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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

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To cite this Article Gut, Rudolf and Rueede, Jürg(1978) 'REACTIONS OF THE SILVER ION IN LIQUID ANHYDROUS HYDROGEN FLUORIDE', *Journal of Coordination Chemistry*, 8: 1, 47 – 53

To link to this Article: DOI: 10.1080/00958977808073069

URL: <http://dx.doi.org/10.1080/00958977808073069>

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REACTIONS OF THE SILVER ION IN LIQUID ANHYDROUS HYDROGEN FLUORIDE

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(Received October 17, 1977)

The silver electrode permits investigations of precipitation and complex-formation reactions in liquid anhydrous hydrogen fluoride (AHF) by potentiometric titrations using AgF solutions as titrants. The weaker solvation of the silver ion by HF relative to H₂O accounts for the low solubility in AHF of salts like AgTaF₆, AgSbF₆ etc., as well as the formation of the sparingly soluble silver halides and silver sulfide. The complexes Ag(PH₃)⁺ and Ag(PH₃)₂⁺ are formed from Ag⁺ and PH₃⁺ in AHF. The formation of Ag(AsH₃)₂⁺ is observed on titration of AsH₃, and with HCN the well known Ag(HCN)₂⁺ complex is obtained. Carbon monoxide and PF₃ form weak 1:1 complexes with Ag⁺. In the presence of AgCl and HCl the silver electrode acts as a fluoride ion electrode which served for the investigation of fluoro-complex formation of NbF₅ and TaF₅ with fluoride ion. The difference between the standard potentials E°_{Ag/Ag⁺} and E°_{H₂/H⁺}(1M F⁻) was re-determined.

INTRODUCTION

The chemistry of silver in anhydrous hydrogen fluoride has many peculiar features. Thus AgF is extremely soluble and a strong electrolyte in AHF, and its high solubility is enhanced still further by the addition of arenes such as benzene, tetraline etc., indicating the formation of silver-arene complexes.^{1,2} Such silver fluorometallates as AgTaF₆ and AgSbF₆, which are formed in AHF from AgF and the corresponding fluoride, are astonishingly insoluble in this solvent, but show great solubility in water. The compounds Ag₂S, AgCl, AgBr and AgI are insoluble in AHF even though the anions exist in this solvent only in the protonated states HX and H₂S. Silver cyanide and Ag(CN)₂⁻ are not decomposed by this highly acidic medium but are protonated; AgHCN⁺ and Ag(HCN)₂⁺ are said to exist as N-coordinated species,³⁻⁵ but AgCN⁺, like AgN₃⁶ or silver acetate,⁷ can be recrystallised unchanged from AHF. Quantitative data for the formation of Ag⁺ complexes has hitherto been reported only for the ligands F⁻ and HCN.

In this investigation the silver electrode turned out to be a very accurate tool for the determination of silver ion concentrations in AHF, and argentometric titrations permitted the quantitative elucidation of solubilities and of formation constants in this medium. The high acidity of the solvent allowed investigations with such ligands as HCN or PH₃,

which deprotonate on formation of silver complexes in aqueous solution. The relatively high solubility of arenes in AHF made an investigation of silver arene complexes possible. These results are dealt with in another publication.⁸

EXPERIMENTAL⁹

Titration Apparatus and Titration Technique

The titration apparatus consists of a 100 ml Kel-F container capped by a screwed-on cover with threaded holes for gas inlet and outlet tubes, indicator- and reference-electrodes, and the 3 ml burette, a graduated Kel-F rod with a precision-drilled 5 mm ϕ hole. Stopcocks used were "Hamilton Inert Valves". Interconnections were made by electrical FEP spaghetti tubing. A 1 mm ϕ Ag wire molded into a piece of FEP tubing served as an indicator electrode. The systems Ag/AgBF₄ (sat), KBF₄ (sat) in AHF ([Ag⁺] \cong 1.1 · 10⁻²), † Ag/AgNbF₆ (sat) ([Ag⁺] \cong 2.4 · 10⁻²), and Ag/AgF (c = 0.25) ‡ have been used as reference electrodes. The electrolyte of the reference electrode was enclosed in a Kel-F tube, the upper end of which was equipped with a silver-wire and the

† [Ag⁺] = concentration of free silver ion in ml⁻¹.
‡ All concentrations are given in ml⁻¹.

lower end of which was closed with a piece of pressed Teflon filter plate that served as a diaphragm. The stability of the reference potential was checked versus an outer reference Ag/AgF ($c = 0.02$), KF ($c = 0.23$) before and after each measurement.

The assembled titration apparatus was placed in a refrigerator (0°) equipped with a clear PVC door with two openings protected by slit rubber diaphragms, through which the apparatus could be handled by rubberglove-protected hands. "Nalge 1600-Teflon FEP" bottles of different sizes with welded on FEP outlets containing a $\frac{1}{2}$ " thread were used in the preparative work.

Approximately 50 ml portions of 0.02 – 0.05 M solutions of the ligands were titrated with ~ 0.5 M AgF solutions in AHF.

Concentrations of dissolved gases (PH_3 , CO, HCl etc.) could in most cases be determined from the endpoints of the titrations. Potassium fluoride or NaNbF_6 served as supporting electrolyte. The part of the titration curve resulting from excess (free) silver ion was well separated in many experiments which allowed a direct calibration of E vs. pAg, independent of the potential of the reference electrode. By analogy, using the silver electrode as a fluoride ion electrode, the excess of fluoride ion permitted the calibration of E vs. pF. All measurements were carried out at 0° with a Methrom Precision Potentiometer E 353 B. Conductivity measurements were carried out at 1000 cps using a Philips PR 9501 conductivity bridge and a cell consisting of a FEP tube with two 3 x 7 mm bright Pt-electrodes molded in 3 mm apart. Materials: Anhydrous hydrogen fluoride distilled from commercial 99.9 percent material in steel tanks was redistilled over AgF to remove traces of H_2S . The conductivity of the double or triple distilled solvent corresponded to a water content of not more than 10^{-4} ml $^{-1}$. Borontrifluoride, AsF_5 , PF_5 , SF_4 from commercial steel tanks were distilled before use. Crude SbF_5 was distilled twice in a Teflon apparatus. Niobium, pentafluoride and TaF_5 were prepared by condensing HF in excess onto the freshly sublimed chlorides and the crude fluorides were sublimed in an FEP tube in a vacuum. The compounds AgNbF_6 , AgTaF_6 , AgPF_6 , AgAsF_6 , AgSbF_6 and AgBF_4 were prepared from AgF and the corresponding fluoride in AHF as solvent and, like some commercial products were recrystallised once or twice from AHF. Methathesis ($\text{NaPF}_6 + \text{AgF} \xrightarrow{\text{HF}} \text{AgPF}_6 + \text{NaF}$) can also be used as a preparative method. Phosphine was obtained by decomposition of PH_4I with water. Arsine was prepared by reducing arsenite with BH_4^- . AgHF_2 : Hydrogen fluoride gas

was condensed in excess on a wet filter cake of freshly precipitated silver oxide and the solution formed was evaporated to dryness by prolonged heating at 150°C in a steam of nitrogen. The lightly colored residue was dissolved in AHF. The solution was then filtered away from traces of metallic silver and cooled to -78°C to obtain large crystals of $\text{AgF}\cdot 5\text{HF}$. The supernatant liquid was discarded. The $\text{AgF}\cdot 5\text{HF}$ crystals melt on warming and upon evaporation of HF at 25°C the melt solidifies as AgHF_2 , a stable, colourless, non-light-sensitive compound which was used as a source of silver fluoride. Further evaporation of HF gives the light sensitive, yellow AgF. Solutions of AgF in AHF have high densities: $d \cong 1 + 0.259 m$ (for molalities $m < 0.7$). To prepare $\text{Ag}(\text{HCN})_2\text{TaF}_6$, 6.57 g (33 mM) $\text{KAg}(\text{CN})_2$ were dissolved in 25 ml AHF and added to 9.10 g (50 mM) TaF_5 in 75 ml AHF while stirring. On cooling in dry ice-acetone, 4.5 g $\text{Ag}(\text{HCN})_2\text{TaF}_6$ separated as thin platelets. The supernatant liquid was decanted, and the crystals were washed once with HF and dried in a stream of nitrogen. Anal. calcd. for $\text{Ag}(\text{HCN})_2\text{TaF}_6$: Ta, 39.61; Ag, 23.61; CN, 11.38. Found: Ta, 40.60; Ag, 22.15; CN, 10.97; Ag:CN = 1:2.06. The high value for Ta is most probably due to the presence of small amounts of KTaF_6 .

RESULTS AND DISCUSSION

1. The Silver Electrode as Indicator Electrode for $[\text{Ag}^+]$

At constant ionic strength the potential of the silver electrode in AHF varies reversibly with the concentration of free silver ion. In a typical experiment 57.4 ml of a 0.0915 M KF solution in AHF were titrated with 0.861 M AgF. Over a variation of pAg ($-\log [\text{Ag}^+]$) from 3.0 to 1.5 the potential varied linearly with pAg giving a slope $\Delta E/\Delta \log [\text{Ag}^+] = 0.0558$ V (theoretically 0.0542 V). This however does not prove the correct response of the electrode at very low equilibrium concentrations of Ag^+ , but many of the titrations described show clearly that the silver electrode works perfectly even at values of $\text{pAg} \approx 20$. Stable potentials were reached very quickly, often in seconds, and were constant over long periods.

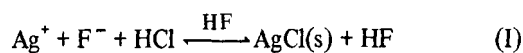
2. The Complex Formation of Ag^+ with F^-

The experiment described under 1., carried out at nearly constant $[\text{F}^-]$ ($I = 0.1$) allows no statement

concerning the formation of an AgF complex. To evaluate the extent of this complex formation, solid NaF was added to an AHF solution 0.00671 M in AgBF₄ and 0.461 M in NaBF₄ to make [NaF] = 0.235 M. The corresponding change in the potential of the inserted silver electrode was +2.5 mV. The same ΔE is observed upon equivalent increase of the ionic strength with NaBF₄ in place of NaF. No net effect due to the formation of AgF is observable under these conditions. The complex formation between Ag⁺ and F⁻ must, therefore, be very slight ($K_{AgF} = [AgF]/([Ag^+][F^-]) \leq 0.1$), and can be neglected for dilute solutions containing Ag⁺ and F⁻. A value $K_{AgF} = 11.5^{13}$ would reflect in a potential change of -30 mV under the conditions of the above experiment.

3. The Silver Electrode as Indicator Electrode for [F⁻]

As is shown later, silver chloride can be formed in AHF by the reaction

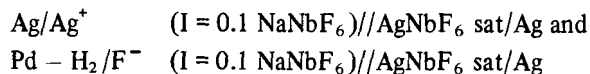


$$K_I = \frac{1}{[Ag^+][F^-][HCl]}$$

In a suspension of AgCl in AHF containing a constant concentration of dissolved HCl the product $[Ag^+][F^-]$ is fixed, and $[Ag^+]$ is inversely proportional to $[F^-]$. Under such conditions the silver electrode will respond to pF values as long as the reaction (1) is not shifted significantly to the left by low fluoride ion concentrations. Correlation of potentials with pF values can be determined experimentally by the addition of excess (free) fluoride ion. This electrode system worked perfectly and permitted a recheck of data for the formation of the fluorocomplexes of NbF₅ and TaF₅ that had been obtained earlier through the use of the hydrogen electrode¹⁴ (see Section 10).

4. The Difference of the Standard Reduction Potentials E°_{Ag/Ag^+} and $E^\circ_{H_2/H^+}(1M F^-)$

The determination of the standard potential of silver was achieved through the use of the systems:



The potentials measured as a function of $[Ag^+]$ and $[F^-]$ respectively were extrapolated to $[Ag^+] = 1$ and $[F^-] = 1$ after correction for the hydrogen pressure,

(only 0.472 atm as a result of the high vapour pressure of HF (0.479 atm at 0°)). The difference in the extrapolated potentials

$$E^\circ_{Ag/Ag^+} - E^\circ_{H_2/H^+}(1M F^-) = +0.611 \pm 0.005 \text{ V} \\ (I = 0.1, \text{ NaNbF}_6, 0^\circ)$$

is in good agreement with the value of 0.64 V reported by Clifford *et al.*^{13,15}

5. Solubilities of Silver Salts of Complex Fluoroanions

Solubilities of silver salts (Table I) were determined by saturation of AHF with the particular compound at 0° followed by chemical analysis of the solution. All of these compounds, which are highly soluble in water, have a much lower solubility in AHF and cannot serve as titrants in place of the highly soluble but alkaline AgF.

TABLE I
Solubility of silver salts of complex fluoroanions in HF at 0° in g/100 g HF

AgNbF ₆	0.752
AgTaF ₆	1.23
AgPF ₆	2.15
AgAsF ₆	2.52
AgSbF ₆	1.80
AgBF ₄	2.02 ¹⁶

In addition, the solubility products for AgNbF₆ and AgTaF₆ were calculated from titrations of AHF solutions of KNbF₆ and KTaF₆ (Figure 1a) with AgF during which solid AgNbF₆ and AgTaF₆ are formed respectively. The ratio of $[Ag^+]$ in solution to $[MF_6^-]$ changed 10 and 50 fold in the course of the two titrations. The constancy of the values obtained for the solubility products:

$$-\log K_{soAgNbF_6} = 3.01 \pm 0.04 \quad (I = 0.15 \pm 0.03)$$

$$-\log K_{soAgTaF_6} = 2.61 \pm 0.06 \quad (I = 0.13 \pm 0.03)$$

indicate that no other equilibria are involved. Unavoidable changes in supporting electrolyte composition and ionic strength lead to relatively large errors.

Solubilities calculated from these solubility products are, as expected due to the salt effect, somewhat higher than the values stated in Table I.

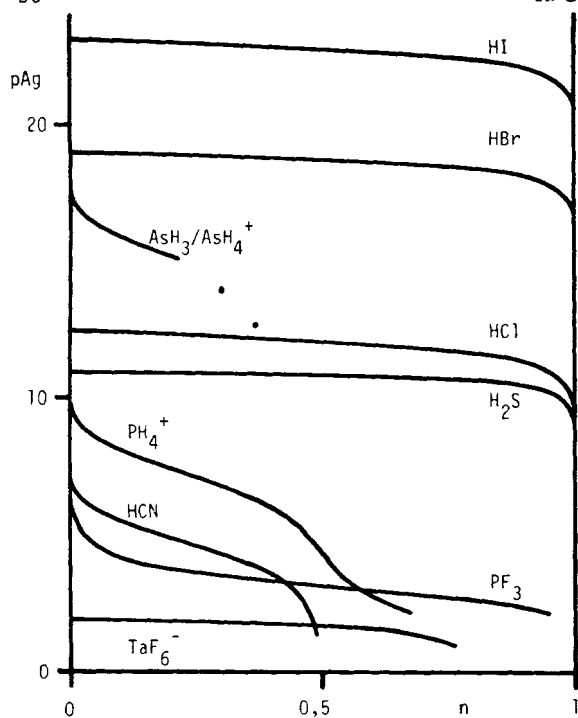


FIGURE 1a

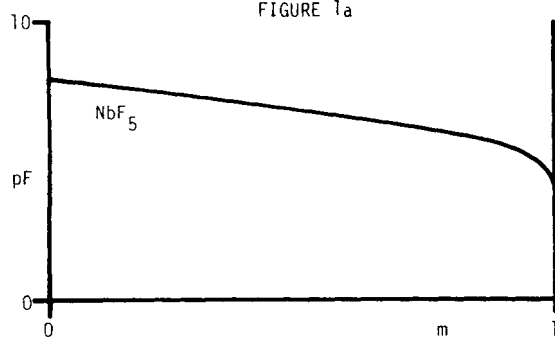


FIGURE 1b

FIGURE 1 a) Argentation curves. b) Fluorocomplex formation of NbF_5 . $n = ([\text{Ag}^+]_t - [\text{Ag}^+])/[\text{Ligand}]_t$. $m = ([\text{F}^-]_t - [\text{F}^-])/[\text{NbF}_5]_t$.

	$[\text{Ligand}]_t$	I (KF)
HI	.0467	.071
HBr	.0399	.073
HCl	.00674	.21
H_2S	.0264	.10
$\text{AsH}_3/\text{AsH}_4^+$.0172	.20
PH_4^+	.154	.35
HCN	.0840	.10
PF_3	.0155	.24
TaF_6^-	.115	—
NbF_5	.0589	—

6. The Formation of AgCl , AgBr , AgI and Ag_2S Precipitates

The halides AgCl , AgBr and AgI are insoluble in basic AHF and can be formed by the reaction of AgF with the undissociated halogen hydride



$$K_{\text{II}} = 1/[\text{Ag}^+][\text{F}^-][\text{HX}]$$

Evaluation of argentation curves† (Figure 1a) obtained from titrations of basic solutions of HX ($[\text{F}^-] = \text{const.}$) provide all concentrations necessary for the calculation of K_{II} :

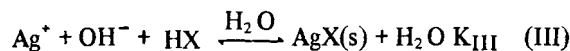
$$\log K_{\text{II}}(\text{AgCl}) = 15.44 \pm 0.02 \quad (I = 0.035, \text{NaF})^{0^\circ}$$

$$\log K_{\text{II}}(\text{AgCl}) = 15.18 \pm 0.05 \quad (I = 0.21, \text{KF})$$

$$\log K_{\text{II}}(\text{AgBr}) = 21.64 \pm 0.10 \quad (I = 0.073, \text{KF})$$

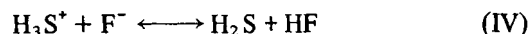
$$\log K_{\text{II}}(\text{AgI}) = 25.56 \pm 0.10 \quad (I = 0.071, \text{KF})$$

The constant K_{II} is not to be confused with the solubility product of the silver halides. K_{III} , the constant corresponding to K_{II} for the analogous reactions in *aqueous* solution is:



The constant K_{III} can be estimated from $\text{p}K_{\text{W}}$, $\text{p}K_{\text{HX}}$ and $\log K_{\text{SO}}(\text{AgX})$. In this way we find $\log K_{\text{III}}(\text{AgCl}) \cong 31$, $\log K_{\text{III}}(\text{AgBr}) \cong 36$ and $\log K_{\text{III}}(\text{AgI}) \cong 40$. These values, although numerically greater, show the same differences as the values of K_{II} .

Hydrogen sulfide is sparingly soluble in AHF, but the solutions are conducting due to partial protonation to H_3S^+ . Conductivity measurements on a solution of H_2S before and after acidification§ with NbF_5^{10} allowed the approximate estimation of K_{IV} :



$$\log K_{\text{IV}} = \log ([\text{H}_2\text{S}]/([\text{H}_3\text{S}^+][\text{F}^-])) \cong 3$$

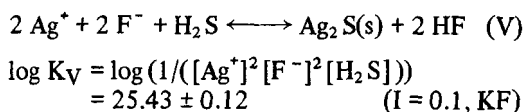
Hydrogen sulfide in basic AHF will therefore be mainly present in the form of H_2S . In the titration of such a solution of AgHF_2 insoluble Ag_2S is formed

† Basic: Fluoride ion added in excess to reactants to keep $[\text{F}^-]$ large and constant.

‡ Argentation curves: Degree of argentation $n = ([\text{Ag}^+]_t - [\text{Ag}^+])/[\text{L}]_t$ plotted versus $\text{pAg}(-\log [\text{Ag}^+])$.

§ Acidified: A fluoride ion acceptor added to keep $[\text{F}^-]$ at low values.

according to



The shape of this argentation curve (Figure 1a) deduced from

$$K_V = \frac{1}{[\text{Ag}^+]^2 [\text{F}^-]^2 [\text{H}_2\text{S}]} ;$$

$$[\text{S}]_t = c \text{ and } [\text{H}_2\text{S}] = c(1 - n)$$

is given by

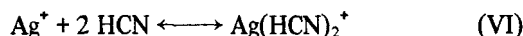
$$\text{pAg} = \frac{1}{2} \log c(1 - n) + \log [\text{F}^-] + \frac{1}{2} \log K_V.$$

The same shape as the well known titration curve of strong base with a strong acid results if $[\text{F}^-]$ is kept constant, but the slope $\Delta \text{pAg} / \Delta \log(1 - n) = 1/2$ is only one half, in exact agreement with the experiment. This observation, together with the analogous ones in the case of silver halides, is evidence for the correct response of the silver electrode at very small equilibrium concentrations of Ag^+ .

7. The Formation of $\text{Ag}(\text{HCN})_2^+$

Hydrogen cyanide in AHF is nonconducting⁴ but can be completely protonated to H_2CN^+ by BF_3 .^{5, 17} In basic solutions hydrogen cyanide will mainly be present in the unprotonated state. According to Dove and Hallett⁴ and to Gillespie⁵ HCN in AHF forms the complexes AgHCN^+ and $\text{Ag}(\text{HCN})_2^+$ in which HCN seems to be N-bonded to silver.

The argentation curve for 5.52 mM HCN in 65.7 ml AHF (0.081 M KF) titrated with 0.665 M AgF (Figure 1a) is due to the reaction



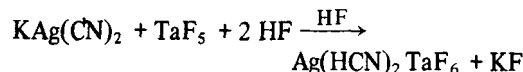
$$\log K_{VI} = \log ([\text{Ag}(\text{HCN})_2^+] / ([\text{Ag}^+] [\text{HCN}]^2))$$

$$= 5.64 \pm 0.03 \quad (I \cong 0.1, \text{KF})$$

Silver ion added in excess of the stoichiometry $\text{Ag}^+ : \text{HCN} = 1 : 2$ does not react; formation of AgHCN^+ could not be observed. Likewise, addition of $\text{KAg}(\text{CN})_2$ to an alkaline solution of AgF does not change the initial pAg value. The comparison of $K_{II}(\text{AgCl})$ with K_{VI} explains the observed reaction of $\text{Ag}(\text{HCN})_2^+$ with HCl to form solid AgCl^3 .

Solid compounds which analyze as HCNAgPF_6 and $\text{HCNAg}_2\text{As}_2\text{F}_{12}$ have been described.⁴ These substances might be mixtures of the sparingly soluble

compounds AgPF_6 and $\text{Ag}(\text{HCN})_2\text{PF}_6$ and of AgAsF_6 and $\text{Ag}(\text{HCN})_2\text{AsF}_6$. Our own preparations revealed that the reaction of equimolar amounts of AgCN and TaF_5 in AHF gives two products: AgTaF_6 and $\text{Ag}(\text{HCN})_2\text{TaF}_6$. The latter can best be prepared according to



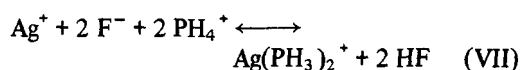
(KF is very soluble, see "Experimental").

Silver azide, like AgCN, is very soluble in AHF and can be recovered unchanged⁶ but in contrast to HCN, Ag^+ is coordinated neither by hydrazoic acid, nor by its protonated form H_2N_3^+ . Silver azide must therefore dissolve in AHF with formation of Ag^+ , F^- and HN_3 , whereas AgCN forms Ag^+ , F^- and $\text{Ag}(\text{HCN})_2^+$ on dissolution.

8. The Formation of PH_3 and AsH_3 Complexes of Silver

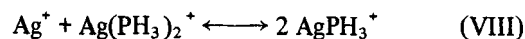
The complex formation of PH_3 with silver cannot be investigated in aqueous systems since deprotonation of the ligand occurs with formation of polynuclear silver compounds. The high acidity of AHF prevents this deprotonation.

According to conductivity measurements, PH_3 dissolves in AHF with complete protonation to PH_4^+ .¹⁸ Soluble PH_3 complexes are formed with silver. The argentation curve (Figure 1a) of PH_4^+ titrated with AgF in a basic AHF-solution shows an initial uptake of Ag^+ with an end point at $[\text{Ag}]_t / [\text{P}]_t = 1/2$ arising from the reaction



$$\log K_{VII} = \log ([\text{Ag}(\text{PH}_3)_2^+] / ([\text{Ag}^+] [\text{F}^-]^2 [\text{PH}_4^+]^2)) = 8.77 + 0.03 \quad (I \sim 0.35, \text{KF}),$$

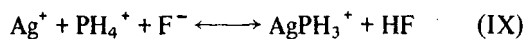
followed by a further but only partially observable uptake of Ag^+ due to the formation of the mono-complex:



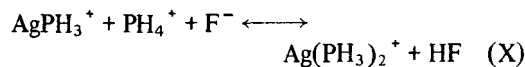
$$\log K_{VIII} = \log ([\text{Ag}(\text{PH}_3)_2^+]^2 / ([\text{Ag}^+] [\text{AgPH}_3^+]^2)) = 0.81 \pm 0.04$$

The value of K_{VIII} is of the same magnitude as the value for the analogous reaction with the ligand NH_3 in the aqueous system ($\log K = 0.85$). From K_{VII} and K_{VIII} the complex-forming constants for the stepwise

coordination are calculated to be:

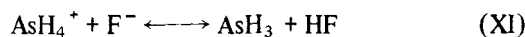


$$\log K_{\text{IX}} = \log \left(\frac{[\text{AgPH}_3^+]}{([\text{Ag}^+][\text{F}^-][\text{PH}_4^+])} \right) = 4.79$$



$$\log K_{\text{X}} = \log \left(\frac{[\text{Ag}(\text{PH}_3)_2^+]}{([\text{AgPH}_3^+][\text{F}^-][\text{PH}_4^+])} \right) = 3.98$$

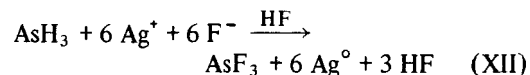
In contrast to PH_3 , arsine in AHF behaves only as a weak base. Although not very precise due to decomposition, conductivity measurements can be interpreted in terms of the reaction



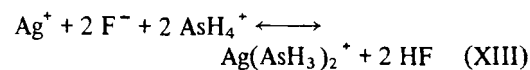
$$\log K_{\text{XI}} = \log \left(\frac{[\text{AsH}_3]}{([\text{AsH}_4^+][\text{F}^-])} \right) \cong 1.7$$

Arsine can be protonated completely by acidifying its AHF solution with NbF_5 or TaF_5 . This opened a method for the preparation of AsH_4^+ compounds.¹⁸

Arsine reduces Ag^+ to the metallic state in aqueous¹⁹ as well as in AHF solutions.



This reaction, used for the analytical determination of AsH_4^+ in arsonium compounds,¹⁸ seems to make an investigation of the complex formation between AsH_3 and Ag^+ impossible. Nevertheless, in a titration of a solution of AsH_3 with AgF (Figure 1a), stable potentials have been observed at values of $n < 0.22$. They become increasingly unstable on further addition of Ag^+ and above $n \cong 0.375$ the reduction to silver metals proceeds quickly. The first few points of this argentation curve are interpreted as due to the reactions

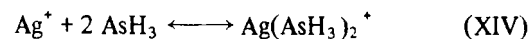


giving

$$\log K_{\text{XIII}} = \log \left(\frac{[\text{Ag}(\text{AsH}_3)_2^+]}{([\text{Ag}^+][\text{F}^-]^2[\text{AsH}_4^+]^2)} \right) = 20.06 \pm 0.12$$

$$(I = 0.2, \text{KF})$$

K_{XI} and K_{XIII} allow the calculation of K_{XIV} :



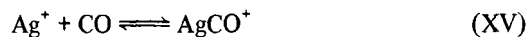
$$\log K_{\text{XIV}} = \log \left(\frac{[\text{Ag}(\text{AsH}_3)_2^+]}{([\text{Ag}^+][\text{AsH}_3]^2)} \right) = 16.66 \pm 0.12$$

The silver complex of AsH_3 is remarkably more stable than that of PH_3 . No complex formation is observed with NH_3 . Arsine is a much better ligand for silver than either phosphine or ammonia.

9. CO , PF_3 , AsF_3 , SbF_3 , SF_4 and Triphenylphosphine as ligands

Souma *et al.*²⁰ demonstrated that silver ion dissolved in AHF ($[\text{Ag}^+]_{\text{total}} = 0.4 \text{ M}$) absorbs carbon monoxide (1 atm.) up to a ratio of $\text{CO}/\text{Ag}^+ = 1.4$ at 0° and $\text{CO}/\text{Ag}^+ = 2$ at -40° , indicating the formation of dicarbonyl-silver(I) ion. The formation constant of this species can only be small.

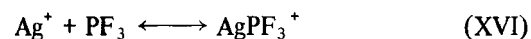
In the titration of an AHF solution of the sparingly soluble carbon monoxide ($[\text{CO}]_{\text{total}} = 0.00595 \text{ M}$) with Ag^+ the only observed reaction is the formation of the monocomplex:



$$\log K_{\text{XV}} = \log \left(\frac{[\text{AgCO}^+]}{([\text{Ag}^+][\text{CO}])} \right) = 3.96 \pm 0.06 \quad (I = 0.26, \text{KF})$$

This is not in contradiction to Souma's results since a reduction of the total concentration of the ligand to be titrated in a stepwise complex formation leads to relative diminution of the concentration of higher complexes compared to lower complexes.

Phosphorus trifluoride has been prepared in situ by addition of PCl_3 to AHF. Small quantities of PF_3 and HCl are lost in this preparation since both gases are sparingly soluble. Phosphorus trifluoride is coordinated by Ag^+ with formation of a weak 1:1 complex (Figure 1a) comparable in stability to the CO -complex:



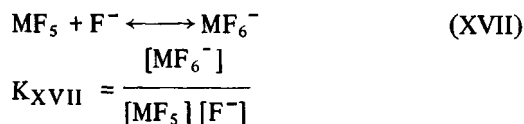
$$\log K_{\text{XVI}} = \log \left(\frac{[\text{AgPF}_3^+]}{([\text{Ag}^+][\text{PF}_3])} \right) = 3.19 \pm 0.1 \quad (I = 0.244, \text{KF})$$

The AgPF_3^+ complex has also been observed to exist in liquid SO_2 .²¹ Arsenic trifluoride, SbF_3 and SF_4 show no sign of complex formation with Ag^+ . Triphenylphosphine, which is very soluble in AHF and undoubtedly present in the protonated state, does not form complexes with Ag^+ .

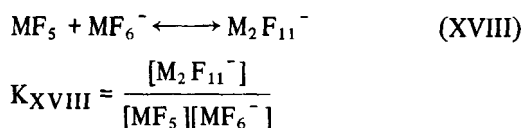
10. The Complex Formation of NbF_5 and TaF_5 with F^-

Gautschi¹¹ investigated the fluorocomplex formation of NbF_5 and TaF_5 in AHF by acidimetric techniques which did not account for the possible formation of

the dinuclear species $M_2F_{11}^-$. The application of the silver electrode as an indicator electrode for $[F^-]$ permitted a completely independent reinvestigation. Anhydrous hydrogen fluoride solutions of MF_5 were titrated with NaF solutions in the presence of solid AgCl and some dissolved HCl. The data obtained (Figure 1b) cannot be explained solely by the reaction



but indicate that the dinuclear species $M_2F_{11}^-$ is formed in the course of the titration:



The species $M_2F_{11}^-$ first observed in the crystal structure of $SeF_3^+Nb_2F_{11}^{2-}$ are known to exist in methylene chloride solutions and in tetra-*n*-butylammonium salts.²³ They will form in AHF when relatively high concentrations of MF_5 and MF_6^- can be achieved simultaneously.

Values calculated for K_{XVII} and K_{XVIII} are:

$$\begin{aligned} \log K_{XVII}(Nb) &= 6.88 \\ \log K_{XVIII}(Nb) &= 1.32 \pm 0.1 \\ \log K_{XVII}(Ta) &= 8.88 \\ \log K_{XVIII}(Ta) &= 1.50 \pm 0.15 \end{aligned}$$

The relatively large uncertainty in K_{XVII} is due to the fact that all errors are reflected in K_{XVIII} only and to the fact that the ionic strength varies in these titrations affecting the first part of the titration curves.

Appropriate correction of Gautschi's K_{XVII} values for the intermediate formation of the dinuclear

$M_2F_{11}^-$ gives:

$$\begin{aligned} \log K_{XVII}(Nb) &= 7.16 \quad (I = 0.2, NaNbF_6) \\ \log K_{XVII}(Nb) &= 6.98 \quad (I = 1.0, KNbF_6) \\ \log K_{XVII}(Ta) &= 9.42 \quad (I = 0.2, NaNbF_6) \end{aligned}$$

in reasonable agreement with the values obtained with the silver electrode.

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