

## Theory of Mixed Backbone Scrambling as Exemplified by Exchange of Chlorine and Bridging Sulfur Atoms between Dimethylgermanium and Dimethylsilicon

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*Cyclic and small linear molecules result from the scrambling of chlorine with bridging sulfur atoms between dimethylgermanium and dimethylsilicon moieties. The pertinent equilibria are treated in terms of stochastic graph theory as extended to mixed-backbone molecules. Proton nuclear magnetic resonance of the non-exchangeable methyl groups bonded to silicon and germanium atoms shows that at equilibrium in this system there is a preference for the chlorine atoms to be bonded to the silicon rather than to the germanium in the chain molecules which are in equilibrium with five different cyclic molecules.*

### Introduction

In previous publications<sup>1-3</sup> from this laboratory, the general groundwork for the study of mixed-backbone families of compounds has been developed. In those investigations, it was demonstrated for the linear halogen-terminated polydimethylgermsiloxanes at equilibrium that the chains were terminated exclusively by germanium atoms; whereas, within the chains, silicon and germanium atoms were distributed nearly statistically. Further, in those areas of composition where there were more than two chlorine atoms per dimethylgermanium group, germanium-free siloxanes were found to be dissolved in dimethyldichlorogermane which was acting as an « inert solvent » while being in equilibrium with the siloxanes with respect to exchange of chlorine (and oxygen) atoms.

In this paper, the theory of such mixed backbone families of equilibrated compounds will be developed for the case of the chloro-terminated polydimethylgermsilthianes. This particular system was chosen for study since an investigation<sup>4</sup> of the equilibria involving the exchange of methylthio groups with chlorine atoms between dimethylgermanium and dimethylsilicon showed that the chlorine atoms were preferentially bonded to the silicon. From this, we would

expect that the role of chain terminator in this family of compounds would be taken preferentially by the silicon rather than by the germanium. Further, recent investigation of cyclic germsilthianes<sup>5</sup> and of the related chlorine-terminated all-silicon<sup>6</sup> and all-germanium<sup>7</sup> families of sulfur-bridged compounds indicate that equilibrated mixtures of chloro-terminated polydimethylgermsilthianes — the subject of this study — ought to exhibit a preponderance of cyclic species, including rings exhibiting both dimethylgermanium and dimethylsilicon groups in their structure.

### Experimental Section

**A. Reagents.** Hexamethylcyclotrisilthiane,<sup>8</sup> hexamethylcyclotrigermanium trisulfide,<sup>9</sup> and dimethyldichlorogermane<sup>10,11</sup> were prepared according to methods of the literature. Dimethyldichlorosilane was purchased from Columbia Organic Chemicals Inc., Columbia S. C., and redistilled before use.

**B. Sample Preparation, Equilibration, and Measurements.** The samples were prepared by mixing in precision-bore nuclear-magnetic resonance (nmr) tubes under anhydrous conditions various proportions of A an equimolar combination of  $[(\text{CH}_3)_2\text{GeS}]_3$  and  $[(\text{CH}_3)_2\text{SiS}]_3$  with varying amounts of  $(\text{CH}_3)_2\text{SiCl}_2$  (experiments 1-7); B  $[(\text{CH}_3)_2\text{GeS}]_3$  with  $(\text{CH}_3)_2\text{SiCl}_2$  (experiments 8-14); and C  $[(\text{CH}_3)_2\text{SiS}]_3$  with  $(\text{CH}_3)_2\text{GeCl}_2$  (experiments 15-21). The samples were equilibrated directly in the sealed nmr tubes by heating at 150° for various lengths of time, until the nmr pattern did not change upon further heating.

In the prior study<sup>7</sup> of the system  $(\text{CH}_3)_2\text{GeCl}_2$ - $[(\text{CH}_3)_2\text{GeS}]_3$ , 12 hrs at 120° was found to be a satisfactory time for equilibration. However, for the system<sup>6</sup>  $(\text{CH}_3)_2\text{SiCl}_2$ - $[(\text{CH}_3)_2\text{SiS}]_3$ , it was found desirable to heat for as long as 20 d at 200°. Preliminary

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studies of the time needed to reach equilibrium in the mixed germanium-silicon system under study here bore out these findings, in that the rates of equilibration were seen to be faster in the high-germanium regions of the system than in the high-silicon regions. The data reported in Table I correspond to 150°, with 80 d of heating for samples A, 21 d for B, and 16 d for C. After quenching to room temperature, the proton nmr spectra of the neat samples (in some cases diluted with 5 parts of CCl<sub>4</sub>) were recorded immediately with a Varian A-60 spectrometer which had been modified to provide a sweep width of 25 cps for the entire scale. Nmr peak areas were determined either by electronic integration or by the technique of cutting out and weighing.

The stoichiometric and statistical calculations were performed on an IBM-7044, using computer programs developed in our laboratory.<sup>12</sup>

### Theory of Mixed-Backbone Systems

Since either of the moieties (CH<sub>3</sub>)<sub>2</sub>Si< or (CH<sub>3</sub>)<sub>2</sub>Ge< may be utilized in the backbone of the molecules making up the (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>-(CH<sub>3</sub>)<sub>2</sub>GeCl<sub>2</sub>-[(CH<sub>3</sub>)<sub>2</sub>SiS]-[(CH<sub>3</sub>)<sub>2</sub>GeS] system, the mathematical treatment of the equilibria of such a system represents an extension of our previously published theory.<sup>13</sup> The general notation and definitions of [13] are extended to mixed-backbone systems as follows<sup>3</sup>.

Consider a set of reactions at equilibria involving the exchange of parts between molecules, where the scrambled moieties may be classified as central (Q-type), bridging (Z-type), and terminal (T-type). Let the different kinds of Q moieties be denoted by Q<sup>1</sup>, Q<sup>2</sup>, . . . , where the superscripts refer to the specific type (e.g. Q<sup>1</sup> = (CH<sub>3</sub>)<sub>2</sub>Ge<, Q<sup>2</sup> = (CH<sub>3</sub>)<sub>2</sub>Si<, . . . , Q<sup>7</sup> = OP<, Q<sup>8</sup> = >Sn<, . . .). Let Z<sup>1</sup>, Z<sup>2</sup>, . . . refer to the different kinds of bridging moieties which may be present, and T<sup>1</sup>, T<sup>2</sup>, . . . to the kinds of terminal moieties. It is assumed that each terminal moiety is joined (bonded) to some Q-type moiety and each bridging moiety is joined to two distinct central moieties which may or may not be of the same kind.

Now let G refer to an environmental graph (as in ref. [13], a molecule or molecular fragment) composed of Q, Z, and T moieties with some particular moiety or join specified to be the origin, e.g. G = T<sup>1</sup>-Q<sup>1</sup>-Z<sup>2</sup>-Q<sup>2</sup>-Z<sup>1</sup>, where Z<sup>2</sup> is the origin and the dot appended to Z<sup>1</sup> indicates that the remainder of the molecule on this bond may be any allowable molecular fragment. Then the abundance of G, Z(G), is defined to be the relative number of times the origin (in this case the Z<sup>2</sup> moiety) is found with this particular environment G.

For a particular Q, Z, or T moiety M, the environmental graph composed of M as origin and all neighboring moieties joined to M is defined to be the first order of environment of M. This definition of T moiety environments agrees with [3] but differs

slightly from [13]. In general, the Θ order of environment of M is the environmental graph encompassing the (Θ-1) order environment of M and those moieties joined to this (Θ-1) environment at its border. Thus T<sup>1</sup>-Q<sup>1</sup>-Z<sup>2</sup>-Q<sup>2</sup>-Z<sup>1</sup> is a second-order environment of Z<sup>2</sup> where Q<sup>1</sup>-Z<sup>2</sup>-Q<sup>2</sup> is its first order. Similarly for an environmental graph with a join as origin, the zero-order environment of that join is the pair of moieties connected by it; and the Θ-order environment of that join is formed by encompassing the (Θ-1) order of environment and its neighboring moieties.

Since there are different kinds of Q, Z, and T moieties, the number of combinatorially distinct environments of the Q and T or of the Z moiety can now increase with each integer value of the order Θ, rather than, as in ref. [13], only with increasing odd or even values of Θ, respectively (e.g. see Table I of ref. [13]). In addition, note that the Θ-order environment of a moiety includes all (Θ-1)-order environments of the moiety's joins and is itself included in the Θ-order environment of any of these joins. Actually the Θ-order environment of a Q or Z moiety represents a structure midway between the (Θ-1)- and Θ-order environments of any of the moiety's joins, so it may equivalently be characterized as a (Θ-1/2) order of environment of a join. Thus the allowable orders of environment of a join will vary in half-integer steps, i.e., Θ = 0, 1/2, 1, 1 1/2, . . .

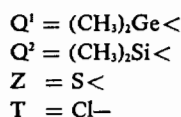
An equilibrated system of molecules has a reorganization heat order of ρ about the moiety (join) when the abundance, Z(G), of every ring-free environmental graph G which contains a ρ-th order environment of one of its moieties (joins) is the randomly expected value determined from the abundances, Z(G<sup>1</sup>), of all ring-free ρ-th order environments of the moieties (joins) and when this condition does not obtain for any order of environment smaller than ρ (see ref. [13] for the meaning of randomly expected value). By the above-mentioned principle relating orders of environments of moieties and joins, it is noted that a reorganization heat order of ρ about the moieties is equivalent to a reorganization heat order of (ρ-1/2) about the joins. Thus a reorganization heat order of an equilibrated system may be given by stating the integral or half integral value of ρ where the condition that this quantity is measured about the join can be assumed. The methods of stochastic graph theory apply only to the ring-free portion of the graphs making up the equilibrated reaction products. However, if various observed ring species are present, then the concentration of each distinct ring may be related to the concentration of specified ring-free molecules by an independent equilibrium constant. In this way, the concentration of all molecules (or graphs) of a scrambling equilibrium may be found by directly evaluating these ring-chain equilibrium constants in addition to determining, by the methods of stochastic graph theory, the concentrations of the molecules in the ring-free portion. We shall now apply this theory to the scrambling of chlorine and bridging sulfur atoms between dimethylsilicon and dimethylgermanium.

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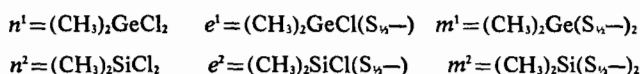
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## Application of theory

**A. Moieties, Building Units, and NMR Identification.** The moieties obtained in the system under study are the following:



The first order of environment of two Q moieties joined by a particular Z moiety overlap in the sense that they both contain this Z moiety. For stoichiometric reasons, it is convenient to associate  $\frac{1}{2}$  of this Z moiety with each Q moiety so that any molecule may be considered to be the stoichiometric sum of building units, defined as follows:



The  $n^i$ ,  $e^i$ , and  $m^i$  are termed *neso*, *end*, and *middle* building units respectively, and the superscript  $i$  refers to the condition that the building unit has a germanium ( $i=1$ ) or silicon ( $i=2$ ) central moiety. The end and middle groups are, of course, constituents of chain molecules of a range of sizes and the middle groups may also be part of various ring molecules.

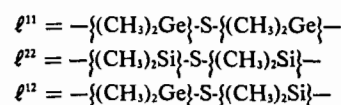
From the prior separate studies of the all-silicon<sup>6</sup> system  $\{(\text{CH}_3)_2\text{SiCl}_2 \text{ vs. } [(\text{CH}_3)_2\text{SiS}]\}$  and the all-germanium<sup>7</sup> system  $\{(\text{CH}_3)_2\text{GeCl}_2 \text{ vs. } [(\text{CH}_3)_2\text{GeS}]\}$ , it is



Figure 1. Schematic proton NMR spectrum of equilibrated mixtures in the system  $(\text{CH}_3)_2\text{SiCl}_2 - (\text{CH}_3)_2\text{GeCl}_2 - [(\text{CH}_3)_2\text{SiS}] - [(\text{CH}_3)_2\text{GeS}]$  referenced to internal tetramethylsilane.

clear that the NMR signals corresponding to the above three dimethylgermanium building units appear within a range of  $-1.17$  and  $-0.90$  ppm whereas the signals of the analogous dimethylsilicon building units lie within  $-0.77$  and  $-0.63$  ppm. This creates the fortunate situation where the range of the proton signals of the dimethylgermanium moieties does not overlap with that of the dimethylsilicon moieties. Since, as shown by the schematic spectrum in Figure 1, the signals due to the *neso* molecule, the end-group cluster, and the middle-group cluster are also fairly well separated from each other in both the  $\text{CH}_3\text{Ge}$  and  $\text{CH}_3\text{Si}$  regions, we can immediately determine the total amounts of the six kinds of building units at equilibrium. In addition, for Eqs. (15) and (23), second-order environments of the end groups are needed. As can be seen from Table I, these may be established *a priori* from the change in relative areas of the two end-group resonances in either the  $\text{CH}_3\text{Ge}$  or  $\text{CH}_3\text{Si}$  regions of the spectrum with a change in  $R' \equiv [\text{Si}]/([\text{Ge}] + [\text{Si}])$  at a constant (or nearly constant) value of  $R \equiv [\text{Cl}]/([\text{Ge}] + [\text{Si}])$ . Thus for example, from experiments 10 and 19 in Table I, it is apparent that the down-field resonance of the germanium end groups corresponds to a germanium atom as nearest neighbor while the upfield resonance corresponds to a silicon nearest neighbor. In a few cases, either of these two germanium end-group resonances could be resolved into a pair of peaks: the downfield one representing the configuration  $\text{ClGeSGeCl}$  (or  $\text{ClGeSSiCl}$ ) with the upfield one of the pair representing  $\text{ClGeSGeS}$  (or  $\text{ClGeSSiS}$ ).

**B. Chain Equilibria.** Since the exchange of bridging sulfur and chlorine on silicon taken by itself<sup>6</sup> and on germanium taken by itself<sup>7</sup> has each exhibited a reorganization heat order of unity, along with a chain equilibrium constant which is not far from the random value, we shall attempt to fit the data of the mixed system on the assumption that  $\rho = \frac{1}{2}$  rather than 1. The building units effectively represent the first-order environments of the central moieties, and it is convenient also to have a shorthand notation for the first-order environments of the bridging moiety. Thus let the linkage or bridging units be defined as follows:



Introducing these bridging units destroys the intuitively convenient principle that a molecule may be stoichiometrically decomposed into independent constituent units, and one is forced to come to grips with the heart of the stochastic graph theory approach, *i.e.* a molecule is composed by merging together, with appropriate overlapping parts, the constituent building and bridging units of the molecule.

The system under study exhibits certain simple rings in addition to the chain population. The *neso* and end units cannot participate in the ring population, however both kinds of middles and all three kinds of bridging units can occur in either chain or ring

Table I. Equilibrium Data in Mole Percentage of Building Units (i.e. Total Methyl Groups) in the System (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> vs. (CH<sub>3</sub>)<sub>2</sub>GeCl<sub>2</sub>, vs. [(CH<sub>3</sub>)<sub>2</sub>SiS] vs. [(CH<sub>3</sub>)<sub>2</sub>GeS] at 150°.

Assignment No.	-1.167		-1.117 to 1.075		-1.055 to -0.945		-0.935		-0.917		-0.900		-0.767		-0.754 to -0.738		-0.725 to -0.667		-0.717		-0.698		-0.646		-0.633				
	Meo ClO <sub>2</sub> Cl		Ends ClO <sub>2</sub> -S-Ge		Meo ClO <sub>2</sub> Cl		Ends ClO <sub>2</sub> -S-Si		Meo ClO <sub>2</sub> Cl		Ends ClO <sub>2</sub> -S-Ge		Meo ClO <sub>2</sub> Cl		Ends ClO <sub>2</sub> -S-Si		Meo ClO <sub>2</sub> Cl		Ends ClO <sub>2</sub> -S-Ge		Meo ClO <sub>2</sub> Cl		Ends ClO <sub>2</sub> -S-Si		Meo ClO <sub>2</sub> Cl		Ends ClO <sub>2</sub> -S-Ge		
1	1.549 <sup>b</sup> (1.502) <sup>c</sup>	0.887 <sup>b</sup> (0.894) <sup>c</sup>	2.3 (0.6)	1.6 (1.6)	0.1 (1.5)	1.0 (1.0)	2.9 (4.2)	3.0 (4.5)	64.7 (64.6)	2.7 <sup>f</sup> (5.2)	13.6 <sup>g</sup> (12.7)	--	--	3.9 (0.2)	1.2 (0.5)	--	--	1.2 (0.5)	--	--	--	--	--	1.6 (2.1)	1.4 (2.1)	--	--	1.6 (2.1)	1.4 (2.1)
2	1.187 (1.196)	0.798 (0.799)	1.6 (0.1)	2.4 (1.6)	1.1 (1.7)	2.7 (2.7)	7.4 (7.6)	3.0 (5.7)	50.3 (48.0)	2.9 <sup>f</sup> (4.8)	12.1 <sup>g</sup> (13.5)	--	--	4.7 (0.4)	1.1 (0.6)	--	--	1.1 (0.6)	--	--	--	--	2.1 (2.1)	3.7 (5.3)	3.0 (5.3)	--	--	3.7 (5.3)	3.0 (5.3)
3	0.968 (0.940)	0.717 (0.723)	1.6 (0.2)	2.4 (1.7)	0.4 (1.5)	4.1 (3.5)	10.0 (10.9)	7.5 (8.3)	35.9 (35.9)	2.5 <sup>f</sup> (5.2)	12.9 <sup>g</sup> (11.8)	--	--	4.5 (0.6)	1.4 (0.6)	--	--	1.4 (0.6)	--	--	--	--	2.1 (2.5)	6.4 (7.2)	5.2 (5.5)	--	--	6.4 (7.2)	5.2 (5.5)
4	0.709 <sup>b</sup> (0.729) <sup>c</sup>	0.727 (0.725)	0.8 (0.1)	1.9 (1.2)	1.0 (1.4)	6.9 (6.0)	10.9 (11.1)	3.1 (3.2)	26.2 (27.4)	3.2 <sup>f</sup> (4.6)	10.6 <sup>g</sup> (10.9)	--	--	3.1 (0.6)	2.2 <sup>h</sup> (0.7)	--	--	2.2 <sup>h</sup> (0.7)	--	--	--	--	6.7 (7.3)	10.7 (11.2)	5.3 (5.5)	--	--	10.7 (11.2)	5.3 (5.5)
5	0.452 (0.405)	0.607 (0.600)	0.5 (0.1)	2.5 (1.1)	0.5 (0.9)	6.7 (6.9)	16.3 (18.1)	11.5 (11.9)	13.7 (15.6)	2.5 <sup>f</sup> (4.1)	7.6 <sup>g</sup> (6.2)	--	--	3.3 (0.5)	3.1 <sup>h</sup> (0.4)	--	--	3.1 <sup>h</sup> (0.4)	--	--	--	--	6.2 (5.9)	12.0 (13.8)	9.6 (9.0)	--	--	12.0 (13.8)	9.6 (9.0)
6	0.265 (0.268)	0.590 (0.541)	0.2 (0.1)	1.1 (0.7)	0.2 (0.7)	8.4 (7.9)	18.8 (22.0)	15.9 (15.9)	8.9 (7.8)	1.9 <sup>f</sup> (3.6)	3.8 <sup>g</sup> (5.6)	--	--	3.5 <sup>h</sup> (0.3)	0.6 (0.3)	--	--	0.6 (0.3)	--	--	--	--	6.5 (6.4)	14.8 (15.8)	11.7 (11.1)	--	--	6.5 (6.4)	14.8 (15.8)
7	0.077 (0.096)	0.513 (0.506)	--	0.2 (0.2)	0.4 (0.5)	11.0 (9.7)	21.7 (24.5)	13.0 (15.4)	1.8 (1.8)	1.0 <sup>f</sup> (1.2)	1.1 <sup>g</sup> (1.2)	--	--	2.2 <sup>h</sup> (0.1)	1.4 (0.1)	--	--	1.4 (0.1)	--	--	--	--	8.6 (8.7)	17.5 (19.5)	14.5 (12.2)	--	--	8.6 (8.7)	17.5 (19.5)
8	1.749 (1.745)	0.874 (0.880)	2.0 (1.0)	1.8 (2.9)	--	--	--	3.0 (2.6)	72.5 (76.2)	4.1 <sup>f</sup> (5.1)	15.4 <sup>g</sup> (7.9)	--	--	5.1 (0.2)	2.2 (0.2)	--	--	5.1 (0.2)	--	--	--	--	--	--	--	--	--	--	--
9	1.464 (1.468)	0.742 (0.756)	1.3 (1.1)	3.5 (3.6)	1.4 (1.0)	--	2.6 (0.5)	11.4 (11.1)	61.8 (61.0)	3.9 <sup>f</sup> (7.5)	8.1 <sup>g</sup> (7.5)	--	--	8.1 (0.1)	2.2 (0.2)	--	--	8.1 (0.1)	--	--	--	--	--	--	--	--	--	--	--
10	1.233 (1.215)	0.646 (0.668)	1.6 (1.2)	4.3 (5.8)	1.3 (1.0)	--	3.2 (1.0)	20.1 (18.3)	47.0 (46.9)	9.6 (8.3)	3.9 <sup>h</sup> (5.6)	--	--	9.6 (0.2)	2.2 (0.2)	--	--	9.6 (0.2)	--	--	--	--	--	--	--	--	--	--	--
11	1.005 (0.981)	0.502 (0.499)	1.4 (1.1)	6.9 (5.3)	0.9 (0.9)	3.0 (0.0)	4.5 (1.8)	31.4 (50.8)	33.4 (35.3)	8.5 (7.9)	2.3 (4.0)	--	--	8.5 (0.2)	2.3 (0.2)	--	--	8.5 (0.2)	--	--	--	--	--	--	--	--	--	--	--
12	0.782 (0.788)	0.543 (0.553)	1.5 (1.1)	5.1 (2.5)	2.9 (3.5)	2.2 (0.0)	6.9 (2.4)	40.7 (42.7)	25.3 (23.1)	6.1 (6.6)	2.2 (2.1)	--	--	6.1 (0.2)	2.2 (0.2)	--	--	6.1 (0.2)	--	--	--	--	--	--	--	--	--	--	--
13	0.312 (0.467)	0.296 (0.266)	0.7 (0.9)	4.4 (1.7)	2.6 (7.3)	3.7 (0.0)	8.2 (3.0)	53.9 (54.3)	15.6 (15.3)	2.5 (4.7)	0.6 (1.0)	--	--	2.5 (0.2)	0.6 (0.2)	--	--	2.5 (0.2)	--	--	--	--	--	--	--	--	--	--	--
14	0.248 (0.170)	0.124 (0.070)	0.3 (0.4)	5.9 <sup>h</sup> (6.4)	1.9 (9.5)	5.7 (0.0)	8.2 (3.0)	85.0 (71.7)	4.5 (3.4)	1.5 (2.1)	1.5 (1.0)	--	--	4.5 (0.2)	1.5 (0.2)	--	--	4.5 (0.2)	--	--	--	--	--	--	--	--	--	--	--
15	0.281 (0.271)	0.675 (0.667)	--	0.4 (0.2)	--	0.1 (1.7)	2.7 (7.5)	71.7 (71.7)	3.4 (3.4)	1.6 <sup>f</sup> (1.6)	6.5 <sup>g</sup> (8.6)	--	--	3.4 (0.1)	1.6 (0.1)	--	--	3.4 (0.1)	--	--	--	--	--	--	--	--	--	--	--
16	0.445 (0.476)	0.772 (0.768)	0.0 (0.0)	1.1 <sup>h</sup> (0.3)	--	0.8 (0.5)	10.5 (8.3)	2.0 (2.2)	16.2 (15.6)	1.2 (1.2)	13.9 <sup>h</sup> (13.4)	--	--	16.2 (0.0)	1.2 (0.0)	--	--	16.2 (0.0)	--	--	--	--	--	--	--	--	--	--	--
17	0.715 (0.724)	0.643 (0.653)	0.7 (0.7)	2.6 <sup>h</sup> (1.8)	0.9 (2.0)	4.4 (4.4)	15.4 (15.1)	12.0 (13.0)	26.7 (22.0)	4.7 (4.7)	11.7 (11.0)	--	--	4.7 (0.2)	2.7 (0.2)	--	--	4.7 (0.2)	--	--	--	--	--	--	--	--	--	--	--
18	0.299 (0.269)	0.280 (0.271)	0.5 (1.0)	6.0 <sup>h</sup> (5.2)	1.6 (3.6)	0.6 (0.5)	8.3 (5.7)	33.0 (27.2)	35.6 (35.2)	8.1 (7.6)	0.1 (3.7)	--	--	8.1 (0.2)	1.8 (0.2)	--	--	8.1 (0.2)	--	--	--	--	--	--	--	--	--	--	--
19	1.293 (1.269)	0.385 (0.391)	10.2 (9.1)	27.2 <sup>h</sup> (24.1)	3.9 (5.3)	17.4 (14.9)	35.0 (34.9)	17.4 (14.9)	35.0 (34.9)	3.0 (3.4)	3.0 (3.5)	--	--	3.0 (0.0)	1.1 (0.0)	--	--	3.0 (0.0)	--	--	--	--	--	--	--	--	--	--	--
20	1.481 (1.474)	0.289 (0.286)	11.6 (11.5)	37.5 <sup>h</sup> (34.4)	2.8 (3.2)	3.0 (0.0)	21.6 (20.5)	21.6 (20.5)	21.6 (20.5)	2.4 <sup>h</sup> (0.9)	0.9 (0.0)	--	--	21.6 (0.0)	0.9 (0.0)	--	--	21.6 (0.0)	--	--	--	--	--	--	--	--	--	--	--
21	1.732 (1.746)	0.134 (0.135)	64.3 (58.0)	23.5 (30.5)	0.4 (1.4)	10.7 (9.9)	10.7 (9.9)	10.7 (9.9)	10.7 (9.9)	0.8 (0.2)	0.8 (0.0)	--	--	10.7 (0.0)	0.8 (0.0)	--	--	10.7 (0.0)	--	--	--	--	--	--	--	--	--	--	--

<sup>a</sup> In ppm relative to internal tetramethylsilane <sup>b</sup> Calculated from the molar data <sup>c</sup> Calculated from the molar data <sup>d</sup> Per cent of total hydrogen as determined by nmr <sup>e</sup> Computed with the equilibrium constants  $K_{Si} = 0.13$ ,  $K_{Ge} = 0.09$ ,  $K_S = 2.0 \times 10^{-3}$ ,  $K_{Si}^0 = (550/3) \text{ } \mu\text{mole, } K_{Ge}^0 = (35/3) \text{ } \mu\text{mole, } K_{Si}^0/K_{Ge}^0 = 15 \text{ } \mu\text{mole, } K_{Si}^0/K_{Ge}^0 = 0.36$ ,  $K_{Si}^0/K_{Ge}^0 = 0.35$  and  $K_S = 0.25$  <sup>f</sup> This resonance appears upfield of the one with the superscript <sup>g</sup> <sup>h</sup> This resonance appears downfield of the one with the superscript <sup>f</sup> <sup>h</sup> Two nmr peaks

molecules. Since the methods of stochastic graph theory are restricted to the ring-free population,<sup>13</sup> it is necessary to distinguish middle and bridging units in chains from those in rings. Hence let  $\bar{m}^i$  and  $\bar{\ell}^{ij}$  refer to middle and bridging units in chains and  $m^{oi}$ ,  $\ell^{oij}$  refer to those units in rings. Now if X is a bridging unit, then let  $\mathfrak{Z}(X)$  be the abundance of the first-order environment represented by this unit, with origin being the Z moiety and normalized so that total Z = 1. If X is a building unit, let  $\mathfrak{Z}(X)$  be the abundance of the first-order environment determined by the building unit (replacing  $\{Z\}_{1/2}$  by Z) normalized so that  $[\text{Si}] + [\text{Ge}] = 1 = \text{sum of abundances of all building units}$ . With these preliminaries and assuming  $\rho = 1/2$ , it is now possible, by the precepts of stochastic graph theory, to express the concentration of any chain molecule in terms of the abundances of the building and bridging units. Let  $[c]$  be the concentration of the chain molecule,  $c$ , assuming that normalization is over total Q (i.e.  $[\text{Ge}] + [\text{Si}] = 1$ ). Then for the case of all-germanium chains we have:

$$\begin{aligned} [e^i(\bar{\ell}^{11}\bar{m}^1)_{j-2}\bar{\ell}^{11}e^i] &= 1/2\mathfrak{Z}(e^i(\bar{\ell}^{11}\bar{m}^1)_{j-2}\bar{\ell}^{11}e^i) = \\ &= 1/2\mathfrak{Z}(e^i) \left\{ \frac{2\mathfrak{Z}(\bar{\ell}^{11})}{2\mathfrak{Z}(\bar{\ell}^{11}) + 3\mathfrak{Z}(\bar{\ell}^{12})} \right\}^{j-1} \cdot \left\{ \frac{2\mathfrak{Z}(\bar{m}^1)}{3(e^i) + 2\mathfrak{Z}(\bar{m}^1)} \right\}^{j-2} \\ &\quad \cdot \left\{ \frac{3(e^i)}{3(e^i) + 2\mathfrak{Z}(\bar{m}^1)} \right\} \end{aligned} \quad (1)$$

Utilizing the following stoichiometric constraint, where  $QcZ$  refers to a Q-Z environment in a chain, and  $\mathfrak{Z}(Q^1cZ)$  is normalized over total Q,

$$\begin{aligned} 3\mathfrak{Z}(\bar{\ell}^{12}) + 2\mathfrak{Z}(\bar{\ell}^{11}) &= 3(Q^1cZ) = \\ [2/(2-R)]\mathfrak{Z}(Q^1cZ) &= [2/(2-R)][3(e^i) + 2\mathfrak{Z}(\bar{m}^1)] \end{aligned} \quad (2)$$

Eq. (1) may be simplified to

$$\begin{aligned} [e^i(\bar{\ell}^{11}\bar{m}^1)_{j-2}\bar{\ell}^{11}e^i] &= \\ 2^{j-3}(2-R)^{j-1}3^j(e^i)3^{j-2}(\bar{m}^1)3^{j-1}(\bar{\ell}^{11}) &/ [3^{2j-2}(Q^1cZ)] \end{aligned} \quad (3)$$

More generally, if  $c(e_\alpha^1, e_\beta^2, \bar{m}_\delta^1, \bar{m}_\gamma^2, \bar{\ell}_i^{11}, \bar{\ell}_j^{12}, \bar{\ell}_k^{22})$  is any chain molecule of the dimethylgermsilthiane system under discussion, the composition of which is made up of  $\alpha$   $e^1$  units,  $\beta = (2-\alpha)$   $e^2$  units,  $\delta$   $\bar{m}^1$  units,  $\gamma$   $\bar{m}^2$  units,  $i$   $\bar{\ell}^{11}$  units,  $j$   $\bar{\ell}^{12}$  units, and  $k$   $\bar{\ell}^{22}$  units, then the concentration of this chain under the assumption  $\rho = 1/2$  is given by

$$\begin{aligned} [c(e_\alpha^1, e_\beta^2, \bar{m}_\delta^1, \bar{m}_\gamma^2, \bar{\ell}_i^{11}, \bar{\ell}_j^{12}, \bar{\ell}_k^{22})] &= \\ \frac{2^{\delta+\gamma-j+\alpha\beta-1}(2-R)^{i+j+k}3^\alpha(e^1)3^\beta(e^2)3^\delta(\bar{m}^1)3^\gamma(\bar{m}^2)3^i(\bar{\ell}^{11})3^j(\bar{\ell}^{12})3^k(\bar{\ell}^{22})}{3^{\delta+i+(j+\alpha)/2}(Q^1cZ)3^{\gamma+k+(j+\beta)/2}(Q^2cZ)} \end{aligned} \quad (4)$$

where in addition to Eq. (2), the following stoichiometric constraint has also been utilized:

$$3\mathfrak{Z}(\bar{\ell}^{12}) + 2\mathfrak{Z}(\bar{\ell}^{11}) = [2/(2-R)]\mathfrak{Z}(Q^1cZ) = [2/(2-R)][3(e^i) + 2\mathfrak{Z}(\bar{m}^1)] \quad (5)$$

Eq. (4) represents a special case of formula (9) of

ref. [13] when due account is taken in (9) of the presence of different kinds of central moieties.

*C. Necessary Equilibrium Constants.* From Eqs. (2), (4), and (5) it is evident that, when  $\rho = 1/2$ , determination of the abundances of the nine distinct building and bridging units suffices to prescribe the concentrations of the chain-molecule population. In general with cyclic molecules,<sup>13,14</sup> it is necessary to have an equilibrium constant for each individual molecular species. Thus if  $r$  different kinds of rings are present, then in total there are  $9+r$  abundances which are sufficient to determine the concentrations of any and all molecules in the system. In fact, fewer will suffice to determine the system since the abundances of the units are not all independent. Two stoichiometric constraints have already been described in Eqs. (2) and (5). The normalization of the system so that total Q is unity implies independence of the total volume of the system and hence gives the constraint.

$$\begin{aligned} \mathfrak{Z}(n^1) + 3(e^1) + \mathfrak{Z}(\bar{m}^1) + \mathfrak{Z}(\bar{m}^{o1}) + 3(n^2) + \\ 3(e^2) + \mathfrak{Z}(\bar{m}^2) + \mathfrak{Z}(\bar{m}^{o2}) = 1 \end{aligned} \quad (6)$$

Also there is a minimum of two composition parameters established by the ratios of starting ingredients. We choose them to be the following constraints:

$$\begin{aligned} R &\equiv [\text{Cl}]/([\text{Si}] + [\text{Ge}]) = 2\mathfrak{Z}(n^1) + 2\mathfrak{Z}(n^2) + 3(e^1) + 3(e^2) \\ R' &\equiv [\text{Si}]/([\text{Si}] + [\text{Ge}]) = 3\mathfrak{Z}(n^2) + 3(e^2) + \mathfrak{Z}(\bar{m}^2) + \mathfrak{Z}(\bar{m}^{o2}) \end{aligned} \quad (7)$$

Because of these five constraints, there are  $(4+r)$  abundances which determine the system and actually  $(4+r)$  independent equilibrium constants are needed.

Now the existence of an equilibrium constant will only be assumed for stoichiometrically balanced reactions between whole molecules. However, by utilizing Eqs. (3) and (4), « equilibrium constants between units » may be derived (see Eq. 27 of reference [13]).

*D. Unmixed-Backbone Equilibrium Constants.* For the balanced molecular reaction between the following germanium backbone chains



there is the following molecular equilibrium constant,

$$K = [n^1][e^i\bar{\ell}^{11}\bar{m}^1\bar{\ell}^{11}e^i]/[e^i\bar{\ell}^{11}e^i]^2 \quad (9)$$

Substituting eq. (3) into (9), it is observed that the following ratio of building units given by  $K_{Ge}$  must also be constant for all  $R$  and  $R'$ .

$$K_{Ge} = \mathfrak{Z}(n^1)\mathfrak{Z}(\bar{m}^1)/3^2(e^i) \quad (10)$$

Since  $K_{Ge}$  must have the same value for any Si to Ge ratio, including the ratio zero (no Si present),  $K_{Ge}$  must have the value 0.09 previously determined<sup>7</sup>

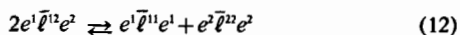
(14) R. M. Levy and J. R. Van Wazer, *J. Chem. Phys.*, **45**, 1824 (1966).

for the  $[(\text{CH}_3)_2\text{GeS}]_n - (\text{CH}_3)_2\text{GeCl}_2$  redistribution reaction. Proceeding similarly for silicon-backbone chains yields

$$K_{\text{Si}} = 3(n^2)\overline{3}(\overline{m}^2)/\overline{3}^2(e^2) \quad (11)$$

where  $K_{\text{Si}}$  has been shown<sup>6</sup> to equal 0.13. It is important to note that for  $\rho \leq 1$ , only two independent constants (e.g.  $K_{\text{Ge}}$  and  $K_{\text{Si}}$ ) can be derived from any molecular reactions based on either all-silicon or all-germanium backbones.

*E. The Linkage Equilibrium Constant.* In the molecular reaction between dimer molecules,



there is the molecular equilibrium constant,

$$K = [e^1\overline{\ell}^{11}e^1][e^2\overline{\ell}^{22}e^2]/[e^1\overline{\ell}^{12}e^2]^2 \quad (13)$$

Substituting (4) into Eq. (13) yields the result that the following ratio of bridging units given by  $K_s$  must be constant for all values of the composition parameters  $R$  and  $R'$ .

$$K_s = \frac{\overline{3}(\overline{\ell}^{11})\overline{3}(\overline{\ell}^{22})}{\overline{3}^2(\overline{\ell}^{12})} \quad (14)$$

This constant,  $K_s$ , which may also be derived from reactions other than (12), will be called a *linkage constant* as it deals with the sorting of silicon and germanium atoms about the sulfur bridges in all chains.

Highly nonrandom values of the constant  $K_s$  will affect the distribution of germanium and silicon in the mixed-backbone chains in the following way.

1.  $K_s \gg 1$ . In this case, the backbone of the chains will consist primarily of long sections of just silicon middles alternating with long sections of just germanium middles. Thus very few short-chain molecules will exhibit a mixed backbone.

2.  $K_s \ll 1$ . In this case, there will be a strong preference for an alternating silicon germanium backbone in all chains. Hence the all-silicon and all-germanium chains will primarily be just short chains.

The preceding two observations suggest the following important general principle: A highly biased preference for certain long-chain molecules need not imply that a reorganization reaction of long chains is highly dependent on the global structure of the whole molecule since this may be purely the consequence of a « neighboring atom » nonrandom bias.

From the near-random values<sup>5</sup> of the constant for the cyclic germsilthianes, it would be suspected that the value of  $K_s$  may be close to random,  $K_{s(\text{rand})} = 0.25$ . However, a highly nonrandom value would still be consistent<sup>14</sup> with the ring-ring constants previously observed, so that a separate determination of  $K_s$  is required.

The abundances of the environmental graphs appearing in Eq. (14) are difficult to determine experimentally, as they each involve a sum of poorly resolved peaks from the NMR spectrum. However, the following equation is equivalent to Eq. (14) for the order

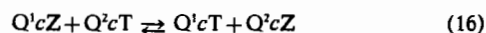
of nonrandomness we are considering, and this equation refers to the abundances of environmental graphs which are each determined from a single clearly resolved peak in the NMR spectrum.

$$K_s = \frac{\overline{3}(T-Q^2-Z-Q^2)\overline{3}(T-Q^1-Z-Q^1)}{4\overline{3}(T-Q^2-Z-Q^1)\overline{3}(T-Q^1-Z-Q^2)} \quad (15)$$

From this equation, the value  $K_s = 0.6 \pm 0.2$  was determined from the experimental data. The rather high standard deviation was not unexpected, as most determinations of  $K_s$  correspond to measurements of concentrations around 2-8% of the total ( $[\text{Ge}] + [\text{Si}]$ ). However, it is evident that no order-of-magnitude deviation from randomness has occurred, so that the random distribution of Ge and Si about S that was observed for the cyclic species appears also to hold (within experimental accuracy) for the ring-free population.

The three constants  $K_{\text{Si}}$ ,  $K_{\text{Ge}}$ , and  $K_s$  deal respectively with the constitution of the all-silicon chains, the all-germanium chains, and the mixed-backbone chains. There is still one degree of freedom remaining for the allocation of the ring-free molecular population.

*F. The Intersystem Constant.* A close examination of the scrambling reactions (8) and (12) reveals the following: These reactions are necessarily balanced in the sense that the number of each kind of Q, Z, and T moiety on each side of the reaction is the same. However, Eqs. (8) and (12) are also balanced in the sense that the total number of each kind of primary chemical bond is the same on each side of the reaction. In a mixed-backbone system with both Z and T moieties present, scrambling reactions will be possible in which the number of each kind of zero-order environments of the joins (thus the primary chemical bonds) are not preserved. This is exemplified by the following reaction between environmental graphs.

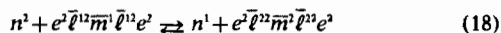


By analogy to the preceding results, it could be hoped that the expression

$$K(R, R') = \overline{3}(Q^1cT)\overline{3}(Q^2cZ)/(\overline{3}(Q^1cZ)\overline{3}(Q^2cT)) \quad (17)$$

would be constant for all values of the composition parameters  $R$  and  $R'$ . However, this is generally not the case even if  $\rho = 1/2$  is assumed. For the case  $\rho = 0$ ,  $K(R, R')$  is constant for all  $R, R'$ .

To determine a final independent equilibrium constant, let us consider a balanced molecular redistribution reaction in which the number of each kind of chemical bond is not preserved, e.g.



The molecular equilibrium constant for this reaction is

$$K = [n^1][e^2\overline{\ell}^{22}\overline{m}^2\overline{\ell}^{22}e^2]/([n^1][e^2\overline{\ell}^{12}\overline{m}^1\overline{\ell}^{12}e^2]) \quad (19)$$

Substituting Eq. (4) into Eq. (19) and collecting

terms yields the result that the following expression, denoted by  $K_I$  and called the *intersystem constant*, will be constant for all values of  $R$  and  $R'$  when  $\rho = 1/2$ .

$$K_I = \frac{3(n^1)3(\bar{m}^1)}{3(n^2)3(\bar{m}^2)} \left( \frac{23(Q^1cZ)3(\bar{\ell}^{22})}{3(Q^2cZ)3(\bar{\ell}^{12})} \right)^2 \quad (20)$$

Note that this expression for  $K_I$  does not amend itself to a simple interpretation as an equilibrium constant between units as did  $K_{Ge}$ ,  $K_{Si}$ , and  $K_s$ . Utilizing Eqs. (2) and (14)

$$\begin{aligned} 3(Q^1cZ)3(\bar{\ell}^{22})/3(\bar{\ell}^{12}) &= 3(\bar{\ell}^{22}) + 23(\bar{\ell}^{12})3(\bar{\ell}^{22})/3(\bar{\ell}^{12}) = \\ &= 3(\bar{\ell}^{22}) + 2K_s3(\bar{\ell}^{12}) \end{aligned} \quad (21)$$

Thus an alternative form for the intersystem constant is

$$K_I = \frac{3(n^1)3(\bar{m}^1)}{3(n^2)3(\bar{m}^2)} \left( \frac{4K_s3(\bar{\ell}^{12}) + 23(\bar{\ell}^{22})}{3(\bar{\ell}^{12}) + 23(\bar{\ell}^{22})} \right)^2 \quad (22)$$

Both (20) and (22) are difficult to work with experimentally since the abundances of the bridging units are not readily determined from the NMR spectra for this system. However, an equivalent form for  $K_I$  which utilizes higher-order environments for which the abundances are directly measurable can be derived as follows. Solving (10) and (11) for  $3(\bar{m}^1)$  and  $3(\bar{m}^2)$  respectively and substituting into (20) yields

$$\begin{aligned} K_I &= \frac{3^2(n^1)3^2(e^1)K_{Si}}{3^2(n^2)3^2(e^1)K_{Ge}} \left( \frac{23(Q^1cZ)3(\bar{\ell}^{22})}{3(Q^2cZ)3(\bar{\ell}^{12})} \right)^2 \\ &= \frac{K_{Si}3^2(n^1)}{K_{Ge}3^2(n^2)} \cdot \left( \frac{3(e^1) \cdot 23(\bar{\ell}^{22})/3(Q^1cZ)}{3(e^1) \cdot 3(\bar{\ell}^{12})/3(Q^2cZ)} \right)^2 \end{aligned}$$

and finally

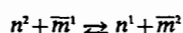
$$K_I = \frac{K_{Si}}{K_{Ge}} \left( \frac{3(n^1)3(T-Q^2-Z-Q^2)}{3(n^2)3(T-Q^1-Z-Q^1)} \right)^2 \quad (23)$$

An obvious asset of formula (23) is that it may be easily used in ring-containing systems, providing, of course, that  $K_{Si}$  and  $K_{Ge}$  are appropriately determined to correspond to their ring-free populations.

An alternative method for evaluating  $K_I$  is first to consider the expression obtained when  $K_s = K_{s(\text{rand})} = 1/4$ . In this case, from Eq. (22)

$$K_I = 3(n^1)3(\bar{m}^1)/[3(n^2)3(\bar{m}^2)] \quad \text{for } \rho = 1/2, K_s = 1/4 \quad (24)$$

Note that this expression for  $K_I$  corresponds to an equilibrium constant for the following reaction between units:



Eq. (24) is limited to the condition  $K_s = 1/4$ ; however, when  $K_s \neq 1/4$ , the behavior of the right-hand side of (24) with variation of  $R$  and  $R'$  will provide useful information for interpreting the reorganization system. Therefore let

$$K_I^*(R,R') \equiv 3(n^1)3(\bar{m}^1)/[3(n^2)3(\bar{m}^2)] \quad (25)$$

Now with  $\rho = 1/2$  and  $K_s \neq 1/4$ , Eq. (22) yields the following bounds for  $K_I(R,R')$ .

$$\begin{aligned} K_I/16K_s^2 &\leq K_I^*(R,R') \leq K_I && \text{for } K_s > 1/4 \\ K_I &\leq K_I^*(R,R') \leq K_I/16K_s^2 && \text{for } K_s < 1/4 \end{aligned} \quad (26)$$

These bounds are tight in the sense that

$$\begin{aligned} \lim_{R' \rightarrow 1} K_I^*(R,R') &= K_I \\ \lim_{R' \rightarrow 0} K_I^*(R,R') &= K_I/16K_s^2 \end{aligned} \quad \text{for any } R \quad (27)$$

Suppose the abundances  $3(n^1)$ ,  $3(n^2)$ ,  $3(\bar{m}^1)$  and  $3(\bar{m}^2)$  may be experimentally determined for various  $R, R'$ . Then Eqs. (27) represent a useful technique for determining both  $K_I$  and  $K_s$ . That is first calculate  $K_I^*(R,R')$  for all data sets  $R, R'$ . Then, if for all  $R$ , the values  $K_I^*(R,R')$  approach a constant  $\alpha$  as  $R'$  approaches 1, and similarly if  $K_I^*(R,R')$  approaches the constant  $\beta$  as  $R'$  approaches zero, then necessarily  $K_I = \alpha$  and  $K_s = (1/4)(\alpha/\beta)^{1/2}$ . The latter equation may be put in the form  $K_s = (\alpha/\beta)^{1/2} K_{s(\text{rand})}$ , from which it is observed that the constant  $K_s$  will deviate from randomness by only half as many orders of magnitude as occur in the range of values taken on by  $K_I^*(R,R')$ . Thus, if only a small variation in the values taken on by  $K_I^*(R,R')$  is observed, this is evidence that  $K_s$  is close to its random value.

Experimentally  $K_I^*(R,R')$  was evaluated from Eq. (25) over the available data points corresponding to various compositions  $R, R'$  (see Table I) and the resulting values were reasonably constant, being equal to  $(2.0 \pm 0.8) \times 10^{-3}$ .

Thus it is reasonable to conclude that  $K_s \approx K_{s(\text{rand})} = 1/4$  and that  $K_I = (2.0 \pm 0.8) \times 10^{-3}$ . Furthermore,  $K_I$  was also calculated directly from Eq. (23) and found to be  $(3.6 \pm 2.2) \times 10^{-3}$ , in agreement, within experimental error, with the preceding value calculated from Eq. (25).

The small value found for  $K_I$  indicates that there is a strong preference for dimethylgermanium moieties to be associated with bridging sulfur atoms and the dimethylsilicon moieties with the halogens at equilibrium. This is in good agreement with data from the study of the equilibria involving the exchange of methylthio sulfur<sup>4</sup> and chlorine between the same two moieties, where an actual molecular equilibrium constant of the form of Eq. (25) with the monofunctional  $\text{CH}_3\text{S}$  replacing the  $Z$  moiety had the value  $(1.02 \pm 0.27) \times 10^{-3}$ .

From Eqs. (10), (11), and (24) assuming  $K_s = 1/4$ , we may calculate additional equilibrium constants for the noncyclic part of the system, thus obtaining a better understanding of the observed preferences seen at equilibrium. Two of these derived constants are shown below, along with the reactions between environmental graphs which they represent:

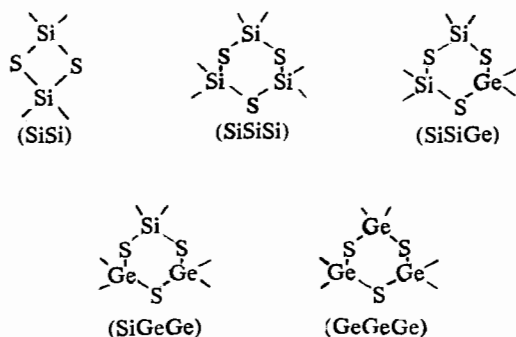
$$\begin{aligned} e^1 + \bar{m}^2 &\rightleftharpoons \bar{m}^1 + e^2 \\ K_a &= \sqrt{K_{Ge}/(K_I K_{Si})} = 18.5 \end{aligned} \quad (28)$$

$$n^1 + e^2 \rightleftharpoons e^1 + n^2$$

$$K_\beta = \sqrt{K_{Si}/(K_1 K_{Ge})} = 26.8 \quad (29)$$

The constant  $K_\alpha$  shows that there is a greater likelihood at equilibrium of the germanium appearing as a middle group and the silicon as an end group rather than vice versa. Similarly, according to the equilibrium expressed by  $K_\beta$ , there is a greater preference for the germanium to be in an end group and the silicon to form the *neso* molecule rather than the contrary. The conclusions to be drawn thus far are that the germsilthiane molecules present in equilibrium mixtures should exhibit the distinct structural feature of having silicon atoms preferred as the ends of the chains. This is most significant since, in the analogous oxygen-bridged system<sup>1</sup> (polydimethylgermsiloxanes) at equilibrium, the germanium atoms are to be found at the terminal position almost exclusively, due to the extremely *large* value of  $K_1$ . Furthermore, the preference for germanium to terminate germsiloxane chain molecules is about  $10^7$  times larger than for silicon to terminate the germsilthianes.

**G. Ring Equilibria.** Ring-chain constants determined in the independent systems of chloro-terminated polydimethylsilthianes<sup>6</sup> and polydimethylgermanium sulfides<sup>7</sup> indicate that in both cases a large portion of the middle groups are to be found as ring molecules. Therefore, ring molecules in this mixed system have to be considered in the quantitative interpretation of the equilibria, unlike in the polydimethylgermoxane system where the presence of cyclics at equilibria could be ignored within most of the composition range. In addition to all-silicon-sulfur and all-germanium-sulfur rings, there will also be present at equilibrium cyclic species containing germanium as well as silicon atoms alternating with sulfur atoms. Equilibria involving these cyclic germsilthianes<sup>8</sup> have been studied in this laboratory by proton NMR with the conclusion that the formation of the mixed-ring molecules is a nearly random statistical process; *i.e.* the controlling equilibrium constants exhibit values close to the random ones. Furthermore, it was concluded that the species present in addition to the dimeric silthiane ring consist of only trimeric cyclic molecules. The all-silicon ring, the all-germanium ring, and the two mixed rings; thus yielding a total of five different kinds of rings in the system. The presence of these rings necessitates the determination of



five more independent and ring-containing equilibrium constants in order to specify the complete molecular apportionment.

Superimposing the NMR pattern obtained from the previous ring-ring equilibrium study<sup>5</sup> [where  $R \equiv [Cl]/([Ge] + [Si]) = 0$ ] on the spectra given by the samples of this system permitted the assignment of the resonances due to middle groups in rings. In accord with this assignment, the following three molecular ring-ring equilibrium constants were determined from the experimental data, with  $(m^{02}l^{022})_3$  denoting hexamethylcyclotrisilthiane;  $(m^{02}l^{022}m^{02}l^{012}m^{01}l^{012})$  hexamethylcyclodisilthiane;  $(m^{02}l^{012}m^{01}l^{011}m^{01}l^{012})$ , hexamethylcyclodigermsilthiane; and  $(m^{01}l^{011})_3$ , hexamethylcyclotrigermanium trisulfide.

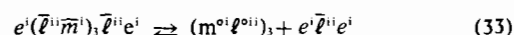
$$K_{3Si/2Si}^{00} = V[(m^{02}l^{022})_3]^2 / [(m^{02}l^{022})_2]^3 = 13 \pm 1.6 \text{ l/mole} \quad (30)$$

$$K_{SiSiGe}^{00} = \frac{[(m^{02}l^{022})_3][m^{02}l^{012}m^{01}l^{011}m^{01}l^{012}]}{[m^{02}l^{022}m^{02}l^{012}m^{01}l^{012}]^2} = 0.38 \pm 0.10 \quad (31)$$

$$K_{SiGeGe}^{00} = \frac{[(m^{01}l^{011})_3][m^{02}l^{022}m^{02}l^{012}m^{01}l^{012}]}{[m^{02}l^{012}m^{01}l^{011}m^{01}l^{012}]^2} = 0.33 \pm 0.10 \quad (32)$$

where  $V$  is the volume per mole. These constants representing the ring-ring equilibrium at  $150^\circ$  agree quite well with the ones previously determined,<sup>5</sup> confirming the fact that the amounts of the mixed trimeric rings at equilibrium correspond to a nearly random distribution ( $K_{rand} = 0.333$ ) of the  $(CH_3)_2Ge$  and  $(CH_3)_2Si$  groups in these trimeric cyclothianes.

Two more independent equilibrium constants involving rings are still needed to define the over-all system. These will be taken to be the ring-chain molecular equilibrium constants corresponding to the following reactions for trimeric cyclo-germanium ( $i=1$ ) and for trimeric cyclosilicon ( $i=2$ ) sulfide.



This reaction is volume dependent and utilizing eq. (3) yields

$$K_{30^i}^{00} = \frac{[(m^{0i}l^{0ii})_3]}{V} \left( \frac{3^i(Q^i c Z)}{2(2-R)\mathfrak{Z}(\bar{m}^i)\mathfrak{Z}(\bar{l}^{ii})} \right)^3 \quad i=1,2 \quad (34)$$

The constant  $K_{30^i}^{00}$  remains fixed for all values of the composition parameters  $R$ ,  $R'$ , so that as  $R'$  approaches unity,  $\mathfrak{Z}(Q^2) \rightarrow$  unity and  $\mathfrak{Z}(Q^2 c Z) \rightarrow (2-R)$ . Hence from the literature,<sup>6</sup>  $K_{3Si}^{00} = (550/3)$  l/mole at  $150^\circ$ ; similarly letting  $R'$  approach zero, one obtains<sup>7</sup>  $K_{3Ge}^{00} = (35/3)$  l/mole estimated for  $150^\circ$ .

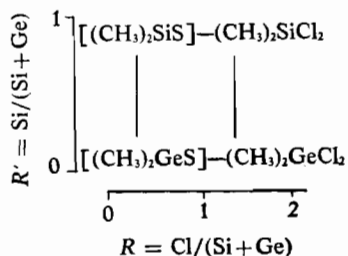
## Results and Discussion

**A. Second-Order Environments in the NMR Spectra.** Since the  $CH_3Ge$  resonances lie downfield from the  $CH_3Si$  ones, it would seem reasonable to assume that germanium in the second order of environment would cause the respective shift to be downfield as compared to the effect of silicon in the second-order environment. This hypothesis was used to make preliminary peak assignments for the chain middle groups.



These assignments and the ones made previously were checked by comparing the observed values of the various NMR peaks with the abundances of the assigned environmental graphs calculated from the nine equilibrium constants evaluated in the preceding sections. This comparison is presented in Table I.

**B. Molecular Distribution.** The system which is the subject of this study may be summarized by the following gross-composition diagram:



As shown by Table I, this system is dominated by the cyclic and *neso* molecules. Thus, at  $R = 0$  with any value of  $R'$ , nothing but cyclic species are detected. At  $R = 1$  with  $R' = 1$ , about 34% of the total Si+Ge is present as cyclic species and 37% as *neso*; at  $R = 1$  with  $R' = 0.5$ , these values are 34 and 36% respectively; and at  $R = 1$  with  $R' = 0$ , they are 14 and 24%. Including the di chains with the *neso* and ring molecules, we find that for  $R = 1$ , this group of small molecules accounts for *ca.* 93% of the total [Si]+[Ge] at  $R' = 1.0$ ; 90% at  $R' = 0.5$ ; and 75% at  $R' = 0$ .

The drastic changes which occur in the system upon complete substitution of the bridging sulfur by bridging oxygen atoms<sup>1</sup> shows up in several ways. First the sulfur-bridged system (as stated above) exhibits few linear molecules longer than the di chain; whereas rather long chains predominate for lower values

of  $R$  in the oxygen-bridged system. Because the values of  $K_1$  are strongly nonrandom (but have opposite signs in the exponent) for both the sulfur- and oxygen-bridged systems, there is a diagonal line of demarcation in the gross-composition diagram. Since  $K_1$  as written in Eq. (24) has a positive exponent for the oxygen-bridged system, this line ranges from pure  $(\text{CH}_3)_2\text{GeCl}_2$  to  $[(\text{CH}_3)_2\text{SiO}]$ ; and, because of the large numerical value of  $K_1$ , only these two species — *i.e.* unreacted mixtures of predominantly chain siloxanes plus dichlorodimethylgermane — are found on the diagonal. Because of the opposite sign of the exponent in  $K_1$  for the sulfur-bridged system, the equivalent diagonal lies at right angles to that of the oxygen-bridged system, going from  $(\text{CH}_3)_2\text{SiCl}_2$  to  $[(\text{CH}_3)_2\text{GeS}]$ . However, due to the fact that  $K_1$  does not have nearly as large an exponent magnitude as in the oxanes, we find on the diagonal not only a mixture of trimeric cyclogermthiane (due to the large ring-chain constant) plus dichlorodimethylsilane but appreciable amounts of other molecules, as shown by experiments 8-14 in Table I.

The large exponent of  $K_1$  causes the diagonal between  $(\text{CH}_3)_2\text{GeCl}_2$  and  $[(\text{CH}_3)_2\text{SiO}]$  to be a sharp dividing line between a region of germsiloxanes (with germanium predominating at the ends of the chains) and a region of germanium-free siloxanes dissolved in dichlorodimethylgermane. Because of the lower exponent magnitude of  $K_1$  in the sulfur-bridged system, the respective diagonal is not a sharp dividing line and the preference for silicon to be present at chain ends is not nearly as pronounced as is the case for germanium in the oxygen system.

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