

Time, min.	0	2	5	14	24
Potential	+6.9	+6.5	+6.2	+5.5	+5.0
Time, hr.	1½	4	5		
Potential	+4.0	3.3	3.0		
Time, days	5	8	11	15	
Potential	+1.74	+1.65	+1.51	+1.45	

It is apparent that the usual potentials acquired by dipping, or potentials of either sign put on by ionized air, all behave in a similar manner.

Summary

Surface potentials can be put on X or Y stearate multi-films by applying a voltage while the films are in a conducting medium as air ionized by po-

lonium. With voltage off, the films lose their charge exponentially. The coulombs represented by the area under the automatically registered discharge curve agree with Langmuir's equation which calculates potential resulting from surface charges.

The slow leakage of charge from X films left in ordinary air can be explained by the natural electrical conductivity of air.

Surface potentials were found to exist on calcium stearate X films deposited on glass.

SCHENECTADY, NEW YORK

RECEIVED JULY 8, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Magnetic Measurements on Hexaphenyldigermene

BY P. W. SELWOOD¹

The molecular weight of hexaphenyldigermene has been reported by Morgan and Drew² as 560 to 566 determined ebullioscopically in benzene. They interpret this as evidence for "no recognizable dissociation" although the value obtained is slightly lower than the molecular weight (606.8) computed for the compound.

A sample of this compound was obtained through the courtesy of Professor Warren C. Johnson of the University of Chicago.

Experimental Part

Magnetic Measurements.—The magnetic susceptibilities were measured by means of the Gouy balance previously described.³ The only modifications were (1) the use of a magnetically damped microbalance, and (2) a modified temperature control. In previous work the temperature of the sample had been maintained through careful injections of liquid air into a lead block surrounding the sample. In the present work oxygen was liquefied by passing it through a condenser surrounded by liquid nitrogen. The oxygen was then allowed to fall, drop by drop, into the lead block. Through control of the rate of flow of oxygen into the condenser, a high degree of temperature control was possible.

All measurements were referred to freshly boiled distilled water, the specific susceptibility of which was assumed to be -0.7200×10^{-6} at 20°.

Preparation of Materials.—Measurements were made on powdered hexaphenyldigermene and on a solution of the digermene in benzene. Some rather interesting experiences were encountered in preliminary tests on the powder, and are described.

(1) The author is indebted to the National Research Council for funds for the construction of a magnet, and to the National Academy of Sciences for a research grant from the Joseph Henry Fund.

(2) Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

(3) Haller and Selwood, *THIS JOURNAL*, **61**, 85 (1939).

The substance gave evidence of having a magnetic susceptibility markedly dependent on field strength. The apparent susceptibility varied from $+1.45 \times 10^{-6}$ at 1000 oersteds to -0.10×10^{-6} at 11,000 oersteds. This behavior strongly suggested the presence of a ferromagnetic impurity. The digermene was therefore recrystallized from benzene, after which the susceptibility became normal, that is, constant, from about 1000 to 17,000 oersteds. A small insoluble residue was found to contain a very few almost microscopic specks of some highly magnetic substance, presumably magnetic oxide of iron. These results are illustrated in Fig. 1 in which Δw , the apparent change in weight on application of the field, is plotted against i , the current through the magnet. While these results have no bearing on the main problem, yet they do show the extraordinary sensitivity of the magnetic method for detecting ferromagnetic impurities and the necessity for excluding iron-bearing laboratory dust from samples under investigation.

The benzene solution used in this work was prepared by shaking the powdered digermene with redistilled thiophene-free benzene. No effort was made to exclude air. The solution was analyzed by evaporating to dryness at 125° and weighing the residue. The density was determined pycnometrically.

Results

The susceptibility of the powdered hexaphenyldigermene at several temperatures is given in Table I.

These results follow the relationship $\chi = A + (C/T + \Delta)$ where χ is the susceptibility, A is the constant diamagnetic part of the susceptibility, C is the Curie constant of the paramagnetic part, T is the absolute temperature, and Δ is the "molecular field constant." In the above relationship $A = -0.47 \times 10^{-6}$ and this is believed

TABLE I

SUSCEPTIBILITY AT FIELD STRENGTH 13,100 OERSTEDS	
Temp., °C.	Susceptibility per gram, $\times 10^6$
20	-0.436
0	-.431
-20	-.423
-40	-.410
-60	-.390
-80	-.357

to be the magnetic susceptibility of undissociated hexaphenyldigermane. The Curie constant is 5.0×10^{-3} and $\Delta = -150^\circ$.

The temperature dependence of the measured susceptibility may be interpreted as evidence for slight dissociation or for the presence of a paramagnetic impurity in very small amount. If triphenylgermanium exists, it may be expected to have a molar paramagnetic susceptibility of about 1270×10^{-6} , corresponding to a single unpaired electron spin.⁴ About 1% of dissociation would then account for the results. However, this is considered improbable because the molecular field constant, Δ , would not be expected to approach -150° for such a compound having, as is likely, no orbital contribution to the susceptibility. On the other hand, molecular field constants of -150° are not unusual for such highly paramagnetic oxides as might be present as impurities to the extent of a few thousandths of a per cent.

Further, if dissociation actually takes place it may be expected to increase sharply with rise in temperature. The data do not indicate such an effect.

The measurements on the powder therefore set an upper limit of 1% as to the extent of dissociation in the solid. The weight of evidence is that no dissociation takes place.

Hexaphenyldigermane is not very soluble in benzene at room temperature. Measurements had therefore to be made as accurately as possible.

TABLE II

Field strength, oersteds	Pure benzene $\chi \times 10^6$	0.00387 <i>M</i> soln. $\chi \times 10^6$
11,450	-0.7024	-0.7017
16,080	-.7027	-.7033
17,100	-.7019	-.7018
Averages	-.7023	-.7023

(4) Van Vleck "Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932, p. 274.

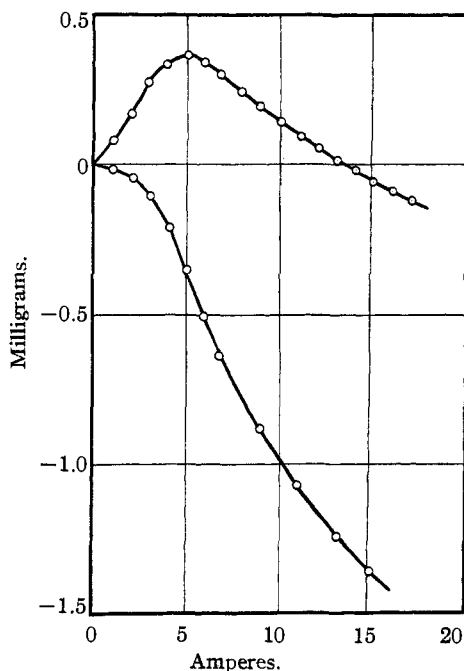


Fig. 1.—Apparent change in weight, Δw , plotted against current through magnet: upper curve, original sample; lower, recrystallized sample.

A single solution 0.00387 *M* in digermane was investigated at 25° . Measurements were made at several field strengths. The results are given in Table II.

The susceptibility of the solution, assuming no dissociation, may be calculated to be -0.7022×10^{-6} , using Wiedemann's law and the observed susceptibility of the solid. On the other hand, the susceptibility of the solution, assuming complete dissociation, may be calculated to be -0.7012×10^{-6} . It is therefore evident that nothing approaching complete dissociation takes place. It is probable that as little as 20% dissociation would have been detected.

Summary

Magnetic measurements on hexaphenyldigermane set upper limits of dissociation at 1% in the solid and 20% in a nearly saturated benzene solution at 25° . It is considered improbable that any dissociation takes place under these conditions.