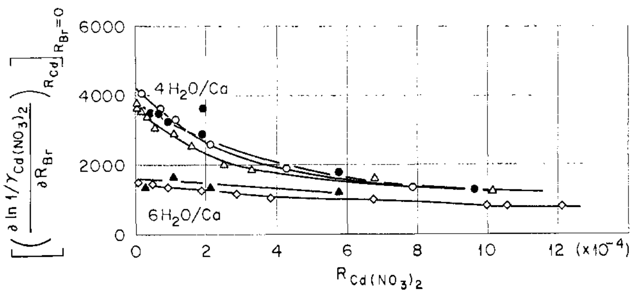

Figure 2.—Evaluation of thermodynamic association constants (at 50°) for $CdBr^+$ in the solvents $KNO_3 + Ca(NO_3)_2 + H_2O$ by graphical extrapolation to infinite dilution of both Cd^{2+} and Br^- of the slopes $[\partial \ln (1/\gamma_{Cd(NO_3)_2})/\partial R_{KBr}]_{R_{Cd(NO_3)_2}}$: △, $Ca(NO_3)_2 \cdot 4H_2O$; ●, $Ca(NO_3)_2 \cdot 4H_2O + 0.5KNO_3$; ○, $Ca(NO_3)_2 \cdot 4H_2O + 1KNO_3$; ▲, $Ca(NO_3)_2 \cdot 6H_2O$; ◇, $Ca(NO_3)_2 \cdot 6H_2O + 0.5KNO_3$.

TABLE I

ASSOCIATION CONSTANTS IN THE MIXTURES $Ca(NO_3)_2 + KNO_3 + H_2O$ at 50° for $Cd^{2+} + Br^- = CdBr^+$ (K_{CdBr^+})

K_{CdBr^+}	Mol of H_2O/mol of Ca^{2+}	Mol of K^+/mol of Ca^{2+}	Mol of H_2O/mol of cation	Mol of H_2O/mol of nitrate
1550	6	0	6	3
1460	6	0.5	4	2.4
3900[a]	4	0	4	2
3880	4	0.5	2.67	1.6
4250	4	1	2	1.33

[a] Reference 7.

Discussion

The principal observation, from Table I and Figure 2, is that, within the experimental error of 5–10%, the association constants appear to depend primarily on the ratio of water to calcium ion (4 or 6) and are virtually independent of the ratio of water to nitrate ion or of the ratio of potassium ion to calcium ion. We have reported similar behavior for partial molar volumes[6] and solute diffusion coefficients.[5] The partial molar volume, at 100°, of $Ca(NO_3)_2 \cdot 4H_2O$ in mixtures with up to 60 mol % potassium nitrate is constant and equal to the molar volume of pure $Ca(NO_3)_2 \cdot 4H_2O$.[6] The polarographic diffusion coefficient of cadmium ion in these mixtures also is independent of the concentration of added potassium nitrate.[5] Pmr studies have shown that, at temperatures up to 100°, the addition of KNO_3 to $Ca(NO_3)_2 \cdot 2H_2O$ does not affect the chemical shift.[10] It therefore may seem reasonable to consider these mixtures to be constituted of K^+, NO_3^-, and $Ca(H_2O)_6{}^{2+}$ or $Ca(H_2O)_4{}^{2+}$, *i.e.*, as analogs of molten salts of weak-field cations.[11]

Raman and infrared spectral studies of concentrated aqueous calcium nitrate solutions, however, have been interpreted in terms of the formation of contact ion pairs $CaNO_3{}^+$.[12] This is not necessarily inconsistent with the thermodynamic and nmr results for the melts with a water to calcium ion ratio of 4:1, since the water molecules could all be bound to the divalent ions and still leave sites in the coordination sphere of the calcium ions for Ca^{2+}–NO_3^- contacts. It is more difficult to reconcile Ca^{2+}–NO_3^- contacts with hexahydrated calcium ions in the melts with higher water contents. Extension of structural as well as thermodynamic studies through this concentration region are needed to elucidate the ion–ion and ion–water interactions in the hydrate melts.

It is clear that when the water content of these mixtures is reduced below that required to form complete hydration shells about the cations, the behavior must approach that of molten salts, with competition between water and anions for sites adjacent to the cations.[3a]

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Thermal Reaction of Silane with Hydrogen Chloride

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Silane and hydrogen chloride react at 100° in the presence of aluminum chloride to produce the chlorosilanes, while no reaction occurs in the absence of a catalyst even at 200°.[1] Purnell and Walsh[2] have demonstrated that the pyrolysis of silane over a silicon mirror is homogeneous at 375°. Further, their results were most consistent with the mechanism

$$SiH_4 \longrightarrow SiH_2 + H_2 \qquad (1)$$

$$SiH_2 + SiH_4 \longrightarrow Si_2H_6 \qquad (2)$$

We have examined the reactions of silane–hydrogen chloride mixtures at 362°. The reaction was very surface dependent. In an uncoated Pyrex reaction vessel, the major products were the three chlorosilanes with little disilane being formed. With silane-d_4 and hydrogen chloride, the products were chlorosilane-d_3, dichlorosilane-d_2, and disilane-d_6. When the reaction vessel was coated with a silicon mirror, the over-all reaction was slower and the disilane to chlorosilanes ratio greatly was increased. These results demonstrate the following points: (1) the thermal reaction between silane and hydrogen chloride is catalyzed by Pyrex to form the chlorosilanes; (2) this catalyzed reaction does not involve silene insertion into hydrogen chloride; (3) if silene is formed during the silane pyrolysis, the insertion of silene into silane is much faster than the insertion into hydrogen chloride.

Experimental Section

Silane was prepared by the lithium aluminum hydride reduction of silicon tetrachloride and treated with water to remove hydro-

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gen chloride. The silane was then distilled through a trap cooled to −160°. The high-pressure (about 400 mm) infrared spectrum of the silane demonstrated that no hydrogen chloride was present.[3,4]

The thermal reactions were carried out in a 21-cm long cylindrical vessel of 1.5-cm radius surrounded by a heating tape and asbestos with a thermometer inserted between the tape and the vessel.

1. **Preparation of Chlorosilane-d_3.**—Chlorosilane-d_3 was prepared from the reaction of silane-d_4 and silver chloride as described for the reaction between silane and silver chloride.[5] The infrared spectrum of $ClSiD_3$ [1600 (s), 702 (vs), 540 (m) cm^{-1}] demonstrated that both silane-d_4[6] and dideuteriodichlorosilane[7] were absent. A mass spectrum of our sample confirmed that the compound was chlorosilane-d_3 and that the dichloro derivative was absent.

2. **Thermal Reaction of SiH_4 with HCl (362°).**—a. Silane (1.24 mmol) and hydrogen chloride (1.23 mmol) were allowed to react at 362° for 1 hr. The volatile fraction was then separated by trap to trap distillation. The fraction condensed in the −196° trap (1.62 mmol) was identified by an infrared spectrum to be a mixture of silane and hydrogen chloride. The fraction condensed in the −160° trap (0.065 mmol) was identified by an infrared spectrum and a mass spectrum to be a mixture of chlorosilane[8] and disilane[9] with $ClSiH_3:Si_2H_6 > 5:1$. The fraction condensed at −130° (0.17 mmol) was identified by an infrared spectrum and a mass spectrum to be primarily trichlorosilane[10] with some dichlorosilane.[11]

b. The inside of the reaction vessel was coated with silicon by the decomposition of 1 mmol of silane. Silane and hydrogen chloride (1.25 mmol each) were again allowed to react for 1 hr at 362°. For this run, the silane–hydrogen chloride fraction recovered was 2.26 mmol. The fraction condensed at −160° (0.032 mmol) was again a mixture of chlorosilane and disilane with $ClSiH_3:Si_2H_6 < 1:5$. No higher chlorosilanes were observed.

c. The inside of the reaction vessel was further coated by four decompositions (1 mmol each) of silane. Silane and hydrogen chloride (1.25 mmol each) were again allowed to react at 362°. The fraction condensed at −160° (0.043 mmol) consisted of disilane with some trisilane and at most a trace of chlorosilane. Nothing had condensed in the −130° trap.

3. **Thermal Reaction of SiD_4 with HCl.**—Silane-d_4 (1.24 mmol) and hydrogen chloride (1.24 mmol) were allowed to react in an uncoated reaction vessel at 360° for 1 hr. The fraction condensed at −196° (2.31 mmol) was a mixture of silane-d_4 and hydrogen chloride. The fraction condensed at −160° (0.023 mmol) was identified by an infrared spectrum to be a mixture of chlorosilane-d_3 and disilane-d_6 with a $ClSiD_3:Si_2D_6$ ratio of about 2. The fraction condensed at −130° (0.01 mmol) was identified by an infrared spectrum to be dichlorosilane-d_2. The silane-d_4 used in these experiments had as an impurity a very small amount of silane-d_3. The ratio of the intensity in the Si–H region ($\sim$2180 cm^{-1}) compared to the intensity in the Si–D region (1600 cm^{-1}) was the same for the starting (silane-d_4 and silane-d_3) mixture and for the deuteriosilanes in the product fractions.

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Proton Magnetic Resonance Spectrum of Diammineplatinum(II) Perchlorate in Dimethyl Sulfoxide

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Complexes of some transition metal and actinide ions with dimethyl sulfoxide (DMSO) as a ligand exhibit metal–DMSO bonding through the sulfur atom in the solid phase. Infrared[1-3] and X-ray[4] studies of *trans*-$PdCl_2 \cdot 2DMSO$, infrared studies of $PtCl_2 \cdot 2DMSO$[2] and of $PtCl_2 \cdot x DMSO$,[3] X-ray studies of *cis*-$Pd(NO_3)_2 \cdot 2DMSO$[5] and of $(C_{15}H_{13}O)IrCl_2 \cdot 2DMSO$,[6] and the color of $[Rh(OAc)_2]_2 \cdot 2DMSO$[7] have shown or indicate that metal–sulfur bonding occurs. Although it is likely that the metal–sulfur bonding is retained when the complex is dissolved (if DMSO is retained as a ligand), there are no studies of solutions to support this expectation at present. Indeed, some studies indicate that changes from metal–oxygen to metal–sulfur bonding can occur when the composition of the compound is altered. Presumably the opposite change could also occur in some cases. For example, infrared studies of $Th(ClO_4)_4 \cdot 12DMSO$[8] and of $UO_2(ClO_4)_2 \cdot 5DMSO$[9] indicate that there are two types of DMSO in these compounds, namely, lattice DMSO and coordinated DMSO. The latter is bound to the metal through the oxygen atom. When the complexes are heated to drive off the lattice DMSO, the compounds $Th(ClO_4)_4 \cdot 6DMSO$ and $UO_2(ClO_4)_2 \cdot 4DMSO$ are formed. In these, lattice DMSO is absent and the infrared spectra indicate metal–sulfur rather than metal–oxygen bonding. In this note we report the results of pmr studies of DMSO solutions of $Pt(NH_3)_2(ClO_4)_2$.

Results and Discussion

The pmr spectrum, taken with an A-60 spectrometer equipped with a Hewlett-Packard 373 A counter, of *cis*-diammineplatinum(II) perchlorate dissolved in DMSO showed three different kinds of protons: those in the free, unbound DMSO, those in coordinated DMSO, and those in the coördinated ammonia molecules. The bound-DMSO proton absorption was a triplet with 1:4:1 intensity ratio. The center peak of this triplet was due to the methyl protons of DMSO bound to

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