ments to be smaller and their estimation less critical than in other approaches.

One immediate result of an identification of intuitive localized pairs with ELMO's might be the estimation of the nature of the repulsive potential for use in Gillespie's model. In this model the pair distributions (rule I above) were arrived at by considering the stable distribution of mutually repulsive points on the surface of a sphere. The repulsive potential was given the form $1/r^n$, where n was positive. The best value for n has not been clear from the empirical evidence, since for up to six points (electron pairs) the stable geometry is independent of n. However, if the position of the point represents the center of a localized orbital, two estimates of n might be made: (1) the interorbital interaction may be largely a Coulomb repulsion, in which case the appropriate value is $n = 1$; (2) a change in r could be thought to be a change in a dimension of each orbital, and, by simple analogy to a particle in a potential well, $n = 2$. In the case of seven-coordination a value between 1 and 2 corresponds to a pentagonal bipyramid (D_{5h}),[25] while higher powers of r require a C_{3v} or C_{2v} symmetry. This conclusion agrees with the known structure of IF_7.[26]

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Notes

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Formation of Polymeric $(GeF_2)_n$ in the Vapor Phase over GeF_2

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Recently the formation of gaseous dimers and trimers of SnF_2 has been reported.[1] There is evidence also for the formation of polyperfluorosilanes and possibly $(SiF_2)_n$ molecules.[2] One might therefore expect a similar behavior for GeF_2.

Gaseous GeF_2 has been formed only at high temperatures and in the presence of excess Ge metal.[3] In this work solid GeF_2, prepared by the reaction of GeF_4 + Ge at 300°,[4] was evaporated under Knudsen conditions (Cu cell) in a mass spectrometer[1] and ions corresponding to $(GeF_2)_n^+$, where $n = 1$–4, were observed over the temperature range 361–403°K. Temperatures were measured using a Pt—Pt-10% Rh thermocouple and could be controlled to ±1°. During the initial heating of the salt $GeOF_3^+$ and $GeOF_4^+$ ions were observed, and the appearance potentials of 15.6 and 13.6 ± 0.5 eV, respectively, suggest the presence of $GeOF_4$ as an impurity. Other oxyfluorides have been found to have high appearance potentials. At higher temperatures GeF_2 showed an increasing tendency to disproportionate to $GeF_4(g)$, Ge(s), and also to GeF(g).

The following appearance potentials (in eV) were recorded: Ge^+, 18.8 ± 0.3; GeF^+, $<9.1 \pm 0.2$ and 14.0 ± 0.3; GeF_2^+, 11.8 ± 0.1; $Ge_2F_4^+$, 10.6 ± 0.3; and $Ge_3F_5^+$, 15.6 ± 0.5. The critical-slope method was used to obtain the GeF_2 ionization potential.

Heats of sublimation and vaporization for GeF_2 and $(GeF_2)_2$ were obtained from Clausius–Clapeyron plots (Figure 1) over the temperature range 335–365°K. Pressures were calculated from the usual relation $P = kI^+T$, where I^+ is the ion intensity signal in arbitrary units and k was determined by a silver calibration. No estimation of relative ionization cross section or multiplier efficiencies was made, so the calculated pressures are considered accurate only to within a factor of 2. At 361°K the following pressures (in mm) were found: GeF_2, 4.4×10^{-4}; $(GeF_2)_2$, 4.0×10^{-5}; $(GeF_2)_3$, 1.6×10^{-6}; and $(GeF_2)_4$, $\lesssim 2.7 \times 10^{-7}$. Table I presents a summary of the thermodynamic properties of these molecules.

The entropy decrease of 51 ± 2 eu for the dimerization of GeF_2 is comparable with a value of 45.5 ± 2 eu found for the SnF_2 case.[1] The entropy change for reaction 4 (Table I) was estimated from that for the analogous SnF_2 reaction and the enthalpy change was then calculated using the measured free energy change. This enthalpy is not significantly different from the value found for SnF_2 association processes.

Several possible structures may be postulated for the polymers, *e.g.*, by analogy with the tetrafluoroethylene structure, $F_2C{=}CF_2$ for dimers with cyclic trimers and tetramers, or by analogy with the halogen-bridged $(BeF_2)_2$ or $(MgF_2)_2$ structures.[5,6] However the former

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[1] K. Zmbov, J. W. Hastie, and J. L. Margrave, in press.

[2] (a) A. S. Kana'an and J. L. Margrave, *Inorg. Chem.*, **3**, 1037 (1964); (b) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.*, **87**, 2824 (1965).

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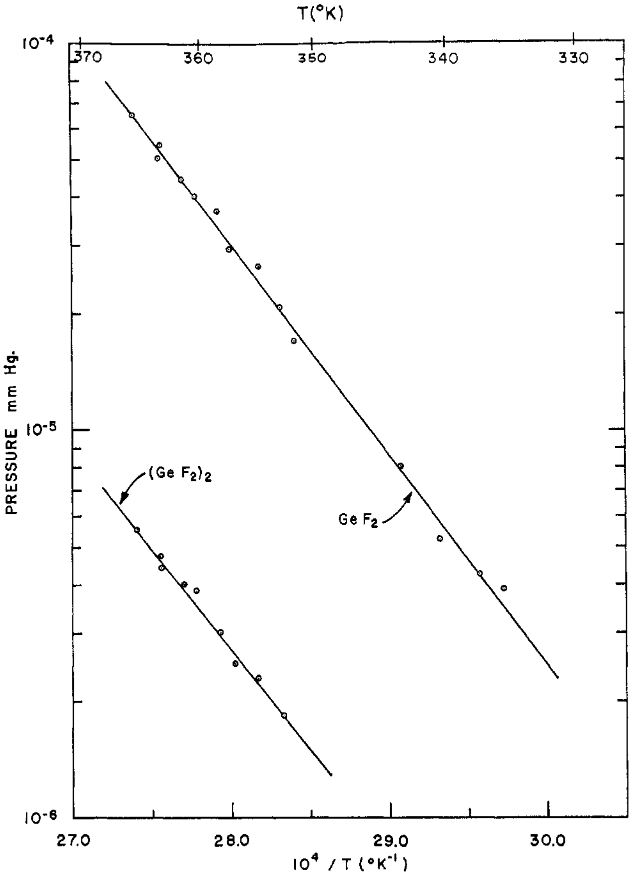

Figure 1.—Variation of GeF_2 monomer and dimer pressures as a function of temperature.

TABLE I

THERMODYNAMIC DATA FOR REACTIONS OF $(GeF_2)_n$

	Reaction	$\Delta H°_{361}$, kcal/mole	$\Delta G°_{361}$, kcal/mole	$\Delta S°_{361}$, eu
1.	$GeF_2(s) \rightarrow GeF_2(g)$	27.0 ± 1	10.4 ± 0.5	46 ± 3
2.	$2GeF_2(s) \rightarrow (GeF_2)_2(g)$	27.0 ± 1	12.1 ± 0.6	41 ± 3
3.	$2GeF_2(g) \rightarrow (GeF_2)_2(g)$	−27.0 ± 1	−8.6 ± 1	−51 ± 2
4.	$GeF_2(g) + (GeF_2)_2(g) \rightarrow (GeF_2)_3(g)$	−24 ± 3	−9.7 ± 1.5	−40 ± 5

possibility seems to be unlikely as a Ge–Ge bond is reported to be stronger than an Sn–Sn bond[7] but the stabilities of the dimers are found to be the reverse. The structure of the solid,[4] for which the unit cell is $(GeF_2)_4$, is also thought to involve a pseudo-tetrahedral arrangement about Ge with a tendency to form chains. Thus the latter type of structure seems very feasible.

If the decreasing stability trend from $(SnF_2)_2$ to $(GeF_2)_2$ continues to $(SiF_2)_2$ one can understand more readily the current lack of conclusive evidence for $(SiF_2)_n$ polymers in the vapor phase, particularly at higher temperatures.[3]

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Monosubstituted Derivatives of Tetracobalt Dodecacarbonyl

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Tetracobalt dodecacarbonyl has both bridge and terminal CO groups.[1] Substitution of two bridging carbonyls by a bidentate ligand, such as an acetylenic compound, has been reported by Krüerke and Hübel;[2] the general formula of these compounds is $Co_4(CO)_{10}(RC_2R')$.

We wish to report the preparation of some new derivatives of $Co_4(CO)_{12}$ by the reaction

$$Co_4(CO)_{12} + L \rightleftarrows Co_4(CO)_{11}L + CO \qquad (1)$$

where L $[= P(C_6H_5)_3,\ As(C_6H_5)_3,\ \text{or}\ Sb(C_6H_5)_3]$ can displace one of the terminal CO groups.

The same reaction had already been carried out by Hieber and Breu.[3] Using more drastic experimental conditions than ours, they obtained the compound $[Co(CO)_3P(C_6H_5)_3]_2$ from $Co_4(CO)_{12}$ and $P(C_6H_5)_3$.

We employed petroleum ether (bp 40–70°) as solvent at room temperature and found that, with $P(C_6H_5)_3$, (1) was shifted completely to the right whereas with $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ equilibrium was soon reached with 70–80% of the start carbonyl still present. As a proof of this, gaseous CO was bubbled through solutions of $Co_4(CO)_{11}L$. With $L = As(C_6H_5)_3$ or $Sb(C_6H_5)_3$, $Co_4(CO)_{12}$ formed but not with $L = P(C_6H_5)_3$. In no case, however, did other carbonyl derivatives form, in particular, polysubstituted derivatives of $Co_4(CO)_{12}$.

Separation of the derivatives from unreacted $Co_4(CO)_{12}$ was accomplished by thin layer chromatography and by further crystallization from *n*-heptane. All of the compounds were obtained as dark brown crystals, relatively stable to air, insoluble in water but soluble in organic solvents such as *n*-heptane, benzene, CCl_4, etc. The brown solutions were found to be as air sensitive as those of $Co_4(CO)_{12}$. The infrared spectra (Table I) show bands in the CO stretching region at 2000–2100 cm^{-1} (terminal CO) and 1800–1900 cm^{-1} (bridging CO) and in the phenyl CH bending out of the plane region at 600–800 cm^{-1}. Figure 1 shows the spectrum of $Co_4(CO)_{11}P(C_6H_5)_3$ in *n*-heptane. The molecular weight determinations carried out in benzene (Mechrolab osmometer) on these compounds are in agreement with the $Co_4(CO)_{11}L$ formulation.

The compounds obtained would appear to be the first known $Co_4(CO)_{12}$ derivatives in which a monodentate ligand replaces a terminal CO group and, in all

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