm in the pressure gives rise to 1 per mil change in the result.

For the *calibration* it is useful to fill the cuvette with N_2 or CO_2 and to close the cuvette with a greased plug. Their volume susceptibilities* are 0.4

and 0.1, respectively. In order to calibrate the instrument we used the following volume susceptibilities at $20^\circ C$: κ (water) = 903.1, κ (air) = -36.9, the difference being 940.

It appeared that the proportionality constant of the torsion balance changed no more than two per mil during a series of some weeks. The error in the adjustment proved to be 0.2 per mil, adding only a small contribution to the error in the susceptibility, which was probably due to a displacement of the balance or ferromagnetic impurities situated on the moving part of the balance.

Comparison of the results of both apparatus helped us to remove systematic errors, as we can expect entirely different errors to be present in the inductance apparatus. We performed two series with the balance, the second one with an improvement, and one series with the inductance apparatus.

Plotting the differences between the values obtained with the different apparatus for the same sample against the density, system differences of the order of some per mil were found. It appeared that during the first series the balance changed its position when the cuvette contained a liquid of different density. In the second series the change in density was compensated by shifting a weight. After that the differences, being three per mil at the most, agreed better with the estimate of the separate errors (Fig. 1).

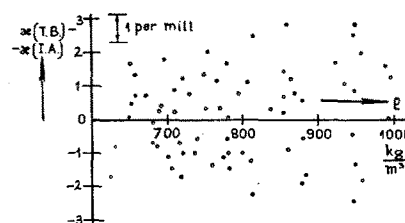


FIG. 1. The difference between the volume susceptibilities, as found with a torsion balance and an inductance apparatus, is plotted vs. the density of the liquids (ρ in kg/m^3).

ρ = density (kg/m^3), μ_0 = permeability of vacuum, and μ_r = relative permeability.

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¹ S. Broersma, *Magnetic Measurements on Organic Compounds* (Martinus Nyhoff, The Hague, 1947). Also Rev. Sci. Inst. 20, 660 (1949).

* We use the rationalized Giorgi system. The susceptibility referring to unit volume is given by $\kappa = \mu_r - 1$, that referring to unit mass by $\chi = \kappa/\rho$. The unit employed is -10^{-8} . The magnetic moment is defined by $M = v\kappa H = v\kappa\mu_0^{-1}B$; v = volume,

TABLE I. Values of the volume, mass, and molar susceptibility, unit -10^{-8} .

	$\kappa = \mu_p - 1$		χ		$\chi_M = M\chi$		C.g.s. units, meas.
	T.B.	I.A.	Average	$= \kappa/\rho$	Meas.	Calc.	Meas. — calc.
n-pentane	687.6		687.6	1.0981	79.23	78.6	+0.6
2-methyl-butane	695.0		695.0	1.1215	80.92	79.9	+1.0
n-hexane	712.1		712.1	1.0799	93.05	92.9	+0.2
2-methyl-pentane	716.9		716.9	1.0975	94.57	94.2	+0.4
3-methyl-pentane	731.7		731.7	1.1013	94.90	94.2	+0.7
2,2-dimethyl-butane	721.8		721.8	1.1118	95.80	95.5	+0.3
2,3-dimethyl-butane	735.5		735.5	1.1115	95.78	95.5	+0.3
n-heptane	730.9	731.0	731.0	1.0690	107.11	107.2	-0.1
2-methyl-hexane	734.0		734.0	1.0815	108.37	108.5	-0.1
2,2-dimethyl-pentane	735.0		735.0	1.0907	109.29	109.8	-0.5
2,3-dimethyl-pentane	762.8		762.8	1.0974	109.96	109.8	+0.2
2,4-dimethyl-pentane	738.4		738.4	1.0972	109.94	109.8	+0.2
2,2,3-trimethyl-butane	764.8		764.8	1.1081	111.03	111.1	0.0
n-octane	747.5	747.7	747.6	1.0631	121.43	121.4	0.0
3-methyl-heptane	760.2	761.7	761.0	1.0781	123.14	122.7	+0.4
2,3-dimethyl-hexane	775.1	774.1	774.6	1.0867	124.12	124.0	+0.1
3,4-dimethyl-hexane	784.7	783.4	784.1	1.0898	124.48	124.0	+0.5
2,5-dimethyl-hexane	751.0	749.2	750.1	1.0798	123.33	124.0	-0.7
2,2,3-trimethyl-pentane	786.3	787.1	786.7	1.0887	125.49	125.3	+0.2
2,2,4-trimethyl-pentane	748.3	749.0	748.7	1.0819	123.57	125.3	-1.7
n-nonane	760.5	761.7	761.1	1.0594	135.87	135.7	+0.2
n-decane	771.1	770.2	770.7	1.0555	150.18	150.0	+0.2
n-hexadecane	806.4	807.4	806.9	1.0412	235.77	235.7	+0.1
2,2,4,7,9-hexamethyl-decane	828.8	828.7	828.8	1.0628	240.66	243.5	-2.8
cyclopentane	790.4		790.4	1.0604	74.37	72.7	+1.7
methyl-cyclopentane	785.0	784.5	784.8	1.0478	88.18	88.3	-0.1
1,2- and 1,3-dimethyl-cyclopentanes	782.8	781.4	782.1	1.0406	102.17	103.9	-1.7
cyclohexane	768.1	768.7	768.4	0.9868	83.05	83.5	-0.4
methyl cyclohexane	775.8	777.6	776.7	1.0100	99.16	99.1	+0.1
ethyl-cyclohexane	794.7	794.7	794.7	1.0201	114.47	113.3	+1.1
isopropyl-cyclohexane	819.7	820.8	820.3	1.0218	128.99	128.9	+0.1
tert. butyl-cyclohexane	837.5	838.9	838.2	1.0311	144.62	144.5	+0.1
heptyl-cyclohexane	823.0	825.4	824.2	1.0158	185.22	184.7	+0.5
octyl-cyclohexane	827.9	825.3	826.6	1.0117	198.66	199.0	-0.4
decalin	856.6	855.9	856.3	0.9699	134.08	133.8	+0.3
dicyclohexyl	864.8	866.5	865.7	0.9771	162.49	162.4	+0.1
1,1-dicyclohexyl-nonane	879.8		879.8	0.9965	291.50	292.2	-0.7
perhydro anthracene	902.0		902.0	0.9540	183.48	184.1	-0.6
benzene	773.3	774.1	773.7	0.8807	68.80	67.5	+1.3
toluene	778.5		778.5	0.9017	83.07	83.1	0.0
ethyl-benzene	797.3	796.4	796.8	0.9138	97.01	97.3	-0.3
n-heptyl-benzene	820.3		820.3	0.9581	168.90	168.7	+0.2
o-xylene	809.0	809.6	809.3	0.9207	97.74	98.6	-0.9
m-xylene	784.9	782.0	783.5	0.9063	96.21	98.6	-2.4
p-xylene	781.8	782.8	782.3	0.9088	96.48	98.6	-2.2
1,3,5-trimethyl-benzene	795.8		795.8	0.9653	110.01	114.2	-4.2
1,6-diphenyl-hexane	865.5	862.9	864.2	0.9058	215.90	216.0	-0.1
1,1-diphenyl-nonane	870.7	872.1	871.4	0.9245	259.26	260.3	-1.0

The physical error in the average value of κ will be of the order of one per mil. The error in the density (<0.5 per mil) has to be added. Chemical errors such as impurities in the form of isomers have only a small effect according to the additivity rule. Assuming a relative proportion of isomers of $3 \cdot 10^{-2}$ and relative differences in the κ of $3 \cdot 10^{-2}$, their effect is one part in thousand at the most.

So for the hydrocarbons, being highly purified, the error in $\chi_M = \chi \cdot M$ will be of the order of 1.5 per mil. The other substances may have a lower purity. Their density and refractive index were observed and compared with a literature. Here the chemical error may be some per mil, the precision of χ_M 2 to 3 per mil.

Tables I and II** contain the susceptibilities, re-

** The compounds mentioned in Table I were put at our disposal by Professor H. I. Waterman and the Bataafsche Petroleum Maatschappij. (Wibaut, Hoog, Langedyk, Overhoff,

referring to the unit volume (κ), mass (χ), and kilomole (χ_M), expressed in units of the rationalized Giorgi system. The last column gives χ_M in c.g.s. units (ratio: $4\pi \cdot 10^{-8}$). All numbers have to be multiplied with -10^{-8} .

Comparison with literature shows large differences. We therefore collected the values found for 18 substances and measured by several investigators. Excepting by the author, only force methods have been used.

On comparing the values no correlation seems to exist between the precision mentioned by the authors and the deviation from the average values. In order to prevent one value from disturbing the estimate of the average, we assigned half the weight to the values lying far away from a preliminary mean. The number of these values was at the most $\frac{1}{3}$ of the total number of values. The rounded-off results are listed in Table III. In the second column the number of values of the main group with weight one is given. The largest deviation in this group from the average value is taken as a measure for the error.

The table shows directly that only for 15 substances the susceptibilities are known with a precision better than 10 per mil. Therefore the values of Table II, referring to compounds measured only once by the author, *viz.*, with the balance and probably not having the high purity of those of Table I, have been rounded off at one or two per mil. Our values differ up to 5 per mil from the averages of Table III, the average deviation being less than 2.5 per mil. In the mean our values lie 1.5 per mil below those found in literature.

II. PURE COMPOUNDS

The best expression for the susceptibility has been given by Van Vleck,² calculating the susceptibility of an assembly of independent molecules. If we omit the paramagnetic term, dependent on the temperature, then:

$$\chi_M \mu_0^{-1} = \frac{2}{3} N \sum_{n'} \frac{|m(n, n')|^2}{h\nu(n', n)} - \frac{1}{4} N \sum_i \frac{e_i^2}{m_i} \langle x_i^2 + y_i^2 \rangle_n. \quad (1)$$

Here N is the number of Avogadro, e_i and m_i are the charge and mass of the i th electron or nucleus, x_i and y_i are its coordinates in a plane perpendicular to the field. $m(n, n')$ represents the high frequency

and Smittenberg, Rec. Trav. Chim. 58, 329 (1939)) measured several other properties of these samples. The compounds in Table II from erythritol up to rhamnose were put at our disposal by Dr. J. van Alphen.

² J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932). Here the equations have been written according to the rationalized Giorgi system.

TABLE II. Values of the volume, mass, and molar susceptibility, unit -10^{-8} .

		κ	χ	$\chi_M = M\chi$			C.g.s. units, meas.
		T.B.	$=\kappa/\rho$	Meas.	Calc.	Meas. — calc.	
chloroform	CHCl_3	930	0.624	74.5			5930
carbon tetrachloride	CCl_4	868	0.544	83.7			6660
prim. propyl chloride	$\text{C}_3\text{H}_7\text{CH}_2\text{Cl}$	795	0.898	70.5	70.1	+0.4	5610
prim. <i>n</i> -butyl chloride	$\text{C}_4\text{H}_9\text{CH}_2\text{Cl}$	807	0.911	84.3	84.4	-0.1	6710
sec. <i>n</i> -butyl chloride	$\text{C}_2\text{H}_5\text{CHClCH}_3$	798	0.915	84.7	84.4	+0.3	6740
bromine	Br_2	1319	0.422	67.4			5360
methylene bromide	CH_2Br_2	1175	0.471	81.8			6510
bromoform	CHBr_3	1191	0.411	103.8			8260
ethyl bromide	$\text{C}_2\text{H}_5\text{Br}$	903	0.631	68.7	67.4	+1.3	5470
ethylene dibromide	$\text{CH}_2\text{BrCH}_2\text{Br}$	1150	0.527	99.0	99.0	0.0	7880
methylene iodide	CH_2I_2	1453	0.437	117.0	117.1	-0.1	9310
methyl alcohol	HCH_2OH	666	0.840	26.9	27.3	-0.4	2140
ethyl alcohol	$\text{CH}_3\text{CH}_2\text{OH}$	723	0.915	42.2	42.2	0.0	3360
prim. propyl alcohol	$\text{C}_3\text{H}_7\text{CH}_2\text{OH}$	760	0.945	56.8	56.5	+0.3	4520
prim. <i>n</i> -butyl alcohol	$\text{C}_4\text{H}_9\text{CH}_2\text{OH}$	768	0.948	70.3	70.7	-0.4	5590
prim. <i>n</i> -hexyl alcohol	$\text{C}_6\text{H}_{13}\text{CH}_2\text{OH}$	800	0.973	99.5	99.3	+0.2	7920
formic acid	HCOOH	662	0.543	25.0	25.3	-0.3	1990
acetic acid	CH_3COOH	698	0.665	40.0	40.2	-0.2	3180
propionic acid	$\text{C}_2\text{H}_5\text{COOH}$	731	0.736	54.6	54.5	+0.1	4350
<i>n</i> -butyric acid	$\text{C}_3\text{H}_7\text{COOH}$	752	0.785	69.2	68.7	+0.5	5510
<i>n</i> -heptoic acid	$\text{C}_6\text{H}_{13}\text{COOH}$	787	0.855	111.3	111.6	-0.3	8860
ethyl formate	HCOOC_2H_5	667	0.729	54.0	53.4	+0.6	4300
methyl acetate	$\text{CH}_3\text{COOCH}_3$	675	0.723	53.6	54.0	-0.4	4260
ethyl acetate	$\text{CH}_3\text{COOC}_2\text{H}_5$	696	0.771	68.0	68.2	-0.2	5410
iso-amyl acetate	$\text{CH}_3\text{COO}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	753	0.863	112.3	112.4	-0.1	8940
glycol	$\text{CH}_2\text{OHCH}_2\text{OH}$	877	0.784	48.7	48.6	+0.1	3880
hexamethylene glycol	$\text{CH}_2\text{OH}(\text{CH}_2)_4\text{CH}_2\text{OH}$		0.896	105.9	105.7	+0.2	8430
glycerol	$\text{CH}_2\text{OHCHOHCH}_2\text{OH}$	979	0.778	71.7	71.0	+0.7	5706
erythritol	$\text{CH}_2\text{OH}(\text{CHOH})_2\text{CH}_2\text{OH}$		0.759	92.7	93.4	(-0.7)	7380
adonitol	$\text{CH}_2\text{OH}(\text{CHOH})_3\text{CH}_2\text{OH}$		0.754	114.7	115.8	(-1.1)	9130
sorbitol	$\text{CH}_2\text{OH}(\text{CHOH})_4\text{CH}_2\text{OH}$		0.744	135.5	138.2	(-2.7)	10780
mannitol	the same		0.767	139.7	138.2	(+1.5)	11120
dulcitol	the same		0.775	141.2	138.2	(+3.0)	11240
arabinose	$\text{OCH}(\text{CHOH})_3\text{CH}_2\text{OH}$		0.718	107.7	107.0	(+0.7)	8570
xylose	the same		0.710	106.6	107.0	(-0.4)	8480
glucose	$\text{OCH}(\text{CHOH})_4\text{CH}_2\text{OH}$		0.716	129.0	129.4	(-0.4)	10260
mannose	the same		0.718	129.3	129.4	(-0.1)	10290
galactose	the same		0.719	129.5	129.4	(+0.1)	10300
fructose	$\text{CH}_2\text{OHCO}(\text{CHOH})_3\text{CH}_2\text{OH}$		0.716	129.0			10260
rhamnose	$\text{OCH}(\text{CHOH})_4\text{CH}_3$		0.760	124.6	123.0	(+1.6)	9920
acetone	CH_3COCH_3	580	0.732	42.5			3380
diethylether	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	671	0.934	69.2			5510
diethyl malonate	$\text{COOC}_2\text{H}_5\text{CH}_2\text{COOC}_2\text{H}_5$	750	0.720	115.3	115.0	+0.3	9180
allyl alcohol	$\text{CH}_2=\text{CHCH}_2\text{OH}$	679	0.794	46.1	46.1	0.0	3670
cyclohexanol	$\text{C}_6\text{H}_{11}\text{OH}$	872	0.920	92.2	91.6	+0.6	7340
phenyl chloride	$\text{C}_6\text{H}_5\text{Cl}$	860	0.777	87.4	87.6	-0.2	6960
benzyl chloride	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	890	0.806	102.1	103.2	-1.1	8120
α -naphthyl chloride	$\text{C}_{10}\text{H}_7\text{Cl}$	992	0.831	135.2	134.7	+0.5	10760
phenyl bromide	$\text{C}_6\text{H}_5\text{Br}$	936	0.625	98.2	99.1	-0.9	7810
α -naphthyl bromide	$\text{C}_{10}\text{H}_7\text{Br}$	1053	0.704	145.7	146.2	-0.5	11590
phenyl iodide	$\text{C}_6\text{H}_5\text{I}$	1038	0.567	115.6	115.6	0.0	9200
nitrobenzene	$\text{C}_6\text{H}_5\text{NO}_2$	759	0.631	77.7			6180
<i>o</i> -cresol	$\text{C}_6\text{H}_4(\text{OH})\text{CH}_3$	872	0.823	89.0	89.7	-0.7	7080
<i>m</i> - and <i>p</i> -cresol	the same	871	0.835	90.3	89.7	+0.6	7190
methyl salicylate (<i>O</i>)	$\text{C}_6\text{H}_4(\text{OH})\text{COOCH}_3$	840	0.712	108.4	107.9	+0.5	8630

TABLE III. Average values of the mass susceptibilities as found in literature. Unit -10^{-8} .

		Giorgi C.g.s.		Giorgi C.g.s.	
water		0.905	72.0	5 per mil	
2 per mil					
carbon tetrachloride	5	0.543	43.2	chloroform	5 0.625 49.7
ethyl acetate	4	0.770	61.3	propyl alcohol	4 0.944 75.1
benzene	8	0.882	70.2	butyl alcohol	4 0.949 75.5
10 to 20 per mil				acetic acid	5 0.668 53.2
acetone	8	0.736	58.6	propionic acid	2 0.737 58.7
methyl alcohol	6	0.842	67.0	n-butyric acid	4 0.789 62.8
ethyl alcohol	6	0.920	73.2	ethyl formate	2 0.729 58.0
formic acid	4	0.543	43.2	methyl acetate	3 0.720 57.3
				propyl acetate	3 0.809 64.4
				toluene	4 0.903 71.9
				nitrobenzene	6 0.630 50.1

elements of the magnetic moment occurring in the atoms and $h\nu(n', n)$ the energy difference of the two states between which a transition occurs. The first term represents a paramagnetic effect which is independent of the temperature. The effect of the nucleus on the diamagnetic term is small.

It can be proven that the paramagnetic term is zero in the case of atoms, if we take their nuclei as a zero point for the coordinates x and y . Now forming the molecules from independent atoms, we can describe the new situation by using for each atom its own nucleus as zero point, and correct the diamagnetic term for changes in the charge distribution. At the same time we add a high frequency term, which is caused by the non-central fields due to the adjoining atoms.

If these extra terms are smaller than the main effect, it is obvious that an additivity rule will be fulfilled in a first approximation. Furthermore, deviations from this rule can be expected to give us information about the structure of the molecule.

Hydrogen atoms represent the simplest case of Eq. (1). For this we find:

$$\chi_H = -\mu_0(Ne^2/2m)a_0^2 = -2.98 \cdot 10^{-8}, \quad (2)$$

in which a_0 is the radius of the smallest orbit in the classical theory of hydrogen. The size of this effect is a convenient unit for both magnetic terms in Eq. (1).

We can estimate the first term by replacing $\nu(n', n)$ by an average frequency ν_0 , for which we write with the aid of Rydberg's constant:

$$\nu_0 = \alpha R c,$$

ν_0 being, in general, of the order of the resonance frequency of hydrogen and hence α of the order of 1.

Now we can replace:

$$\sum_{n'} |m(n, n')|^2 = m^2(n, n) = (geh/4\pi m)^2 P^2(n, n),$$

where $P(n, n)$ is the angular momentum measured in units $h/2\pi$. Furthermore, we have

$$\langle x_i^2 + y_i^2 \rangle_{Av} = \frac{2}{3} \langle r_i^2 \rangle_{Av}.$$

TABLE IV. The dia, para, and total molar susceptibility of H_2 .

	Dia	Para	Total
Van Vleck (1929)	5.92	-0.64	5.28
Witmer (1942)	5.17	-0.12	5.05
Experimental			5.03
Two H atoms	5.96		5.96

Substituting this in (1) we get

$$\chi_M = \frac{1}{2} \chi_H \left[\sum_i (r_i/\alpha_0)^2 - 2g^2 P^2(n, n)/\alpha \right]. \quad (3)$$

Equation (3) has been applied for the calculation of the effect of hydrogen molecules. Here refractive data give $\alpha = 1.23$, while $g = 1$. Applying known wave functions, Van Vleck and Frank³ found the first row in Table IV. The value of Witmer⁴ agrees better with the experimental results.

For inert gases there exists a rather large difference between the calculated and measured values. This is mainly due to the fact that the largest contributions come from the outer electrons for which the calculations are less reliable. Obviously, in other cases the computations will be even more difficult.

Therefore, the main result obtainable from theory is that we can expect an additivity rule to hold while deviations due to atomic interaction occur. The latter will often reproduce for different molecules and can be introduced as separate terms. Extensive experimental investigations of Pascal⁵ first established this additivity rule.

In this section we shall consider some pure compounds, mainly hydrocarbons. After that the effects on mixing will be discussed, showing the molecular interactions, and also the application to mixtures of unknown structure.

According to the *additivity rule* the following holds:

$$\chi_M = \sum_k n_k \chi_M^k, \quad (4)$$

where n_k is the number of contributing elements of the kind k present in the molecules. In this chapter we shall try to derive the values χ_M^k which represent the separate terms in Eq. (1) and which are due to the several elements, from the experimental values of χ_M , obtained for the several compounds.

We shall start with the homologous series. The main contribution is given by the CH_2- group. In Fig. 2 we have plotted $\chi_M - n \cdot 14.3$ against n , the number of CH_2- groups present in the molecule. In a graphic representation the deviations are easily recognizable, the more so as we subtract the average

³ J. H. Van Vleck and H. Frank, Proc. Nat. Acad. Sci. **15**, 539 (1929).

⁴ E. E. Witmer, Phys. Rev. **61**, 387 (1942).

⁵ P. Pascal, see Auwers, Jahrbuch der Radio aktivitat und Elektronik **17**, 181 (1921).

effect of the CH_2 - group (14.3) and hence obtain almost horizontal lines.

The normal aliphatic compounds (a) show only small deviations from a straight line. The mean slope corresponds to a value for the CH_2 - group of 14.28, with a precision of about 2 per mil. Only *n*-pentane shows an important deviation. The other lines representing the average increment in other series of compounds, apart from *k*, were drawn parallel to this line.

On comparing compounds with an equal number of branches (b), larger deviations appear. On the basis of their magnetic behavior such compounds can be further divided into a few groups, *viz.*, with respect to the position of the branches in the chain. We shall discuss this below.

The series of cyclohexane (c) also shows deviations as regards additivity. For the higher compounds this may be due to impurities. For cyclohexane itself it can be real. In (d) compounds with 2 cyclohexane rings are represented. Benzene and its homologues (e) show a similar additivity. The values of the alcohols (f) and the acids (g) fit the drawn lines rather well. Line (h) represents the position of the values of some esters. Glycol and homologous compounds (i) show good agreement with the assumed average effect of a CH_2 - group.

Though lines with different inclination could also have been drawn, a change by 5 per mil in the CH_2 - value would already cause large deviations from the points indicated. A comparison with literature, however, shows far larger differences. For the CH_2 - group values have been found ranging from 14.28,⁶ 14.43,⁷ 14.63,⁸ 14.66,⁹ up to 14.69.¹⁰ The fact that we examine longer molecules than the other authors can partially explain why our value is among the lower ones.

Line (k) in Fig. 2 gives the results for the alcohols from glycerol up to mannitol and isomers (the average of the isomers has been used). For each CHOH -group 22.4 is subtracted. The deviations are not very large.

For calculations with *other compounds* the estimate of a mean value for a chain branching is very convenient. It appears to be about 1.3. For two branches roughly double this value is found, also on attaching the branches to the same carbon atom. Sometimes this value was already applied in the data of Fig. 2.

For a further analysis we shall distinguish between primary, secondary, tertiary, and quarternary

⁶ S. S. Bhatnagar, N. G. Mitra, and G. D. Tuli, *Phil. Mag.* **18**, 449 (1934).

⁷ B. Cabrera and H. Fahlenbrach, *Zeits. f. Physik* **85**, 568 (1933).

⁸ J. Farquharson and M. V. C. Sastri, *Trans. Faraday Soc.* **33**, 1472 (1937).

⁹ D. B. Woodbridge, *Phys. Rev.* **48**, 672 (1935).

¹⁰ W. R. Angus and W. K. Hill, *Trans. Faraday Soc.* **39**, 187 (1943).

C-atoms, depending upon the number of C-C-bonds starting from these carbon atoms. We shall use the value for a secondary C-atom in a long chain as a basis and attribute to the other C-atoms an extra effect equal to the difference with this value.

In Fig. 2 the points of intersection of the several lines with the axis of ordinate directly yield the value for the different groups. They are given in Table V. We observe that these values include both the effect of a group and a term related to the structure, so that another step has to be done in order to find the single contributions.

Considering formic acid and methylalcohol in Fig. 2, *f*, *g*, and *h*, we see that their points lie somewhat below the drawn lines. In formic acid only the COOH - group is present, connected to hydrogen, without further C-atoms. In methylalcohol there is only the CH_2OH - group and hydrogen. We shall therefore assume that these observed differences in the series *f*, *g*, and *h* account for the effect of a primary C-atom, which is 0.6 on the average. Now, also, the other values χ_M^k can be derived.

We find for H, 3.0. As has been mentioned, the calculated value for H-atoms is 2.98; half the experimental value of pure H_2 is 2.52; the contribution of

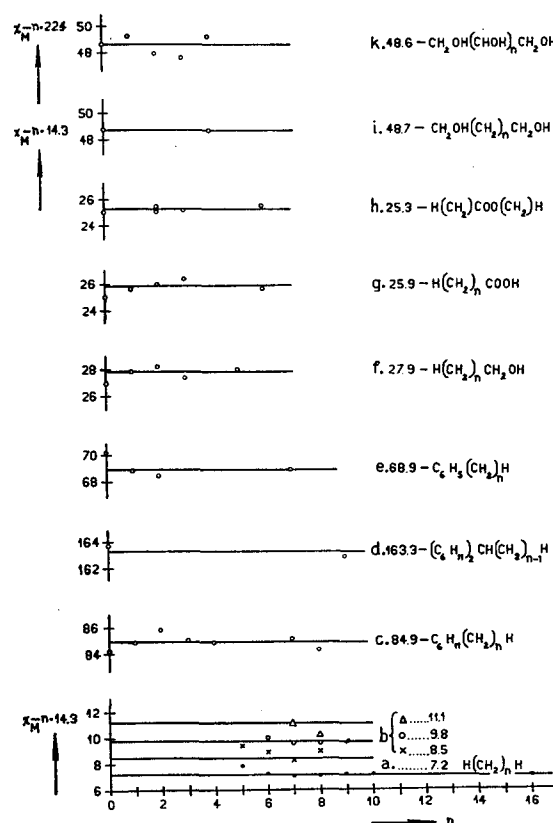


FIG. 2. The molar susceptibilities of members of homologous series are plotted *vs.* the number of carbon atoms. A constant amount is subtracted for each CH_2 - group present; the unit is $\cdot 10^{-8}$.

TABLE V. Contributions to the molar susceptibility as found in Fig. 2.

H+primary C-atom	3.6	HCH ₂ OH+primary C-atom	27.9
Chain branching	1.3	HCOOH+primary C-atom	25.9
C ₆ H ₁₂ +branch	84.9	HCOOH+prim. C-atoms (esters)	25.3
C ₆ H ₁₁ -C ₆ H ₁₁ +branch	163.3	CH ₂ OH (CH ₂ -homologs)	24.3 ⁵
C ₆ H ₆ +branch	68.9	CHOH (CHOH-homologs)	24.3
		CHOH	22.4

C is 8.3. For some sorts of pure carbon one has found $\chi_M = 7.6$. These values agree more or less.

From the average value of 1.3 for a branch there follows, after subtraction of the effect of a primary C-atom, the value of a tertiary C-atom: +0.7.

Now we can examine the saturated rings. The extra contribution due to the 6-membered ring in the cyclohexane series (Table I) appears to be -2.1. From dicyclohexyl follows 2·-2.3, from decalin 2·-2.1, and from perhydroanthracene 3·-2.4. This gives an average value of -2.2 for the 6-membered ring.

The 5-membered ring shows more irregular contributions to the magnetic effect. As an order of magnitude we can use +1.3 for the few compounds available.

Examining the homologs of benzene, we find an effect due to the ring of -0.2. For 1,6-diphenylhexane we obtain 2·-0.4, for 1,1-diphenyl-nonane 2·-0.8. Benzene itself and 1, 3, 5-trimethylbenzene give positive values. The xylenes demonstrate the large influence of the relative position of branches in the ring.

The mono-substituted compounds with Cl show fairly constant contributions for chlorine, ranging for 6 substances from 22.0 to 23.7. In chloroform and carbon tetrachloride the Cl-atoms give different effects: 21.1 and 18.8, respectively.

Bromine shows effects ranging from 33.7 to 35.9 in 4 compounds. It becomes lower when there is more Br in the molecule. For pure bromine we find 2·33.7.

The value for the COOH-group is found, considering the homologs of formic acid and the esters. The former give 22.3, the latter 21.2. We shall assume 22.3 for COOH and subtract 1.1 for esters. This means that the effect of H in CH₂ is different from that in COOH.

Examining the alcohols, we find for the CH₂OH-group 24.3; from glycerol-homologs with CH₂ substituted there follows 24.3⁵; substances with CHOH-groups substituted give 24.3. The CHOH-group then also can be derived.

For these compounds, containing electric dipoles, interaction effects occur, and the values found might depend upon the temperature. Below we shall examine this by mixing the liquids. Effects of the order of 5 per mil may occur.

Investigation of some sugar solutions suggests that the effect of stereo-isomerism probably will not

TABLE VI. Contributions by the several groups; unit -10^{-8} .

	Giorgi	C.g.s.		Giorgi	C.g.s.		Giorgi	C.g.s.
CH ₂	14.28	1136	primary C-atom	0.6	50	COOH	22.3	1770
H	3.0	238	tertiary C-atom	0.7	60	esters	-1.1	-90
C	8.28	659	double bond	(-4.4)	(-350)	CH ₂ OH	24.3	1930
Cl	23.1	1840	saturated 5-ring	(+1.3)	(+100)	CHOH	22.4	1780
Br	34.6	2750	saturated 6-ring	-2.2	-180	OCH	15.5	1230
I	51.1	4070	benzene ring	-0.2	-20			
			naphthalene ring	+7.8	+620			

exceed 10 per mil, being about the precision of measurement here.

Table VI contains the results as concerns the several contributions to the susceptibility. In Tables I and II they have been applied. The differences between the measured and calculated values of χ_M are most often smaller than 8 per mil, less than 5 per mil on the average. We omitted the calculated values of those compounds, of which the measured value had not been taken into account in the previous calculation of the group values.

Up to now we used an average value for a *branch* consisting of the effect of a primary and a tertiary C-atom. As the aliphatic hydrocarbons containing branches have been extremely purified, it has significance to extend the analysis somewhat. We have 20 hydrocarbons at our disposal and therefore can introduce some new variables.

Apart from the effect of an isolated branch (r), one can have the extra effect on attaching two primary C-atoms to the same C-atom in a chain (p_0), on attaching them to two neighboring C-atoms (p_1), and on attaching them to two atoms with one secondary in between (p_2). Furthermore, there is the extra effect of a quaternary C-atom compared with two tertiary apart (t_0), of two neighboring tertiary C-atoms (t_1) and of two tertiary C-atoms with one secondary in between (t_2).

For a definite compound we then have to count the number of times such relative positions occur. By successive approximation the unknown values can be estimated. In Table VII the results are given. The three rows with p refer to the position of the primary C-atoms, the following three (t) to the position of the tertiary C-atoms.

Using these constants we get an agreement with the measured values within 2 per mil; applying an average value for a branch alone, the differences are 4 per mil.

The two branches themselves contribute about 20 per mil to the effect. Though the gain is not large, having introduced another 5 constants, still we can expect that the data of Table VII reveal some of the peculiarities in the susceptibility of the compounds. In the calculation of χ_M as given in Table I, these data were not applied.

We also performed this analysis with the data of the Faraday effect, obtained by the author

measuring the same hydrocarbons.¹¹ Although the effects are far stronger here, the agreement is much better, compared with the application of one single value for a branch (D in Table VII). Only 3 more constants are needed here. With one constant the deviations are 25 per mil, which is roughly equal to the total effect of two branches. With 4 constants the deviation is 4 per mil only.

In the last four rows of Table VII we give the total effect of two branches placed in different positions in a long chain. In both magnetic data an oscillating effect may be seen.

III. MIXTURES

In II we investigated the susceptibilities of pure compounds. Here, we shall examine the influence of the interaction effects between the molecules. These effects can be examined in the dependence of the susceptibility upon the temperature and on melting, also by diluting a liquid with other liquids.

When there are no dipoles, association is not likely to occur, and on mixing the liquids the susceptibility will be linearly related to the concentration. When there are dipoles, non-linearities will appear on mixing, and the susceptibility will also depend upon the temperature.

We shall again apply Eq. (4), now supposing n_k to be the fraction of the k th component. For the mean molecular weight the following equation holds:

$$M = \sum_k n_k M_k, \quad (5)$$

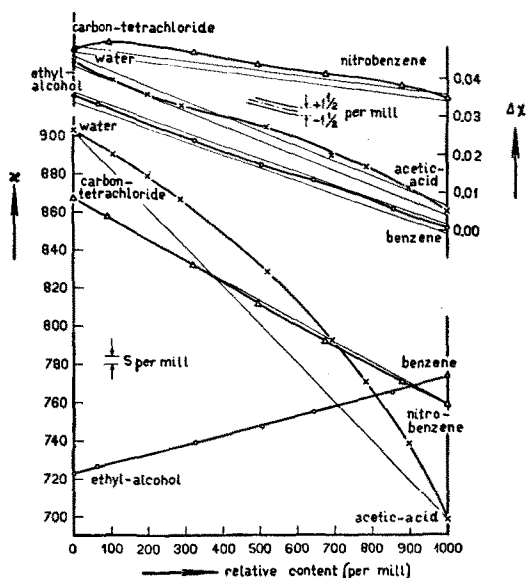


FIG. 3. The volume and mass susceptibilities of liquid mixtures, containing molecules with electric dipoles, plotted vs. the relative content of mass (in parts per thousand).

¹¹ Broersma, Waterman, Westerdyk, and Wiersma, *Physica* 10, 97 (1943).

TABLE VII. The dependence of the contributions upon the relative positions of the branches in the molecule.

		χM	D
C	r	+1.2	+2.2
XXXXX C	p_0	—	+1.45
XXXXX CC	p_1	+0.3	—
C C XXXXX	p_2	+0.1	—
X XXCXX X	t_0	-0.5	+1.1
XX XXCCXX	t_1	-0.5	-3.8
X X XXCXCXX	t_2	-0.6	—
C XXCXX C	$(r+p+t)_0$	1.9	7.0
CC XXCCXX	$(r+p+t)_1$	2.2	0.4
C C XCXCX	$(r+p+t)_2$	1.9	4.4
C C XCXCXCX	$(r+p+t)_3$	2.4	4.4

so that we easily find

$$\chi = \sum_k m_k \chi^k, \quad (6)$$

where m_k is the fraction of mass of the k th component and χ^k the susceptibility per unit mass. Hence χ is linearly related with the fraction of mass. The same follows for the susceptibility per unit volume κ and the fraction of volume v_k , provided no contraction occurs.

For the investigation mixtures were chosen of which one or both of the components contained electric dipoles, viz., ethyl alcohol-benzene, carbon tetrachloride-nitrobenzene, water-acetic acid, and water-ethyl alcohol.

In Figs. 3 and 4 the results are given. The points representing the two pure compounds have been connected by two straight lines at a distance +1.5 and -1.5 per mil from the average.

In Fig. 3, κ and $\Delta\chi$, the difference between χ and a constant value for each of the systems, both have been plotted against the relative content of mass. We see that the values for ethyl alcohol-benzene mixtures deviate less than 1 per mil from a straight line. The mixtures of carbon tetrachloride and nitrobenzene show a deviation in χ of 6 per mil. Although the κ -curve of water-acetic acid shows

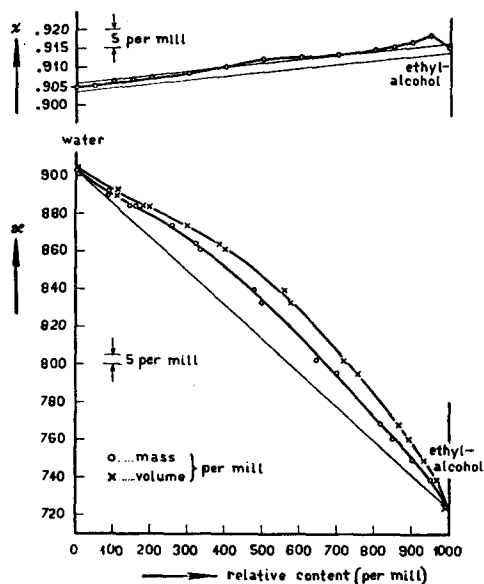


FIG. 4. The volume and mass susceptibilities of ethylalcohol-water mixtures plotted vs. the concentration (in parts per thousand).

departures up to 40 per mil from the straight line, still the χ -curve deviates no more than 4 per mil.

Figure 4 gives the volume susceptibility of water-ethyl alcohol mixtures plotted against the relative content of mass and relative content of volume. There are deviations of 25 and 40 per mil, respectively. The χ -curve, however, shows only a deviation of 5 per mil for high alcohol concentrations; for low concentrations the curve follows the straight line.

Roughly speaking, the observed maximum deviations are about 5 per mil. We can expect the effects of the interaction in pure compounds to be of this order of magnitude, which is also, as Table I and II show, the limit of the applicability of the additivity rule, using the constants of Table VI.

After this we performed measurements with 7 sets of mixtures of hydrocarbons. In Fig. 5 the measurements with the torsion balance (T.B.) and inductance apparatus (I.A.) are indicated. The following maximum deviations from the average of the values occur:

<i>n</i> -heptane— <i>n</i> -octane	0.5 per mil,
<i>n</i> -heptane—2,2,4-trimethyl-pentane	1.0 per mil,
<i>n</i> -heptane— <i>n</i> -hexadecane	1.0 per mil,
<i>n</i> -heptane—methyl-cyclohexane	1.5 per mil,
cyclohexane—methyl-cyclopentane	1.0 per mil,
cyclohexane—methyl-cyclohexane	1.5 per mil,
decalin—methyl-cyclohexane	1.0 per mil.

This means that within the precision of measurement there exists a linear relation between the susceptibility and the concentration. As no dipoles are present here and no contraction occurs, the deviations will probably be even much smaller.

The above data and results have been applied to experiments dealing with *research on mixtures of hydrocarbons*, such as oil fractions which cannot be separated by means of the normal chemical or physico-chemical methods. The range of molecular weights in these mixtures is about 150 to 350, so that the number of C-atoms present will be 10 to 25, giving the possibility of a great number of isomers.

The best description of these mixtures can be given by means of a statistical analysis.¹² The fact that the magnetic susceptibility has additive properties and is not affected by mixing makes statistical analysis a convenient tool for this purpose. Also, other physical quantities can serve for the purpose. They are needed because there are several variables, such as have been listed in Table VI. Furthermore, by means of slow chemical reactions, e.g., hydrogenation, one has been able to remove some properties without changing other aspects of the constitution—such as, e.g., saturated rings. Therefore, we shall only examine saturated hydrocarbons, consisting of carbon and hydrogen atoms, rings, and branches.

Waterman and collaborators determined already several constants for the three series: tin I (7 fractions), tin V*** (7 fractions), and tin VIII (5 fractions). The mean molecular weight is known with an accuracy of about 10 per mil, the other data within a fraction of one per mil.

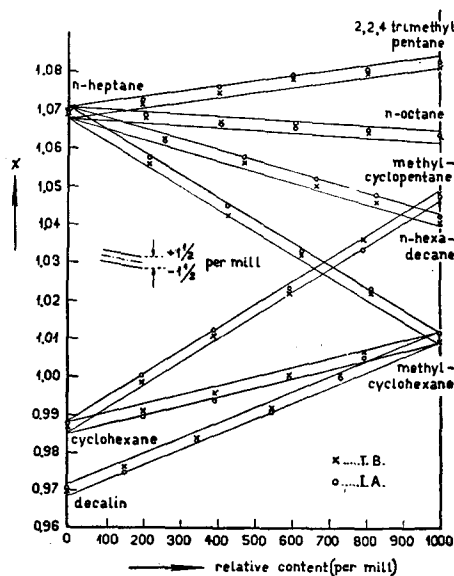


FIG. 5. The mass susceptibilities of hydrocarbon mixtures plotted vs. the relative content, showing a linear relation.

¹² Waterman, Vlugter, Van Westen, J. Inst. Petr. Tech. 21, 661, 701 (1935); Waterman, Leendertse, J. Inst. Petr. Tech. 24, 16 (1938).

*** The word "tin" refers to a sample of crude oil taken from a certain well. Here we are only interested in a comparison of the physical data of some of the fractions, obtained from three of those samples.

As the precision of M is far less than that of the other constants, we shall change the expression for the additivity rule somewhat, by using Eqs. (4) and (5). Furthermore, in connection with the valency picture, the introduction of certain elements will change the number of H-atoms. From C_nH_{2n+2} there follows $n_H = 2n_c + 2$. The introduction of double bonds, saturated rings, and the coupling of rings, will decrease n_H by 2 for each change so that

$$n_H = 2(n_c + 1 - n_k'),$$

in which n_k' indicates the number of these constitutive elements.

With these three equations n_H and n_c can be eliminated. We then obtain:

$$(\chi - A)M = B + \sum_k n_k'(\chi_k' - B) + \sum_k n_k''\chi_k'', \quad (7)$$

where

$$A = (\chi/M)CH_2 \quad \text{and} \quad B = \chi_{H_2} - M_{H_2} \cdot A. \quad (8)$$

A represents the effect of the CH_2 - group, the main element in long chains. B indicates the change in the content of hydrogen in the molecule. The property with a double prime affects the susceptibility, without changing the hydrogen content.

Formula (7) is very well adapted to our problem. The influence of the molecular weight agrees with its precision of measurement. The main effect due to the CH_2 - group is eliminated from the start, although its precise knowledge of course is necessary. Obviously the formula holds for every additive property.

The molecular refraction has been shown to be additive within a high precision, while only a small number of structural effects are of interest. The influence of the rings and other constitutional effects prove to be much smaller than the effect of the carbon and hydrogen atom itself. Applying Eq. (7), only A and B are important. If n_r is the number of rings and R_s the specific refraction, we find

$$(R_s - A_r)M = B_r(1 - n_r).$$

Waterman and collaborators carried out the analysis more empirically and were able to determine the number of rings with an accuracy of about 5 percent. Applying our formula to their published data, we get

$$(R_s - 0.3294)M = 1.50(1 - n_r).$$

The values of A and B thus found agree with the values found for pure compounds by applying Eq. (8). We find: $A = 0.3292$; $B = 1.54$.

The parachor has been investigated in the same way. According to Sugden this quantity is roughly additive and appears to be very sensitive for structural effects. Following Waterman *et al.*, the number of tertiary C-atoms can be estimated with it, as-

TABLE VIII. Structural and magnetic data of unknown hydrocarbon mixtures.

	M	n_r	n_t	n_p	κ	χ	χ_r $\chi_b = 1.3$	a_r $a_b = 2$
Tin I								
1	166	0.9	2 ^s	2 ^s	832	1.0406	+0.2	-0.2
2	185	0.9	3	3 ^s	843	1.0428	0.0	-2.4
3	201	1.0	3	3	847	1.0390	+0.2	-2.3
4	235	1.0	3 ^s	3 ^s	851	1.0378	0.0	-2.3
5	247	1.1	4	4	857	1.0373	+0.1	-2.6
6	275	1.1	4	4	862	1.0359	+0.1	-2.6
7	304	1.3	5	4 ^s	869	1.0360	+0.4	-4.1
Tin V								
1	164	0.7	2	2 ^s	819	1.0402	-0.9	+0.3
2	175	0.8	2	2 ^s	832	1.0448	+1.2	+1.2
3	199	0.9	3	3	839	1.0407	+0.2	-4.8
4	219	0.9	3 ^s	3 ^s	847	1.0391	-0.1	-4.1
5	240	1.0	4	4	852	1.0365	-1.2	-3.4
6	277	1.1	4 ^s	4 ^s	852	1.0263	-2.9	-5.7
7	300	1.3	4 ^s	4	858	1.0222	-2.2	-4.8
Tin VIII								
1	176	1.1	3	2 ^s	849	1.0327	-0.3	-1.3
2	205	1.5	4	3	872	1.0326	0.0	-2.6
3	255	1.9	5	3 ^s	888	1.0280	+0.3	-2.5
4	303	2.2	7	5				
5	351	2.6	8 ^s	5	907	1.0219	-0.5	-2.1
Effect 5-ring							(+1.3)	1.1
Effect 6-ring							-2.2	-4.0
Difference when changing χ_M or D by 1 per mil							0.2	0.2

suming a special sort of rings. The values for the constants of Eq. (7) again agree with those found with (8) from pure compounds.

After this the number of primary C-atoms can be calculated, assuming a certain molecular model (see 11, p. 124). The values for n_r , n_t , and n_p thus obtained are given in Table VIII; n_t and n_p are less precise than n_r and have been rounded off for that reason. Table VIII contains also the measured susceptibilities, χ has not been rounded off.

Now we shall have to adapt Eq. (7) to these results. This gives 18 equations of the form

$$(\chi - A)M = B(1 - n_r) - \chi_r n_r - \chi_p n_p - \chi_t n_t, \quad (9)$$

containing the variables A , B , χ_r , χ_p , and χ_t . By successive approximation these values can be estimated.

It appears that A agrees within 2 per mil with the result for the pure substances and B within 5 per mil, while the order of magnitude of the other quantities fit well.

Applying now the values found for the pure compounds, we can start with

$$(\chi - 1.018)M = 3.95(1 - n_r) + \chi_r n_r + \frac{1}{2}(n_p + n_t)\chi_b + \epsilon,$$

where $\chi_b = \chi_p + \chi_t$, while $\epsilon = \frac{1}{2}(n_t - n_p)(\chi_t - \chi_p)$ is small and can also be substituted.

Now only the constants χ_r and χ_b are left, while both 5-rings and 6-rings can occur in the mixtures.

We shall assume that the ratio n_{5r} to n_{6r} is constant for each of the tins separately. In the preliminary calculation we assumed it to be constant for all of the mixtures. We then examine the reproducibility of χ_r for the several mixtures of one tin, applying some different values for χ_b .

It appears that χ_r has a fairly constant value for the tins if $\chi_b = 1.3 \pm 0.1^5$, while then $\chi_r = +0.1$ for tin I and $\chi_r = -0.1$ for tin VIII. According to Table VII, $\chi_{6r} = -2.2$ and an average value of $\chi_{5r} = +1.3$ so that both 5-membered and 6-membered rings are present.

The author also measured the constant D , as given by the Faraday effect (see 11), and applied Eq. (7) to it. The analysis shows that the effect of the ring, a_r (last column in Table VIII), as present in the mixtures, is constant for the fractions 1-6 of tin I, and 2, 3, and 5 of tin VIII. This result agrees to that obtained with the susceptibility, although

there are differences in the relative concentration of 5-rings and 6-rings. Tin V shows irregularities for both effects; probably non-magnetic data are disturbing here.

As a result we can state that the magnetic data seem to be able to give some additional information as concerns the structure of the substances. The results for mixtures, applying also other physical constants, agree in several respects with those obtained for pure compounds.

The work described was carried out in the Laboratory for Technical Physics in the department of the late Professor E. C. Wiersma during and after the war years. His valuable criticism and guidance will always remain in my memory. The experimental problems were often discussed with Professor P. van der Leeden. The physico-chemical possibilities of the magnetic work were proposed by Professor H. I. Waterman and Professor R. Kronig.

The Ultraviolet Absorption and Luminescence of Decaborane*

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The ultraviolet absorption spectrum of decaborane in cyclohexane shows a broad absorption with a maximum molecular extinction coefficient of $3200 \pm 100A$ at wave-length $2720 \pm 50A$. The luminescence of decaborane dissolved in a glass at $77^\circ K$ shows a continuous fluorescence extending from $3630 \pm 50A$ to about $6000A$ with a broad maximum at $4520A$. No further luminescence was observed at wave-lengths shorter than $9000A$. The 0-0 transition is located at $3600 \pm 50A$. The energy levels of a particle in a rectangular, hemispherical, and spherical box were used to test the applicability of a metallic model to decaborane. Agreement with the absorption spectrum and the molecular dimensions was obtained.

THE structure of decaborane has recently been determined by x-ray analysis.¹ Silibiger and Bauer concluded that the structures inferred by extrapolation from the lighter boron hydrides² cannot be correct. Kasper, Lucht, and Harker¹ then determined the structure, and it is fundamentally different from the earlier proposals.

Decaborane may be described as a ten-atom fragment of boron metal with hydrogen atoms around the outside. Thus each boron is bound to five or six other atoms. A study of the electronic spectrum of decaborane³ is particularly interesting as a means of investigating the electronic binding associated with this structure.

* This work was supported by the ONR under contract N 7 onr-295, Task Order X as Project No. NR-058-097. This aid is gratefully acknowledged.

¹ G. Silibiger and S. H. Bauer, *J. Am. Chem. Soc.* **70**, 115-119 (1948); Kasper, Lucht, and Harker, *ibid.* **70**, 881 (1948).

² B. V. Nebrasov, *J. Gen. Chem. (U.R.S.S.)* **10**, 1021, 1156 (1940); K. S. Pitzer, *J. Am. Chem. Soc.* **67**, 1126 (1945); and other references there cited.

³ This spectrum was also of interest in connection with an attempt, so far unsuccessful, to obtain spectroscopic evidence for BH_3 in diborane at elevated temperatures.

EXPERIMENTAL RESULTS

Decaborane was prepared by heating diborane at $140-160^\circ C$ for about one hour.⁴ The product was sublimed twice into a receiver at $0^\circ C$ with rejection of very volatile and non-volatile portions. The melting point of the final product was $98.1-99.6^\circ C$ (corr); the reported melting point is $99.7^\circ C$.

The ultraviolet spectrum was taken in cyclohexane solution with a Beckmann spectrometer. Absorption was observed with a maximum molecular extinction coefficient of 3200 ± 100 at wave-length $2720 \pm 50A$. The absorption curve as observed between $2200A$ and $3700A$ is shown in Fig. 1a.⁵

The fluorescence spectrum of decaborane at the temperature of liquid nitrogen was also taken. A few

⁴ H. Schlesinger and A. B. Burg, *Chem. Rev.* **31**, 13 (1942).

⁵ The decaborane solution of highest concentration, 0.1601 m/l, as well as all fluorescence solutions were made up using a sample of decaborane (m.p. $99.3-99.6^\circ C$, corr.) kindly furnished by Dr. D. Harker, Research Laboratory, General Electric Company, Schenectady, New York. In view of the sharp melting point of this sample, it seems unlikely that the longwave tail of the absorption could be due to impurities.