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**Thermodynamic Stability of Complexes of BF_3 ,
 PF_5 and AsF_5 with Chlorine Fluorides, Oxyfluorides,
and Related Compounds**

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LOCKHEED MARTIN UTILITY SERVICES
Paducah, KY and Portsmouth, OH**

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**MANAGED BY
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
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**Thermodynamic Stability of Complexes of BF_3 , PF_5 , and AsF_5
with Chlorine Fluorides, Oxyfluorides, and Related Compounds**

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July 1996

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Under contract USECHQ-93-C-0001
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ABSTRACT

The recent discovery of solid, water sensitive, arsenic-containing deposits in auxiliary process piping in the PGDP led to a search for explanations that could account for such accumulated material. A plausible explanation for the deposits is the formation of complexes of AsF_5 with one or more gases that may have been present as a result of cascade equipment cleanup activities. A literature search on the above subject was begun at PGDP and later expanded by the author. The target of the search was literature that would provide information on the dissociation pressure of complexes of AsF_5 or its hydrolysis products with any gases that may be (at least intermittently) present in the cascade location where the deposits were found. While the precise information sought (namely reliable, accurate dissociation pressures of such complexes at cascade temperatures) was not found in the detail desired, other information on these or similar complexes was obtained which permits prediction of the conditions under which the complexes might form, dissociate, or migrate, and how they might behave in the presence of atmospheric moisture.

Information was gathered on potential AsF_5 complexes with ClF , ClF_3 , ClF_5 , ClF_3O , ClO_2F , and ClO_3F . Information was also collected on many other related complexes as it was encountered, particularly for series of complexes which could assist in predicting chemical trends. Thermodynamic analysis and property estimation methods have been used to generate provisional estimates of the dissociation pressures of the two complexes $\text{ClF}_3 \cdot \text{AsF}_5$ and $\text{ClO}_2\text{F} \cdot \text{AsF}_5$. In addition, several hydrolysis species have been identified, and stability properties of the most relevant such complex ($\text{H}_3\text{O} \cdot \text{AsF}_6$) have similarly been estimated. While the predicted dissociation pressures are somewhat uncertain, they do lead to a tentative picture of the formation and behavior of such complexes in a cascade cleanup environment.

1. INTRODUCTION

Recently, in the PGDP purge cascade, several pounds of a solid deposit was found. The deposit fumed in air, reacted explosively with moisture, and was found by chemical analysis to contain a considerable proportion of arsenic. Upon exposure to air, a portion of it appeared to liquefy, and a white precipitate came out of the solution. The likely source of arsenic dates to the late 1980s, at a time when UF_6 feed was received with elevated levels of arsenic in the form of AsF_5 . This was discovered when severely accelerated cylinder valve corrosion was observed¹. Subsequently, the concentration of AsF_5 in the feed was reduced back to its lower historical levels by the feed manufacturer.

A literature search on the above subject was begun at PGDP² and later expanded by the author. The target of the search was literature that could provide information on the dissociation pressure of complexes of AsF_5 or its hydrolysis products with any gases that may be at least intermittently present in the cascade location at which the deposits were found. While the precise information sought (namely dissociation pressures of such complexes at cascade temperatures) was not found, other information on these or similar complexes was obtained which permits prediction of the conditions under which the complexes might form, dissociate, or migrate, and how they might behave in the presence of atmospheric moisture.

The search and analysis focuses primarily on complexes of AsF_5 with ClF_3 and ClO_2F , and on their hydrolysis products. In addition, we evaluate analogous complexes. The analogous potential combinations examined are primarily those of BF_3 , PF_5 , and AsF_5 complexing with ClF , ClF_3 , ClF_5 , ClF_3O , ClO_2F , and ClO_3F , but many other related complexes were examined as data were encountered, particularly for series of complexes that could assist in predicting chemical trends. Thermodynamic analysis and property estimation methods have been used to generate provisional estimates of the dissociation pressures of the two complexes $\text{ClF}_3 \cdot \text{AsF}_5$ and $\text{ClO}_2\text{F} \cdot \text{AsF}_5$. In addition, several hydrolysis species have been identified, and stability properties of the most relevant such complex ($\text{H}_2\text{O} \cdot \text{HF} \cdot \text{AsF}_5$) have similarly been estimated.

From the literature examined to date, it is evident that many of the possible combinations of Lewis acids and Lewis bases form stable adducts, sometimes termed a complex, per the general equation:

For example, ClF_3 and AsF_5 are known to form a complex which structurally is generally thought of as $\text{ClF}_2^+ \text{AsF}_6^-$, though this is often written as $\text{ClF}_2 \text{AsF}_6$ or $\text{ClF}_3 \cdot \text{AsF}_5$. In this complex, ClF_3 acts as the

Lewis base, donating F to the Lewis acid AsF_5 . Equation (1) is written with the complex being a solid species, indicated by "(s)", and its components being gases, indicated by "(g)". These are the usual phases for the species considered in this report, but this is not necessarily always the case. For example, KF(s) and $\text{BF}_3\text{(g)}$ form the well-known compound KBF_4 , which can be thought of as just such a complex.

The stability of a complex will depend on the energetics of the fluoride ion transfer and lattice energy in the crystal formed, a measure of which is its dissociation pressure. At one extreme, the complex will be thermodynamically unable to form, as seems to be the case for the combinations of ClO_3F with BF_3 , PF_5 , and AsF_5 . Attempts to form such complexes have been unsuccessful^{3,4}. More favorable energetics allow complexes to form with marginal stability at low temperature. For such complexes, the gaseous components, in equilibrium with the solid according to equation (1), will exhibit a measurable dissociation pressure (that is to say, the sum of the partial pressures of the gas components in equilibrium with the solid). An example of such a complex is ClF_2BF_4 (that is, $\text{ClF}_3 \cdot \text{BF}_3$), whose dissociation pressure has been measured over the temperature range -30 to $+20^\circ \text{C}$ to range from about 26 to 1630 Torr.⁵ More stable compounds exhibit lower dissociation pressures, sometimes immeasurably low.

Measurements of dissociation pressure over a reasonable range of temperature provide what is generally the best available data for characterizing the behavior and thermodynamic stability of such compounds. Consequently, it is for the less stable complexes, those exhibiting measurable dissociation pressures at temperatures easily accessible in the laboratory (e.g. -78°C to room temperature) for which the most detailed stability data is available. For more stable compounds, dissociation pressure information may be very qualitative or completely lacking. Several of the AsF_5 complexes of most interest and all SbF_5 complexes fall into this category, having little or no quantitative dissociation pressure data. Qualitative pressure data might consist of a statement that "the material dissociates at 50°C " or "the complex slowly sublimates at 120°C " leaving the reader to speculate on what pressure might correspond to the phrase "slowly subliming."

Our literature search has concentrated on complexes formed from any of BF_3 , PF_5 , AsF_5 and SbF_5 with ClF_3 and F_2 , and with their derivatives and potential reaction products. Where fairly extensive information is available for complexes of another gas with several of these Lewis acids, we have also incorporated the relevant information into the analysis to assist in establishing chemical trends. Such compounds include several of the alkali metal fluorides, other interhalogen fluorides (e.g. BrF_3), SF_6 , and a few nitrogen oxyfluorides. Of these species, Table 1 gives an overview of those combinations for which information on the formation (or definitive information on the non-formation) of complexes was

Table 1. Literature Information on Stability of Complexes

	BF ₃	PF ₅	AsF ₅	SbF ₅	Notes
ClF	Yes	-	Yes	Yes	[A] [D]
ClF ₃	Yes	Yes		Yes	
ClF ₅	No	-	Yes	Yes	
"ClF ₇ ,"	No	Yes	Yes	Yes	[C]
ClF ₃ O	Yes	Yes	Yes	Yes	
ClO ₂ F	Yes	Yes	Yes	Yes	
ClO ₃ F	No	No	No	Yes	
ClO ₂ F ₃	Yes	-	Yes	-	
BrF ₃	-	-	-	Yes	[D]
BrF ₅	-	-	Yes	Yes	[D]
BrF ₇	-	-	Yes	-	
IF ₇	Yes	-	Yes	Yes	
NF ₃	-	-	Yes	Yes	
"NF ₅ ,"	Yes	Yes	Yes	Yes	[C]
NF ₃ O	Yes	-	Yes	Yes	
NOF	Yes	Yes	Yes	Yes	
NO ₂ F	Yes	Yes	Yes	Yes	
SO ₂ F ₂	Yes	-	Yes	Yes	
SF ₆	Yes	Yes	Yes	Yes	
SO ₂ F ₂	-	-	Yes	Yes	
POF ₃	-	-	Yes	-	
LiF	Yes	-	-	Yes	
NaF	Yes	Yes	Yes	Yes	
KF	Yes	Yes	Yes	Yes	
RbF	Yes	Yes	Yes	-	
CsF	Yes	Yes	Yes	Yes	
O ₂ F ₂	Yes	Yes	Yes	Yes	
H ₂ O ₂ F ₂	Yes	-	Yes	Yes	[B]

H_2OF_2	-	-	Yes	Yes	[B]
UO_2F_2	-	-	Yes	Yes	[B]
TcO_2F	-	-	Yes	-	

Notes: "Yes" : Complex has been observed
 "No" : All reported synthesis attempts were unsuccessful
 " - " : No reports located on this combination
 [A] 2 ClF(g) form Cl_2F^+ cation
 [B] Cationic component decomposes to 2 constituents
 [C] Cation precursor does not exist as stable gas phase species;
 $\text{MF}_x \cdot \text{NF}_y$ decomposes to $\text{F}_2 + \text{MF}_{x-2} + \text{NF}_y$
 [D] Complex formed is at other than a 1:1 ratio of components

found. Except as they proved useful in establishing chemical trends helpful in estimating properties of the AsF_5 complexes with chlorine fluorides and oxyfluorides, this report does not attempt to comprehensively treat other complexes.

Another related class of complexes involving chlorine fluorides and oxyfluorides exists, namely those in which the chlorine-containing species acts as a Lewis acid. An example of such a species is K^+ClF_4^- (i.e. $\text{KF} \cdot \text{ClF}_3$).⁶ While of potential relevance to uranium enrichment in gas separations, these compounds are considered outside the scope of this study and will not be included in this review.

For the chlorine fluoride and oxyfluoride complexes, virtually all exhibit one common property, namely that they are sensitive to hydrolysis and will fume on contact with moist air. These compounds generally react explosively on contact with condensed water or condensed organic materials.

Literature preparation methods usually fall into two categories: (1) precipitation from a solution in anhydrous HF and (2) formation from the condensed phase of the gases frozen at low temperatures. While there were a few cases in which the constituent gases were simply mixed and allowed to stand, resort to condensed phase methods suggests that the actual formation of the complex may be speeded by availability of a participating condensed phase.

The object of this report is to make the most reliable estimate possible from the available data of the stability of complexes of AsF_5 with ClF_3 and its plausible reaction products. Stability, in this context, means predicting whether, under any specified conditions of temperature, pressure, and concentration of $\text{AsF}_5(\text{g})$ and $\text{ClF}_3(\text{g})$ (or reaction product), the complex will tend to form or will tend to dissociate if already present. The relevant thermodynamic property for predicting this stability is the equilibrium constant, K_p . For the dissociation reaction

(essentially the reverse of equation (1)), K_p is given to good approximation by

$$K_p = P_A P_B \quad (3)$$

where P_A and P_B are the equilibrium partial pressures of gases A and B, and the pressure is expressed in multiples of the thermodynamic standard state, 1 bar (1 bar = 0.9872 atm = 750.06 Torr = 14.504 psia). While not precisely correct to put it this way, the units of P can be considered to be in bar and thus K_p in this case is in units of bar². K_p will be a function of temperature and of thermodynamic constants of the reactants and products. Our goal in this report is, for each relevant complex, to determine values for such of the thermodynamic constants as are unavailable so as to derive an equation for K_p as a function of temperature. Appendix A discusses the details of the derivation of the requisite properties from K_p (or vice versa).

Literature data pertinent to this evaluation are those which give dissociation pressures either as data (pressure-temperature data pairs) or in the form of a temperature dependent equation. Such an equation can be converted into an equation for K_p by reference to equation (3). For the binary compound dissociation depicted in equations (2) and (3), the dissociation pressure is

$$P_{dis} = P_A + P_B, \quad (4)$$

and since we assume stoichiometric dissociation:

$$P_A = P_B \quad (5)$$

so that in this case,

$$K_p = P_{dis}^2 / 4 \quad (6)$$

Other reaction equations would produce variations on this functional relationship, as indicated in Appendix A. It is not unreasonable to suppose that there will be some undissociated or other polymeric species in the vapor phase over some complexes. Authors who have considered this possibility for the particular complexes discussed here have not found overt evidence of such gas phase adducts. however.

For purposes of predicting stability of a complex in the presence of variable partial pressures of its component gases (as might be the case in cell treatment gas disposal, for example), a formula for K_p as a function of temperature is the appropriate function to utilize. For that reason, and to avoid confusion of the two forms, we will derive and present functions for K_p rather than dissociation pressure in the remainder of this report.

Frequently literature data on dissociation pressure are analyzed to produce values for ΔH°_{dis} and ΔS°_{dis} the enthalpy and entropy of dissociation of the complex. These in turn may be used with literature values for the constituent compounds' entropy and enthalpy of formation to deduce entropy and enthalpy of formation for the complex. This is substantially what is intended in the analysis in this document. To avoid inconsistencies in the values of the source component data, and in the interest of generating formulae which can be more accurately extrapolated, we will use the original pressure data or equation, and recalculate the thermodynamic properties of the complexes, rather than using the literature values. Differences in results were generally minor and readily traced to differences in the degree of refinement of the data treatment or in the values used for ΔH°_f and S° the constituent compounds.

Often (alas), detailed pressure-temperature data aren't available for a complex. Sometimes a single pressure is reported (or more than one, but very closely spaced in temperature). Other times, only qualitative dissociation pressure information is given, e.g. a report that a particular material "dissociated" in a thermogravimetric analysis environment over a particular temperature range, or that the material "readily sublimed" at some temperature. In such cases, lacking better data, an estimate will be made of the approximate dissociation pressure, recognizing that such an estimate may well be off as much as an order of magnitude. In the worst case, the only information available is that a complex "is stable" at some temperature or "shows no measurable dissociation pressure". In such a case, all that can be done is to estimate the upper limit on the dissociation pressure that is consistent with the statement (given the particular experimental equipment used), and treat the resulting information as an upper bound on dissociation pressure. In such cases, it may be possible to make an estimate of the stability of that particular complex by reference to stability trends in various chemical series for which better analyses can be made.

2. ANALYSIS OF SPECIFIC COMPLEXES

While references to a very large number of complexes were found in the literature search (as indicated in Table 1), this report is primarily directed at elucidating the properties of complexes of AsF_5 with compounds that might be present in a GDP cleanup treatment environment. Complex forming gases in this category are ClF_3 and its plausible reaction products with UO_2F_2 , UF_6 , or moisture. Complexes discussed in detail will be those of AsF_5 with such species. We will also discuss related complexes that exhibit similar properties, from which chemical trends can be deduced which allow estimation of otherwise unavailable properties of AsF_5 complexes. Complexes of BF_3 and PF_5 exhibit behavior similar to that of AsF_5 complexes, but they are generally somewhat less stable than the corresponding AsF_5 complex, and consequently are often more thoroughly studied (from a stability standpoint). SbF_5 complexes are generally much more stable than the corresponding AsF_5 complexes and therefore generally haven't been studied from a thermal stability standpoint in a manner sufficiently quantitative to be useful in estimating trends for AsF_5 compounds.

ClO_3F , a common reaction product of ClF_3 , seems not to form stable complexes with Lewis acids such as AsF_5 .

For each complex discussed here, we will report the source of the literature data, evaluate that information so as to provide an equation of $K_p(T)$, and calculate values for the enthalpy and entropy of dissociation of one mole of the complex, and (at standard thermodynamic reference conditions of 1 bar and 298.15K (25°C or 77°F) the enthalpy of formation, the entropy, and heat capacity per mole of complex. These parameters are implicit in the constants of the K_p equation, but are also useful for carrying out computational thermodynamics calculations with a view to estimating equilibria in more complex mixtures of species, or deducing the heats of reaction. The analytical methods used for deducing these thermodynamic properties (referred to below as the "2nd Law" and "3rd Law" methods) are discussed in Appendix A.

Uncertainties are listed for the derived or estimated thermodynamic properties of the dissociation process and the complex. The uncertainties listed are those inherent in the estimates for C_p and S° and in the statistics of the fit, but do not contain contributions for uncertainties in literature values of the properties of the constituents, e.g. for DH_f° of AsF_5 . Appendix A contains a more complete description of error estimation and propagation. As will be obvious from the magnitude of the uncertainties, values have not been rounded to remove all but significant digits. For example, in the first complex discussed, Cl_2FBF_4 , the enthalpy of dissociation, $\text{DH}^\circ_{\text{dis}}$, is listed as "99145 $\pm$ 5892", rather than "99100 $\pm$ 5900". The statistically insignificant digits are retained in the interest of allowing one to reproduce the data from

which they were derived.

In the following analyses an "independent estimate of S° and C_p " is referred to but not elaborated upon. The source of each particular estimate is, however, indicated in Appendix C and the general methods used are described in Appendix B.

Unless otherwise specified, temperatures are in kelvin, pressures are in bar, enthalpies are in joules per gm-mole, and entropy and heat capacity are in joules per gm-mole per degree (K). Estimated or derived values for these parameters are:

ClF -- BF₃

The existence of a 2:1 complex of ClF and BF₃, which more properly should be considered an ionic compound whose constituents are Cl₂F⁺ and BF₄⁻, was reported by Christie⁷. The complex exhibits a high dissociation pressure, but experimental difficulties prevented obtaining reliable pressure-temperature data. Only very limited information was therefore reported on the dissociation pressure of this complex. The following statements will be interpreted as indicated:

1. "The complex is stable at -127°C" will be taken to indicate that at -127°C, $P = 1 \times 5^{\pm 1}$ Torr.
2. "...complex exhibits a measurable dissociation pressure at -112°C" will be taken to indicate that at -112°C, $P = 5 \times 5^{\pm 1}$ Torr.

A synthetic data set was generated embodying the above interpretations for purposes of estimating thermodynamic properties of this complex. Due to the extremely limited data, the 2nd law method cannot be used to provide a reliable equation for K_p or estimates of the related thermodynamic parameters for the dissociation of this complex. An independent estimate of entropy for the complex is used to allow calculation of K_p per the third law method as outlined in Appendix A. The resulting equation for K_p is:

$$\ln K_p = 91.6238 - 13345.6 / T - 4.76693 \ln T$$

For this complex,

$$K_p = P(\text{ClF})^2 P(\text{BF}_3)$$

The calculated values for enthalpy of dissociation and formation, along with the associated entropy and heat capacity values used are:

Dissociation	DH [°] _{dis} J/mol J/mol K	DS [°] _{dis} J/mol K	DCP _{dis}
(3rd Law)	99145 ± 5892	496.349 ± 13.450	-39.635 ± 21.550
	DH [°] _f J/mol J/mol K	S [°] J/mol K	C _p
(3rd Law)	-1335350 ± 5892	193.882 ± 13.450	157.431 ± 21.550

ClF -- PF₅

No report of the complex Cl₂F⁺PF₅⁻ was found in the literature reviewed. From correlations and trends among the properties of other (known) complexes containing Cl₂F⁺ or PF₅⁻, estimates for each of the relevant thermodynamic properties of this (hypothetical) complex can be made.

	DH ^o _f	S ^o	C _p
	J/mol	J/mol K	
	J/mol K		
(Estimate)	-1796287 ± 8538	259.310 ± 17.322	205.211 ± 23.077

Combining these with properties for the dissociation products ClF(g) and PF₅(g) (Appendix C), we derive the change in thermodynamic properties for the dissociation reaction to be:

Dissociation	DH ^o _{dis}	DS ^o _{dis}	DC _{p,dis}
	J/mol	J/mol K	
	J/mol K		
(Estimate)	101294 ± 8538	477.376 ± 17.322	-55.484 ± 23.077

from which, in turn, K_p can be derived:

$$\ln K_p = 102.1087 - 14172.4 / T - 6.67313 \ln T$$

For this complex,

$$K_p = P^2(\text{ClF}) P(\text{PF}_5)$$

Naturally, the uncertainty in the prediction of K_p or dissociation pressure prediction is rather large. From this equation for K_p, however, we would predict that the dissociation pressure of this complex would reach 1 bar (ca. 1 atmosphere) at a temperature of -65 ± 20°C. This is consistent with the lack of observation of the compound. To test this prediction, experimental investigation of the behavior of the constituents below this temperature range would be necessary. To reiterate, the properties listed above are purely estimates, and have no direct basis in experimental evidence for the existence of this compound.

ClF -- AsF₅

The existence of a 2:1 complex of ClF and AsF₅ was reported by Christie⁸, who on spectroscopic grounds interpret the complex as an ionic compound of the cation Cl₂F⁺ and AsF₆⁻. Its dissociation pressure was measured over a temperature range of -64 to -18 °C and fit to the equation:

$$\log_{10} P(\text{Torr}) = 11.71240 - 2391.6 / T(\text{K})$$

The data from which this was derived were also reported. We have analyzed these data per the second law method (but incorporating the additional heat capacity dependent parameter, as outlined in Appendix A). The resulting equation for K_p is:

$$\text{(2nd Law)} \quad \ln K_p = 118.7872 - 18835.0 / T - 9.14018 \ln T$$

An independent estimate of entropy for the complex is used to allow calculation of K_p per the third law method as outlined in appendix A. The resulting equation for K_p is:

$$\text{(3rd Law)} \quad \ln K_p = 121.3467 - 19433.3 / T - 9.14018 \ln T$$

For this complex,

$$K_p = P(\text{ClF})^2 P(\text{AsF}_5)$$

At 20°C, these K_p equations predict a dissociation pressure on the order of 5 atmospheres. It is not likely, therefore, that this complex will be of direct relevance to GDP cleanup operations, the only conceivable exception being in cryogenic systems.

The calculated values for enthalpy of dissociation and formation, along with the entropy and heat capacity values used are:

Dissociation	DH ^o _{dis} J/mol J/mol K	DS ^o _{dis} J/mol K	DCP _{dis}
(2nd Law)	133945 ± 2448	478.666 ± 9.999	-75.996 ± 23.882
(3rd Law)	138920 ± 4077	499.947 ± 17.322	-75.996 ± 23.882

	DH _f ^o J/mol J/mol K	S ^o J/mol K	CP
(2nd Law)	-1471278 ± 2448	280.591 ± 9.999	237.185 ± 23.882
(3rd Law)	-1476252 ± 4077	259.310 ± 17.322	237.185 ± 23.882

Statistically, the two sets of derived values are consistent with one another; based on the lower uncertainty levels, the values derived by the 2nd law method are recommended. Either set should reproduce the experimental data within the measured region with high precision. It is only in extrapolations or in use of the data for other purposes (e.g. reaction heat evolution calculations) that one set differs from the other.

The existence of a complex of ClF_3 and BF_3 was reported by Selig⁹. The adduct, which should be considered a complex of the ions ClF_2^+ and BF_4^- , has a melting point of 30°C. Dissociation pressures of the solid were measured over the temperature range of -30 to 20°C. The authors fit their dissociation pressure data to the following equation:

$$\log P(\text{Torr}) = 12.000 - 2576 / T(\text{K})$$

The data from which this was derived were not, however, reported in the referenced article. A synthetic data set was generated over the above-mentioned temperature range. These synthetic data points were analyzed per the second law method (but incorporating the additional heat capacity dependent parameter, as outlined in Appendix A). The resulting equation for K_p is:

(2nd Law) $\ln K_p = 85.2770 - 13668.9 / T - 6.77690 \ln T$

An independent estimate of entropy for the complex is used to allow calculation of K_p per the third law method as outlined in Appendix A. The resulting equation for K_p is:

(3rd Law) $\ln K_p = 87.6573 - 14307.2 / T - 6.77690 \ln T$

For this complex,

$$K_p = P(\text{ClF}_3) P(\text{BF}_3)$$

The calculated values for enthalpy of dissociation and formation, along with the entropy and heat capacity values used are:

Dissociation	$\text{DH}^\circ_{\text{dis}}$ J/mol J/mol K	$\text{DS}^\circ_{\text{dis}}$ J/mol K	DCP_{dis}
(2nd Law)	96851 ± 747	331.650 ± 2.617	-56.347 ± 22.698
(3rd Law)	102157 ± 4467	351.441 ± 16.611	-56.347 ± 22.698

	ΔH_f° J/mol J/mol K	S° J/mol K	CP
(2nd Law)	-1391338 ± 747	204.305 ± 2.617	173.053 ± 22.698
(3rd Law)	-1396644 ± 4467	184.514 ± 16.611	173.053 ± 22.698

The 2nd Law-derived values fall within one standard deviation of the 3rd-Law values. There is no particular reason to reject the apparently more precise 2nd Law values, though it should be recognized that much of the apparent precision may be artificially exaggerated due to use of the synthetic data set.

The existence of a complex of ClF_3 and PF_5 was reported by Christe and Pavlath¹⁰. The resulting adduct is considered to consist of an ionic complex of ClF_2^+ and PF_6^- . Dissociation pressures were measured and fit to the following equation

$$\log P(\text{Torr}) = 10.53 - 1798 / T(\text{K})$$

Neither the data from which this was fit nor the temperature range of the data were listed in the referenced article. For purposes of analysis, a synthetic data set was generated from the above equation over the temperature range -90 to -40°C (which yields pressures over the range typically reported by the second of the above authors). These synthetic data points were analyzed per the second law method (but incorporating the additional heat capacity dependent parameter, as outlined in Appendix A). The resulting equation for K_p is:

$$(2\text{nd Law}) \quad \ln K_p = 88.8410 - 10068.9 / T - 8.68309 \ln T$$

An independent estimate of entropy for the complex is used to allow calculation of K_p per the third law method as outlined in appendix A. The resulting equation for K_p is:

$$(3\text{rd Law}) \quad \ln K_p = 98.6141 - 12103.2 / T - 8.68309 \ln T$$

where for this complex,

$$K_p = P(\text{ClF}_3) P(\text{PF}_5)$$

The calculated values for enthalpy of dissociation and formation, along with the entropy and heat capacity values used are:

Dissociation	$\text{DH}^\circ_{\text{dis}}$ J/mol J/mol K	$\text{DS}^\circ_{\text{dis}}$ J/mol K	DCP_{dis}
(2nd Law)	62193 ± 2251	255.132 ± 8.977	-72.196 ± 24.263

(3rd Law)	79107 ± 4828	336.391 ± 22.148	-72.196 ± 24.263
	$\Delta H_{f,0}$	s^0	C_P
	J/mol	J/mol K	
	J/mol K		
(2nd Law)	-1815468 ± 2251	327.278 ± 8.977	220.833 ± 24.263
(3rd Law)	-1832382 ± 4828	246.019 ± 22.148	220.833 ± 24.263

In this case, the entropy for the compound deduced using the 2nd Law method is so far removed from the entropy estimate based on the entropy-density correlation (4 standard deviations), that the 3rd Law results are likely to provide a better estimate for the properties, and thus will be the ones accepted.

The existence of a complex of ClF_3 and AsF_5 was reported by several groups. Information relative to the stability of the complex was reported by Seel¹¹ and by Christe¹². The adduct should be considered to be an ionic complex of ClF_2^+ and AsF_6^- . No melting point was reported, but the material is reported to be violently reactive with water or organic materials. Exposure of the complex to traces of moisture leads to the conversion of this complex to the complex ClO_2AsF_6 (i.e. $\text{ClO}_2\text{F}^+\text{AsF}_5^-$)¹³, at least in (nearly) anhydrous HF.

Only very limited information was found relating to the dissociation pressure of this complex. The following statements will be interpreted as indicated:

1. "Dissociation pressure at 20°C is about 5 Torr" (Seel)
will be taken to indicate that at 20°C, $P = 5 \times 1.1^{\pm 1}$ Torr.
2. "...in 2-3 hrs at 40-50°C, 5 grams can be sublimed" (Seel)
will be taken to indicate that at 45°C, $P = 10 \times 4^{\pm 1}$ Torr.
3. "...no significant dissociation pressure at room temperature" (Christe)
will be taken to indicate that at 22°C, $P = 0.5 \times 4^{\pm 1}$ Torr.

Normally even a single dissociation pressure (as in statement 1) would allow application of the third law method to allow estimation of K_p and the enthalpy of dissociation of the complex. Seel's listed dissociation pressure was made in a review article which reported similar values for many other such compounds, including a few for which detailed pressure-temperature measurements were later made (see section on $\text{SF}_6 \cdot \text{AsF}_5$, below). Unfortunately, it was often the case that Seel's reported dissociation pressures were somewhat higher than that of later more extensive work. It is likely that reaction with materials of construction generated gaseous reaction products artificially raising the pressures he observed. On the other hand, the report of sublimation probably accurately reflect what was observed, indicating that this complex, at room temperature, is on the verge of generating measurable dissociation pressures. In Christe's work of the period of the referenced article, the pressure measurement equipment and reporting behavior would lead one to interpret a statement that there was "no significant pressure" to mean that the pressure was less than one half to one Torr. The third statement should provide an upper limit only, but considering it in combination with the Seel data, we will assume that the actual pressure

is within a factor of 8 of Christe's probable detection limit.

A synthetic data set was generated incorporating the interpretations above. Due to the extremely limited and qualitative nature of most of the data, the 2nd law method cannot be used to provide a reliable equation for K_p or estimates of the related thermodynamic parameters for the dissociation of this complex. An independent estimate of entropy for the complex is used to allow calculation of K_p per the third law method as outlined in appendix A. The resulting equation for K_p is:

$$(3rd\ Law) \quad \ln K_p = 117.2871 - 19948.79 / T - 11.15014 \ln T$$

where for this complex,

$$K_p = P(ClF_3) P(AsF_5)$$

The calculated values for enthalpy of dissociation and formation, along with the entropy and heat capacity values used are:

Dissociation	DH°_{dis} J/mol J/mol K	DS°_{dis} J/mol K	DCP_{dis}
(3rd Law)	138224 ± 9898	354.264 ± 22.571	-92.708 ± 25.101
	DH°_{fO} J/mol J/mol K	S°_{O} J/mol K	CP
(3rd Law)	-1533838 ± 9898	250.717 ± 22.571	252.806 ± 25.101

Since the predicted dissociation pressure of this complex is only 1 Torr at 20°C and 8 Torr at 40°C, formation of this complex is credible at conditions that might prevail during, for example, disposal of cascade cleanup gases.

ClF_5 and BF_3 are reported not to form a stable complex^{14,15}. From the experimental methods commonly used by that group, this can be taken to imply that such a complex, if it can form, would have a dissociation pressure in excess of an atmosphere or so at -78°C or below. From correlations and trends among the properties of other (known) complexes containing either ClF_4^+ or BF_4^- , estimates for each of the relevant thermodynamic properties of this (hypothetical) complex can be made.

	DH_f°	${}_s\text{O}$	CP
	J/mol	J/mol K	
	J/mol K		
(Estimate)	-1430710 ± 8581	247.590 ± 23.069	182.668 ± 18.428

Combining these with properties for the dissociation products $\text{ClF}_5(\text{g})$ and $\text{BF}_3(\text{g})$ (Appendix C), we derive the change in thermodynamic properties on dissociation:

Dissociation	$\text{DH}^\circ_{\text{dis}}$	$\text{DS}^\circ_{\text{dis}}$	DCP_{dis}
	J/mol	J/mol K	
	J/mol K		
(Estimate)	58653 ± 8581	317.504 ± 23.069	-32.600 ± 18.428

from which, in turn, K_p can be derived:

$$\ln K_p = 64.4467 - 8223.2 / T - 3.92080 \ln T$$

For this complex,

$$K_p = P(\text{ClF}_5) P(\text{BF}_3)$$

Naturally, the uncertainty in the prediction of K_p or of dissociation pressure is rather large. From this equation for K_p , however, we would predict that the dissociation pressure of this complex would reach 1 atmosphere at a temperature of $-90 \pm 30^\circ\text{C}$. Since the vapor pressure of ClF_5 is only about 0.014 atm and that of BF_3 about 1.7 atm at -90°C , it is not clear that this compound would be stable (with the

predicted thermodynamic properties) relative to the liquid phases of the constituents. This is consistent with the lack of observation of the compound. To reiterate, the properties listed above are purely estimates, and have no direct basis in experimental evidence for the existence of this compound.

No report on the existence or stability of this compound was found in the literature search. From correlations and trends among the properties of known complexes containing either ClF_4^+ or PF_5^- , estimates for each of the relevant thermodynamic properties of this (hypothetical) complex can be made.

	DH_gO	s°	CP
	J/mol	J/mol K	
	J/mol K		
(Estimate)	-1896587 ± 10072	305.156 ± 28.433	230.448 ± 20.405

Combining these with properties for the dissociation products $\text{ClF}_3(\text{g})$ and $\text{PF}_5(\text{g})$ (Appendix C), we derive the change in thermodynamic properties on dissociation:

Dissociation	$\text{DH}^\circ_{\text{dis}}$	$\text{DS}^\circ_{\text{dis}}$	DCP_{dis}
	J/mol	J/mol K	
	J/mol K		
(Estimate)	65742 ± 10072	306.393 ± 28.433	-48.449 ± 20.405

from which, in turn, K_p can be derived:

$$\ln K_p = 75.8773 - 9644.2 / T - 5.82700 \ln T$$

For this complex,

$$K_p = P(\text{ClF}_3)P(\text{PF}_5)$$

Naturally, the uncertainty in the prediction of K_p or of the dissociation pressure is rather large. From this equation for K_p , however, we would predict that the dissociation pressure of this complex would reach 1 atmosphere at a temperature of $-64 \pm 35^\circ\text{C}$. Experimental investigation of the behavior of the constituent gases at below this temperature range would be necessary to determine the validity of this prediction. To reiterate, the properties listed above are purely estimates, and have no direct basis in experimental evidence for the existence of this compound.

ClF₅ -- AsF₅

The existence of a complex of ClF₅ and AsF₅ was reported by Christie¹⁶. The adduct should be considered a complex of ClF₄⁺ and AsF₆⁻. Like related compounds, it reacts violently with water or organic materials.

Christie measured dissociation pressures over the temperature range -31 to 10°C and fit the data to the following equation:

$$\log P(\text{Torr}) = 12.2008 - 2763.6 / T(\text{K})$$

The data from which this was derived were also reported. Those data contained an apparent typographical error (a listed value of 226 Torr most probably should have been listed as 266 Torr - otherwise that point lay considerably outside the apparent scatter in the other measurements about the fitted equation).

The reported data points (with the one probable typographical error corrected) were analyzed per the second law method (but incorporating the additional heat capacity dependent parameter, as outlined in Appendix A). The resulting equation for K_p is:

$$(2\text{nd Law}) \quad \ln K_p = 96.0670 - 14901.1 / T - 8.29405 \ln T$$

An independent estimate of entropy for the complex was made and used to calculate an equation for K_p per the third law method as outlined in Appendix A. The resulting equation for K_p is:

$$(3\text{rd Law}) \quad \ln K_p = 94.1696 - 14398.7 / T - 8.29405 \ln T$$

For this complex, K_p = P(ClF₅) P(AsF₅)

The calculated values for enthalpy of dissociation and formation, along with the entropy and heat capacity values used are:

Dissociation	DH ^o _{dis}	DS ^o _{dis}	DC _{p,dis}
	J/mol	J/mol K	

	J/mol K		
(2nd Law)	103335 ± 917	336.878 ± 3.298	-68.961 ± 21.447
(3rd Law)	99157 ± 7727	321.101 ± 29.166	-68.961 ± 21.447
	DH _f ^o	S ^o	CP
	J/mol	J/mol K	
	J/mol K		
(2nd Law)	-1576519 ± 917	297.243 ± 3.298	262.421 ± 21.447
(3rd Law)	-1572342 ± 7727	313.019 ± 29.166	262.421 ± 21.447

The two sets of values are statistically consistent with one another. There seems to be no reason to reject the 2nd Law-derived values which have much lower apparent uncertainty. For this reason, the second law values above are recommended.

Gaseous ClF₃ can occur in equilibrium with ClF and F₂. The equilibrium constant for this process has been measured and fit to the following equation¹⁷:

$$\ln K_p = 9175 / T - 21.30$$

where

$$K_p = \frac{P(\text{ClF}_3)}{P(\text{ClF}) P(\text{F}_2)}$$

and the units of P here are atm (not bar). The data were taken over the temperature range 211 to 271°C. Extrapolation of this K_p to room temperatures suggests that mixtures of ClF₃ and F₂ will form ClF nearly to the extent permitted by the available reactants, but in general, this seems to be kinetically inhibited below about 200°C. The ClF₃*AsF₅ complex has a relatively high dissociation pressure (ca. 2/3 bar at 20°C and about 4 bar at 50°C), much higher than the corresponding ClF₃*AsF₃ complex. The ClF₃*AsF₅ complex should not be expected to play a significant role in cascade cleanup operations unless by some heretofore unobserved phenomenon (such as catalysis of formation of ClF₃) were to occur.

Christe¹⁸ reported the existence of the complex $\text{ClF}_6 \text{AsF}_5$ (and also an analogous SbF_6 complex). This might be thought of as being formed from AsF_5 and ClF_7 -- except that ClF_7 apparently does not exist as a stable gaseous species. This complex is only formed under circumstances in which significant chemical energy is provided by the reactants. Christe's synthesis involved reacting AsF_5 with KrF_2 to form $\text{KrF}^+\text{AsF}_6^-$. When this in turn was exposed to ClF_5 the $\text{ClF}_5^+\text{AsF}_6^-$ complex formed. These processes were carried out at -78°C and -142°C respectively. The complex, however, was stable to thermal decomposition to 110°C , dissociating above that temperature to AsF_5 , ClF_5 and F_2 . This stability is probably kinetic rather than thermodynamic, so no attempt will be made to deduce properties for this complex, which is unlikely to play any role in GDP operations.

The existence of a complex of ClO_2F and BF_3 (that is, $\text{ClO}_2^+\text{BF}_4^-$) has been reported by several groups. On the subject of thermal stability, Schmeisser¹⁹ reported only that the complex was volatile above -78°C . Christe²⁰, however, measured dissociation pressures over the temperature range -23 to 22°C and fit to the following equation:

$$\log P(\text{Torr}) = 11.1482 - 2623.1 / T(\text{K})$$

Rosenthal²¹ also measured dissociation pressures over a narrower temperature range (11 to 23°C), obtaining results in agreement with Christe's work. In both cases, the pressure and temperature data were reported. These data are analyzed per the second law method (but incorporating the additional heat capacity dependent parameter, as outlined in Appendix A) yielding an equation for K_p of:

$$\text{(2nd Law)} \quad \ln K_p = 62.6859 - 13163.7 / T - 3.9208 \ln T$$

In addition, an independent estimate of entropy for the complex is used to allow calculation of K_p per the third law method as outlined in Appendix A. The resulting equation for K_p is:

$$\text{(3rd Law)} \quad \ln K_p = 66.4772 - 14229.4 / T - 3.9208 \ln T$$

For this complex,

$$K_p = P(\text{ClO}_2\text{F}) P(\text{BF}_3)$$

The calculated values for enthalpy of dissociation and formation, along with the entropy and heat capacity values used are:

Dissociation	$\text{DH}^\circ_{\text{dis}}$	$\text{DS}^\circ_{\text{dis}}$	DCP_{dis}
	J/mol	J/mol K	
	J/mol K		
(2nd Law)	99730 ± 592	302.864 ± 2.072	-32.600 ± 17.091
(3rd Law)	108591 ± 5038	334.387 ± 17.856	-32.600 ± 17.091

	ΔH_f°	s°	C_p
	J/mol	J/mol K	
	J/mol K		
(2nd Law)	-1260621 ± 592	229.865 ± 2.072	142.039 ± 17.091
(3rd Law)	-1269482 ± 5038	198.342 ± 17.856	142.039 ± 17.091

The complex's entropy as derived by the 2nd Law method differs by nearly two standard deviations from the value via the density-entropy correlation (and used in the third law method). The statistics for the 2nd Law values are very good however, and the temperature range reasonably wide. The 2nd law values are therefore (with some reservations) recommended.

Dissociation pressures for the complex of ClO_2F and PF_5 (i.e. $\text{ClO}_2\text{F} \cdot \text{PF}_5$) were reported by Rosenthal²², were measured over the temperature range -5 to 9°C. The data from which this was derived were also reported. The narrow temperature range of this data suggests that 2nd Law results should be viewed with caution.

The experimental data points were analyzed per the second law method (but incorporating the additional heat capacity dependent parameter, as outlined in Appendix A). The resulting equation for K_p is:

$$\text{(2nd Law)} \quad \ln K_p = 76.2466 - 13024.2 / T - 5.82700 \ln T$$

An independent estimate of entropy for the complex is used to allow calculation of K_p per the third law method as outlined in appendix A. The resulting equation for K_p is:

$$\text{(3rd Law)} \quad \ln K_p = 78.5086 - 13647.7 / T - 5.82700 \ln T$$

For this complex,

$$K_p = P(\text{ClO}_2\text{F}) P(\text{PF}_5)$$

The calculated values for enthalpy of dissociation and formation, along with the entropy and heat capacity values used are:

Dissociation	$\text{DH}^\circ_{\text{dis}}$ J/mol J/mol K	$\text{DS}^\circ_{\text{dis}}$ J/mol K	DCP_{dis}
(2nd Law)	93845 ± 1496	309.464 ± 5.411	-48.449 ± 18.839
(3rd Law)	99029 ± 6227	328.271 ± 22.589	-48.449 ± 18.839
	$\text{DH}^\circ_{\text{fo}}$ J/mol J/mol K	S° J/mol K	CP

(2nd Law)	-1713524 ± 1496	269.720 ± 5.411	189.819 ± 18.839
(3rd Law)	-1718708 ± 6227	250.913 ± 22.589	189.819 ± 18.839

Though the temperature range of the data is only 14° degrees, the 2nd Law results (perhaps fortuitously) fall well within the estimated uncertainty band of the 3rd law-derived values, and there is no particular reason to reject their temperature dependent information in favor of apparently less certain values derived from 3rd law method.

The existence of an adduct of ClO_2F and AsF_5 (an ionic complex of ClO_2^+ and AsF_6^-) has been reported numerous times. Like other such complexes, ClO_2AsF_5 reacts explosively on contact with (condensed) water or organics.

Data relevant to the thermal stability of the complex was reported by Christe²³ and by Schmeisser^{24,25}. These sources contain only very limited information relevant to the dissociation pressure of this complex. The following statements (from the above references, in order) will be interpreted as indicated:

1. "...no significant dissociation pressure at room temperature"
will be taken to indicate that at 22°C , $P = 0.5 \times 4.0^{\pm 1}$ Torr.
2. "...volatile in high vacuum at 50°C "
will be taken to indicate that at 50°C , $P = 20 \times 3^{\pm 1}$ Torr.
3. "...complex melts at 80°C [in a sealed vial]"
will be taken to indicate that the material is still somewhat stable at that temperature, and has not completely sublimed; from this we will infer that at 80°C , $P = 150 \times 5^{\pm 1}$ Torr.

The first and third observations would ordinarily be taken to indicate only upper limits to the dissociation pressure, but considering the positive observation of volatility in the second statement, it is likely that the actual pressures lie in the range indicated.

A synthetic data set was generated embodying the above-mentioned interpretations, and treated according to the third law method. Due to the extremely limited and subjective nature of the data, the 2nd law method cannot be used to provide a reliable equation for K_p or estimates of the related thermodynamic parameters for the dissociation of this complex. The 3rd law method equation for K_p is:

$$\text{(3rd Law)} \quad \ln K_p = 97.3892 - 19052.8 / T - 8.29405 \ln T$$

where for this complex.

$$K_p = P(\text{ClO}_2\text{F}) P(\text{AsF}_5)$$

The calculated values for enthalpy of dissociation and formation, along with the entropy and heat capacity values used are:

Dissociation	$\text{DH}^{\text{a}}_{\text{dis}}$ J/mol J/mol K	$\text{DS}^{\text{a}}_{\text{dis}}$ J/mol K	DCP_{dis}
(3rd Law)	137854 ± 10059	347.871 ± 22.856	-68.961 ± 19.727
	DH_{fo} J/mol J/mol K	s^{o} J/mol K	CP
(3rd Law)	-1399872 ± 10059	253.885 ± 22.856	221.793 ± 19.727

These values are necessarily rather uncertain given the qualitative and subjective nature of the data. The above estimates, however, suggest a dissociation pressure for this complex at 20° of 1 Torr and at 50°C of 13 Torr (with a predicted error of about 30%). Since ClO_2F is a common reaction product of the reaction of ClF_3 with the products of moist air inleakage (water vapor itself, water of hydration or UO_2F_2), the complex ClO_2AsF_6 could clearly play a role in the behavior of cleanup treatment gases if AsF_5 were locally present to any significant degree. Furthermore, ClF_2AsF_6 (the complex of ClF_3 and AsF_5), when exposed to moisture (with the complex in excess) will be converted to ClO_2AsF_6 .²⁶

The existence of a complex of ClF_3O and BF_3 was reported by Christe²⁷. The resulting adduct should be considered a complex of ClF_3O^+ and BF_4^- . The complex is a white, crystalline substance that reacts violently with liquid water. The only comment made relative to the thermal stability of this complex was that "no dissociation pressure was observed at 20°C". Based on other work of Christe's of this period, we will take this to mean that the dissociation pressure was less than a Torr or so, but this provides only an upper limit to the pressure.

Quantitatively, we will estimate that at 20°C, $P \leq 0.5 \times 4^{\frac{1}{2}}$ Torr (that is, the dissociation pressure is less than 0.5 Torr, times or divided by 4). A synthetic data set embodying this interpretation was generated and analyzed via the third law method using an independent estimate of the entropy derived from the density-entropy correlation discussed in Appendix B and C. Since there is no temperature-dependent data, the 2nd law method cannot be used here. The resulting equation (or actuality, inequality) for K_p is:

$$(\text{3rd Law}) \ln K_p \leq 70.5115 - 18835.5 / T - 3.92080 \ln T$$

where

$$K_p = P(\text{ClF}_3\text{O}) P(\text{BF}_3)$$

Ignoring the data altogether, and using the interpolation method described in Appendix B for estimation of the enthalpy of formation of the complex based on interpolation within the $\text{ClF}_3\text{O}^+\text{MF}_x$ series, we obtain the K_p formula:

$$(\text{Estimate}) \ln K_p = 70.5115 - 16719.0 / T - 3.92080 \ln T$$

The calculated values for enthalpy of dissociation and formation, along with the entropy and heat capacity values used are:

Dissociation	$\text{DH}^{\circ}_{\text{dis}}$	$\text{DS}^{\circ}_{\text{dis}}$	DCP_{dis}
	J/mol	J/mol K	
	J/mol K		
(3rd Law)	$\geq 146888 \pm 7461$	367.930 ± 17.131	-32.600 ± 17.761

(Estimate)		129291 ± 11149	367.930 ± 17.131	-32.600 ± 17.761
		$DH_{f,0}$	S^0	CP
		J/mol	J/mol K	
		J/mol K		
(3rd Law)	$\leq$	-1430809 ± 7461	190.295 ± 17.131	163.291 ± 17.761
(Estimate)		-1413212 ± 11149	190.295 ± 17.131	163.291 ± 17.761

The ("3rd Law") limiting values for the enthalpies lie about one and a half standard deviations outside the estimated error band of the purely estimated value, not a particularly large discrepancy considering the dearth of actual data. The implication of the two estimates is that the limiting value derived by the 3rd law method approximates the actual value. Hence the recommended value will be the 3rd Law estimate, with the " $\leq$ " or " $\geq$ " signs dropped.

ClF₃O -- PF₅

The existence of a complex of ClF₃O and PF₅ was reported by Bougon²³, the adduct being interpreted as a complex of ClF₂O⁺ and PF₆⁻. The only information reported regarding the thermal stability of this compound was that the dissociation pressure at 25°C was 3.5 Torr. Obviously the 2nd law method cannot be used in this case, but using an independent estimate of entropy for the complex, the third law method can be applied to yield an estimate for K_p:

$$(3rd\ Law) \quad \ln K_p = 81.9204 - 18140.1 / T - 5.82700 \ln T$$

where for this complex

$$K_p = P(ClF_3O) P(PF_5)$$

The calculated values for enthalpy of dissociation and formation, along with the entropy and heat capacity values used are:

Dissociation	DH ^o _{dis} J/mol J/mol K	DS ^o _{dis} J/mol K	DCP _{dis}
(3rd Law)	136381 ± 6717	356.638 ± 22.528	-48.449 ± 19.636
	DH _{f,o} J/mol J/mol K	s ^o J/mol K	CP
(3rd Law)	-1879090 ± 6717	248.042 ± 22.528	211.071 ± 19.636

ClF₃O -- AsF₅

A complex of ClF₃O and AsF₅ was reported by Christie²⁹. It is a white, crystalline, hygroscopic material which reacts violently with liquid water. No explicit information was found regarding the thermal stability of this complex other than the comment that there was no significant dissociation pressure exhibited at 20°C. This will be interpreted to indicate that at 20°C, $P \leq 0.5 \times 10^{-1}$ Torr.

Using this limit and an independent estimate of entropy for the complex, we obtain

$$(3rd\ Law) \quad \ln K_p \leq 100.1909 - 20253.3 / T - 8.29405 \ln T$$

where

$$K_p = P(ClF_3O) P(AsF_5)$$

Ignoring the data altogether, and using the interpolation method described in Appendix B for estimation of the enthalpy of formation of the complex by interpolation within the ClF₃O*MF_x series from chemical trends in similar complex series, we obtain the K_p formula:

$$(Estimate) \quad \ln K_p = 100.1909 - 23396.9 / T - 8.29405 \ln T$$

The corresponding values for enthalpy of dissociation and formation, along with the entropy and heat capacity values used are:

Dissociation	DH ^a _{dis}	DS ^b _{dis}	DCP _{dis}
	J/mol	J/mol K	
	J/mol K		
(3rd Law)	≥ 147835 ± 8725	371.166 ± 23.054	-68.961 ± 20.609
(Estimate)	173973 ± 10088	371.166 ± 23.054	-68.961 ± 20.609
	DH _f ^c	S ^d	CP
	J/mol	J/mol K	
	J/mol K		

(3rd Law)	$\leq$	-1532884 ± 8725	256.086 ± 23.054	243.045 ± 20.609
(Estimate)		-1559022 ± 10088	256.086 ± 23.054	243.045 ± 20.609

The pure estimates (annotated as "Estimate", above) lie in on the correct side of the limits derived by the 3rd law method. Uncertain as they are, these estimated values represent the best available thermal stability parameters for this complex.

The above recommended equation for K_p suggests that the dissociation pressure of $\text{ClF}_2\text{OAsF}_6$ will be 0.002 Torr at 20°C and 0.06 Torr at 50 C. Only above 100 to 150 C does the dissociation pressure reach an appreciable fraction of an atmosphere. This high stability would favor its formation in a GDP cleanup environment except for the fact that the precursor, ClF_3O , is apparently quite unstable itself relative to other chlorine oxyfluorides or fluorides. Its reported syntheses routes³⁰ involve energy input (in the form of UV radiation, or starting with very unstable reactants such as Cl_2O) so it is not likely to be present in GDP applications. The author knows of no direct observation of ClF_3O in a cascade-related environment. For this reason, it is likely that this complex will not play a role in AsF_5 -related chemistry in the GDPs.

2.1 FO_2 Complexes

A complex of FO_2 with BF_3 was described by Keith³¹ and complexes of FO_2 with PF_5 and AsF_5 were described by Young³². All are formed by reaction of F_2O_2 with MF_x ($M = \text{B}, \text{P}, \text{or As}$) form $\text{O}_2^+ \text{MF}_{x+1}^-$ and F_2 . The complexes are stable at temperatures ranging up to room temperature, but thermally decompose per

at varying temperatures (the BF_3 complex at 0 to 25°C; the AsF_5 complex in the vicinity of 100°C). This decomposition does not appear to be reversible, so it is plausible that temperature effects are kinetic and temperature-dependent behavior can therefore not be reasonably used to estimate thermodynamic parameters for the complexes. Since these complexes are formed only from a highly unstable precursor, it is unlikely that they will play a role in GDP environments.

H₃O⁺ -- BF₃

The existence of a complex of H₂O, HF, and BF₃ was reported by Christie³³. The complex is considered to be a complex of H₃O⁺ and BF₄⁻. It was formed by precipitation from a solution of BF₃ in anhydrous HF when traces of moisture were added to the solution.

Only a single dissociation pressure was reported for this complex, namely 4 Torr at 22°C. Since the melting point of the complex is reported to be 0°C, this pressure is actually for the liquid (or perhaps solution). For lack of ready means of estimating the thermodynamic properties of this liquid complex, the property estimation method assumed the condensed phase to be a solid. From an independent estimate of entropy and heat capacity for the complex K_p is calculated per the third law method as:

$$(3rd\ Law) \quad \ln K_p = 72.1246 - 22569.7 / T - 2.57658 \ln T$$

where, for this complex,

$$K_p = P(H_2O) P(HF) P(BF_3)$$

The resulting values for enthalpy of dissociation and formation, along with the entropy and heat capacity estimates used are:

Dissociation	DH ^o _{dis} J/mol J/mol K	DS ^o _{dis} J/mol K	DCP _{dis}
(3rd Law)	181269 ± 4367	456.198 ± 14.602	-21.423 ± 8.734
	DH _f ^o J/mol J/mol K	S ^o J/mol K	CP
(3rd Law)	-1831262 ± 4367	160.771 ± 14.602	137.044 ± 8.734

No report of the existence of this complex was found in the literature reviewed, though based on general stability trends, it is likely to be stable. From correlations and trends among the properties of other (known) complexes containing either H_3O^+ or PF_5 , estimates for each of the relevant thermodynamic properties of this (hypothetical) complex can be made.

	DH_3O	${}_s\text{O}$	CP
	J/mol	J/mol K	
	J/mol K		
(Estimate)	-2301882 ± 8481	218.337 ± 19.830	184.824 ± 11.721

Combining these with properties for the dissociation products (Appendix C), we derive the change in thermodynamic properties on dissociation:

Dissociation	$\text{DH}^\circ_{\text{dis}}$	$\text{DS}^\circ_{\text{dis}}$	DCP_{dis}
	J/mol	J/mol K	
	J/mol K		
(Estimate)	193101 ± 8481	445.087 ± 19.830	-37.272 ± 11.721

from which, in turn, K_p can be derived:

$$\ln K_p = 83.5552 - 24561.1 / T - 4.48278 \ln T$$

For this complex,

$$K_p = P(\text{H}_2\text{O}) P(\text{HF}) P(\text{PF}_5)$$

Naturally, the uncertainty in the prediction of K_p or of the dissociation pressure of this complex is rather large. From this equation for K_p , however, we would predict that the dissociation pressure of this complex at 25°C would be about 1 Torr, and based on chemical trends, this complex should readily form under the proper conditions. To reiterate, the properties listed above are purely estimates, and have no direct basis in experimental evidence for the existence of this compound.

A complex of H_2O , HF , and AsF_5 was observed by Christie³⁴, who considered it as a complex of the ionic species H_3O^+ and AsF_6^- . Related complexes ($\text{H}_2\text{O AsF}_5$ and H OFAsF_5) were also observed^{35,36}. These can be considered analogs of the H_3O^+ complex in which the H_2O component is replaced with H_2O_2 and HOF , respectively). These two complexes are less stable than $\text{H}_2\text{O-HF-AsF}_5$, tend to thermally decompose to it, and will not be treated further.

For the $\text{H}_2\text{O-HF-AsF}_5$ complex, only very limited stability information was reported, namely that "thermal dissociation occurred in a DSC [differential scanning calorimeter] at 193°C ". This statement will be taken to indicate that at 193°C , $P = 300 \times 3^{\pm 1}$ Torr.

Due to the extremely limited and qualitative data, the 2nd law method cannot be used. From an independent estimate of entropy for the complex (using the density-entropy correlation discussed in Appendix B and C), a formula for K_p can be derived:

$$(3\text{rd Law}) \quad \ln K_p = 101.8475 - 30388.3 / T - 6.94983 \ln T$$

where for this complex,

$$K_p = P(\text{H}_2\text{O}) P(\text{HF}) P(\text{AsF}_5)$$

The associated values for enthalpy of dissociation and formation, along with the entropy and heat capacity values used are:

Dissociation	DH^{dis} J/mol J/mol K	DS^{dis} J/mol K	DCP^{dis}
(3rd Law)	235435 ± 12886	459.796 ± 20.364	-57.784 ± 13.057
	DH_{eO} J/mol J/mol K	S^{O} J/mol K	CP

(3rd Law)

-1986556 ± 12886

226.199 ± 20.364

216.798 ± 13.057

The predicted dissociation pressures at 20°C and 50°C are 0.002 and 0.05 Torr. Thermal removal of this compound would require fairly high temperatures, though it would probably be susceptible to fluorination (attack of the H₂O component by F₂ or ClF₃). It is a plausible product of the continued hydrolysis of ClO₂AsF₅, particularly if the process occurred in a solution phase. It is not clear from the literature how readily this material will form from the gaseous constituents absent a liquid phase.

SF₄ -- BF₃

The series of complexes whose cationic precursor is SF₄ are probably not of direct relevance to uranium enrichment processes. These complexes, however, have been more thoroughly studied than most, and their data form a more complete picture of the differences in stability within a complete series MF_x⁺BF₄⁻... MF_x⁺PF₆⁻... MF_x⁺AsF₆⁻. Thermodynamic values for the SF₄ series improve the reliability of predictions of the properties of similar complexes for which stability information is limited or lacking altogether, and it is for this reason that the SF₄ series has been examined.

Stability data on the complex of SF₄ and BF₃ was reported by Seel³⁷ and by Bartlett³⁸. Seel measured dissociation pressures over the temperature range 1 to 56°C and fit that data to the following equation:

$$\log P(\text{Torr}) = 11.3400 - 2783.0 / T(\text{K})$$

Except for the highest and lowest data points, Seel did not list the data from which this equation was derived in his article. Bartlett likewise measured dissociation pressures and fit them to a similar equation:

$$\log P(\text{Torr}) = 11.1100 - 2716.0 / T(\text{K})$$

but did not list either the pressure data nor the temperature range over which it was taken. The calculated dissociation pressures for the two equations lie within 5% of one another throughout the data range of Seel's work.

A synthetic data set was generated over Seel's reported temperature range by use of the two reported endpoints and computed pressures between those extremes. Synthetic data points were calculated from both Seel's equation and from Bartlett's, such that there were an equal number from each equation. This synthetic data set was analyzed per the second law method, incorporating the additional heat capacity dependent parameter as outlined in Appendix A. The resulting equation for K_p is:

$$\text{(2nd Law)} \quad \ln K_p = 63.15544 - 13775.3 / T - 3.92080 \ln T$$

An independent estimate of entropy for the complex was also made and used to allow calculation of K_p per the third law method as outlined in Appendix A. The resulting equation for K_p is:

$$(3\text{rd Law}) \quad \ln K_p = 66.9576 - 14915.6 / T - 3.92080 \ln T$$

where for this complex,

$$K_p = P(\text{SF}_4) P(\text{BF}_3)$$

The corresponding values for enthalpy of dissociation, entropy, and heat capacity for these two methods are:

Dissociation	$\text{DH}_{\text{dis}}^{\text{B}}$ J/mol J/mol K	$\text{DS}_{\text{dis}}^{\text{B}}$ J/mol K	DCP_{dis}
(2nd Law)	104815 ± 542	306.768 ± 1.824	-32.600 ± 17.750
(3rd Law)	114287 ± 5851	338.381 ± 19.411	-32.600 ± 17.750
	DH_{rO} J/mol J/mol K	s^{O} J/mol K	CP
(2nd Law)	-2003598 ± 542	247.231 ± 1.824	162.944 ± 17.750
(3rd Law)	-2013070 ± 5851	215.618 ± 19.411	162.944 ± 17.750

The 2nd Law derived value for the entropy is more than two standard deviations different from the estimated entropy used in the 3rd Law method, and in the direction one might expect of the plausible type of systematic error one might encounter in these systems (namely the presence of a low partial pressure of reaction product gases, which proportionally might raise the lowest pressures more than the higher ones. There is, however, no overt indication in either reference for such a problem, and the two equations agree fairly well within the data range, as evidenced by the fairly small uncertainties in the derived 2nd Law enthalpy and entropy parameters (though [synthetic] data from two sources was used).

With some reservations, then, the 2nd Law values will be adopted for this system for purposes of further analysis.

The existence of a complex of SF_4 and PF_5 was reported by Rosenthal³⁹. Dissociation pressures for the complex were measured over the temperature range 0 to 24°C and the data from which this was derived were also reported. This data set is analyzed per the second law method, incorporating the additional heat capacity dependent parameter as outlined in Appendix A. The resulting equation for K_p is:

$$\text{(2nd Law)} \quad \ln K_p = 76.5781 - 13365.3 / T - 5.82700 \ln T$$

From an independent estimate of the entropy for the complex, K_p is also calculated using the 3rd Law method:

$$\text{(3rd Law)} \quad \ln K_p = 77.0621 - 13504.0 / T - 5.82700 \ln T$$

where for this complex,

$$K_p = P(\text{SF}_4) P(\text{PF}_5)$$

The corresponding values for the enthalpy of dissociation and formation, along with the entropy and heat capacity are:

Dissociation	$\text{DH}^\circ_{\text{dis}}$ J/mol J/mol K	$\text{DS}^\circ_{\text{dis}}$ J/mol K	DCP_{dis}
(2nd Law)	96681 ± 1456	312.220 ± 5.079	-48.449 ± 19.623
(3rd Law)	97835 ± 7337	316.244 ± 25.586	-48.449 ± 19.623
	$\text{DH}^\circ_{\text{fo}}$ J/mol J/mol K	S° J/mol K	CP

(2nd Law)	-2454252 ± 1456	288.234 ± 5.079	210.724 ± 19.623
(3rd Law)	-2455406 ± 7337	284.210 ± 25.586	210.724 ± 19.623

The temperature range of the data was fairly narrow, but the parameter values generated by the two methods agree very well. There seems no reason to reject the (superficially, at least) more precise 2nd Law results; these will be the values recommended.

The existence of a complex of SF_4 and AsF_5 was reported by Bartlett⁴⁰ and by Seel¹. The adduct should be considered a complex of SF_3^+ and AsF_6^- . Bartlett measured dissociation pressures and fit that data to the following equation:

$$\log P(\text{Torr}) = 10.26 - 3376 / T(\text{K})$$

Neither the data nor its temperature range were specified in the referenced article. For purposes of analysis, the relevant temperature range will be assumed to be 60 to 185°C (which yields dissociation pressures commonly encountered in such studies).

Seel made the following statements regarding stability of the complex:

1. "The vapor pressure at 20°C is about 10 Torr"
2. "The complex sublimates readily at 90°C"

The first statement is definitely at odds with Bartlett's equation, which predicts a dissociation pressure of 0.3 Torr at 20°C. The second is sufficiently vague that it may be consistent with Bartlett's predicted dissociation pressure of 2.6 Torr at 90°C, though that seems low for a "readily sublimable" material. Seel's work was done in a quartz system, and there is thus the possibility of reactions with materials of construction generating reaction product gases that confuse the measurement of dissociation pressure. This observation unfortunately throws into doubt the only quantitative reported value for the dissociation pressure of $\text{ClF}_3 \cdot \text{AsF}_5$, which was also reported in this same Seel article.

In the following analysis, a synthetic data set was generated over the above-mentioned temperature range using the equation of Bartlett, above. The Seel and Detmer points were not incorporated into the analysis.

This data set was analyzed per the second law method (incorporating the additional heat capacity dependent parameter, as outlined in Appendix A). The resulting equation for K_p is:

$$(2\text{nd Law}) \quad \ln K_p = 90.4098 - 18768.8 / T - 8.29405 \ln T$$

Using an independent estimate of the entropy for the complex, K_p was also calculated per the 3rd law method. The resulting equation is:

$$(3rd\ Law) \quad \ln K_p = 96.2436 - 21033.1 / T - 8.29405 \ln T$$

where for this complex,

$$K_p = P(SF_4) P(AsF_5)$$

The corresponding values for the enthalpies of dissociation and formation, along with the entropy and heat capacity values derived or used are:

Dissociation	DH°_{dis} J/mol J/mol K	DS°_{dis} J/mol K	DCP_{dis}
(2nd Law)	135493 ± 1947	289.841 ± 5.758	-68.961 ± 20.594
(3rd Law)	154319 ± 10136	338.346 ± 25.628	-68.961 ± 20.594
	DH°_{fO} J/mol J/mol K	S°_{O} J/mol K	CP
(2nd Law)	-2135404 ± 1947	333.185 ± 5.758	242.698 ± 20.594
(3rd Law)	-2154230 ± 10136	284.679 ± 25.628	242.698 ± 20.594

The 2nd Law values for the entropy of the complex is about two standard deviations different from the estimated entropy used for the 3rd Law method. It is quite possible that the relatively small uncertainties listed for the 2nd law-derived parameters is an artifact of use of a synthetic data set over a (perhaps inappropriately) wide temperature range. Nevertheless, there is no overt indication of systematic error in Bartlett's pressure-temperature data outside of this discrepancy between calculated and empirically estimated entropy, and one is loathe to discard apparently valid experimental data. The 2nd Law values will therefore be used for the purposes of further analysis, though with reservations.

2.2 Other Complexes

Table 1 indicates most of the complexes of AsF_5 for which literature reports were found. The intent of this report is to locate, determine, or estimate stability properties for AsF_5 complexes which conceivably could be a factor in cleanup treatments involved in GDP operations. Many of the complexes listed are not relevant largely because a reactant is not likely to be present in any significant quantity in such cleanups. Some complexes, however, *could* be relevant in other areas of GDP operations. Complexes with NaF or MgF_2 , for example, may be relevant to chemical trapping operations. A study of such complexes is, however, outside the scope of the present report. Two complexes that can be considered potentially relevant to the present study are those formed between AsF_5 and TcO_3F or UO_2F_2 .

$\text{TcO}_3\text{F} \text{ -- } \text{AsF}_5$

A stable complex of TcO_3F and AsF_5 was reported by Franklin⁴². It was formed in anhydrous HF solution and was reported to be "stable to vacuum pumping at room temperature for 2 hrs". This statement provides only a qualitative upper limit to the dissociation pressure of the complex. Tc compounds were not the focus of this report, and no other information was found from which one could make a reasonable estimate of thermodynamic properties for the complex, though it is possible that a more thorough search for such information would turn up such information. Certainly the appropriate experiments would be relatively straightforward, if complicated by radiological concerns in the use of TcO_3F .

Lacking any usable information at this time, however, no attempt will be made here to estimate K_p or thermodynamic values for this complex, though it may well be relevant to GDP operations.

A complex of approximate composition $\text{UO}_2\text{F}_2 \cdot 2\text{AsF}_5$ was reported by Katayama¹³ to be formed in anhydrous solution of HF. The solid complex was stable at -78°C , but dissociated at room temperature. Katayama estimated the free energy of dissociation of this complex as -9 kJ/mole , from which we can estimate the dissociation pressure at 298.15K (25°C) as being about 6 bar. This is not sufficiently stable to be a factor in GDP cleanup applications.

SUMMARY

The most relevant complexes within the present report's scope of concern are $\text{ClF}_2^+ \text{AsF}_6^-$, $\text{ClO}_2^+ \text{AsF}_6^-$ and $\text{H}_3\text{O}^+ \text{AsF}_6^-$; at low temperatures (i.e. in a cold trap) $\text{Cl}_2\text{F}^+ \text{AsF}_6^-$ might also become important. Figure 1 depicts the dissociation pressures of these complexes (assuming stoichiometric dissociation of the pure complexes) as a function of temperature, along with the estimated standard deviation of that each dissociation pressure. Of course, these three complexes could not simultaneously exist, as H_2O would quickly react with ClF_3 , and there would be competition for AsF_5 if more than one cation precursor (e.g. ClF_3 , ClO_2F , or ClF) were present. Prediction of behavior of a system containing multiple components would have to simultaneously consider the equilibria of the various potential competing processes. This can readily be accomplished using the thermodynamic values for each compound or component developed in this report using computational thermodynamics methods, for example the computer program SOLGAS⁴⁴.

Table 2 summarizes the values for the parameters used to calculate K_p from the equation

$$\ln K_p = A + B/T + C \ln T$$

where K_p is in bar^n and T is in K. In all cases discussed in this report, the parameter C is independently estimated. For parameter sets identified by the notation "2L", A and B are fitted from literature data per the "second law" method; in "3L" sets, the parameter A is derived from an independent estimate of the entropy of the complex, and B is fit from literature pressure vs. temperature data via the "third law" method. Parameter sets indicated by the notation "Est" contain values are estimated purely from chemical trends within this series of complexes without reference to any explicit data on the particular complex in question.

Next to each set of parameters (A, B, C) is the covariance matrix for the three parameters in that set. The entries in the matrix are:

$$\text{Covar} = \begin{vmatrix} \sigma_A^2 & \sigma_{AB} & \sigma_{AC} \\ \sigma_{AB} & \sigma_B^2 & \sigma_{BC} \\ \sigma_{AC} & \sigma_{BC} & \sigma_C^2 \end{vmatrix}$$

Entries such as σ_A^2 are the square of the standard deviation (or more properly "s", the estimate of " σ ") for the indicated parameter; terms such as σ_{AB} are covariance elements. This matrix is useful in estimating the standard deviation of the function $\ln K_p$ at any value of T . The values of the matrix elements derive from consideration of the statistics of the data fit and the uncertainty of estimated thermodynamic properties. The details of the use of the covariance matrix are discussed in Appendix A.

Conversion of K_p to dissociation pressure P_{dis} (under the assumption of stoichiometric dissociation of the pure complex) depends on the number of gaseous molecules formed per "molecule" of complex dissociating:

If	$AB(s) = A(s) + B(g)$	then	$K_P = P_{\text{dis}}$
If	$AB(s) = A(g) + B(g)$	then	$K_P = \frac{1}{4} P_{\text{dis}}^2$
If	$A_2B(s) = 2 A(g) + B(g)$	then	$K_P = \frac{4}{27} P_{\text{dis}}^3$
If	$ABC(s) = A(g) + B(g) + C(g)$	then	$K_P = \frac{1}{27} P_{\text{dis}}^3$

In Table 2, the recommended set of parameters are shown in boldface type; any others are entered in normal font.

Table 3 summarizes the values determined for the thermodynamic properties for each complex, along with their estimated standard deviation and notations indicating the method of derivation or estimation. The recommended set of values are indicated in boldface.

Figure 1 - Predicted dissociation pressures of some AsF_5 complexes

Table 2 **Summary of Kp parameters and covariance matrix elements**
Recommended parameter set is in boldface

Complex	Source	A	B	C	s ² (A)	s ² (B)	s ² (C)	s(AB)	s(AC)	s(BC)
CI2FBF4	(3L)	91.62377	-13345.6	-4.76693	303.9663	927868.7	6.717882	-11890.1	-44.9937	1715.24
CIF2BF4	(3L)	87.65725	-14307.2	-6.7769	338.2912	941770.8	7.452435	-15846.8	-49.9134	2206.24
	(2L)	85.27703	-13668.9	-6.7769	323.3976	529870.3	7.452435	-13085	-49.0921	1986.023
CIF4BF4	(Est)(X)	64.44665	-8223.22	-3.9208	228.0493	1501790	4.912211	-9809.14	-32.9	1464.576
CIO2BF4	(3L)	66.47724	-14229.4	-3.9208	194.1461	740647.3	4.225221	-9710.09	-28.2988	1256.218
	(2L)	62.6859	-13163.7	-3.9208	184.5572	315501.4	4.225221	-7610.98	-27.9226	1150.475
CIF2OBF4	(3L)	70.51152	-18835.5	-3.9208	208.9376	1210762	4.563136	-10355.3	-30.562	1360.307
H3OBF4	(3L)	72.12462	-22569.7	-2.57658	52.58021	373993	1.1034	-3113.53	-7.39013	328.9621
SF3BF4	(3L)	66.95757	-14914.5	-3.9208	209.8778	898541.8	4.557231	-10712.6	-30.5225	1355.624
	(2L)	63.15544	-13775.3	-3.9208	204.8357	412315	4.557231	-9155.74	-30.5494	1363.691
CI2FPF6	(Est)(X)	64.44665	-8223.22	-3.9208	228.0493	1501790	4.912211	-9809.14	-32.9	1464.576
CIF2PF6	(3L)	98.6141	-12103.2	-8.68309	389.0785	1013425	8.515416	-17574.2	-57.0328	2403.426
	(2L)	88.841	-10068.9	-8.68309	341.372	362399.6	8.515416	-11111.8	-53.914	1754.284
CIF4PF6	(Est)(X)	75.87726	-9644.24	-5.827	281.8745	2002704	6.023038	-12027.3	-40.3399	1795.769
CIO2PF6	(3L)	78.50858	-13647.7	-5.827	237.6749	1014541	5.133869	-12255.1	-34.3846	1526.008
	(2L)	76.24663	-13024.2	-5.827	225.1667	417845.1	5.133869	-9449.04	-33.9702	1411.779
CIF2OPF6	(3L)	81.92036	-18140.1	-5.827	257.5374	1148437	5.577542	-13326.5	-37.3561	1662.944

Table 2 Summary of Kp parameters and covariance matrix elements
Recommended parameter set is in boldface

Complex	Source	A	B	C	s ² (A)	s ² (B)	s ² (C)	s(AB)	s(AC)	s(BC)
H3OPF6	(Est)(X)	83.55523	-24561.1	-4.48278	94.82914	1217126	1.987191	-3968.2	-13.3094	592.4811
SF3PF6	(3L)	77.06208	-13504	-5.827	259.3235	1272633	5.569908	-13824.9	-37.305	1658.761
	(2L)	76.57812	-13365.3	-5.827	246.8456	481478.7	5.569908	-10656.6	-37.0526	1586.384
Cl2FAsF6	(3L)	121.3467	-19433.3	-9.14018	374.4158	934013.9	8.249967	-17041.2	-55.255	2392.914
	(2L)	118.7872	-18835	-9.14018	343.5532	489232.3	8.249967	-12488.6	-53.167	1904.919
ClF2AsF6	(3L)	117.2871	-19948.8	-11.1501	416.2158	2169381	9.114278	-20412.3	-61.0438	2715.254
	(2L)	105.865	-16497.7	-11.1501	1209.779	7.3E+07	9.114278	-259127	-61.2799	2786.612
ClF4AsF6	(3L)	94.16958	-14398.7	-8.29405	310.7848	1445435	6.653918	-16435.2	-44.5653	1967.44
	(2L)	96.067	-14901.1	-8.29405	286.9626	456259.8	6.653918	-11415.3	-43.6937	1736.665
ClO2AsF6	(3L)	97.38917	-19052.8	-8.29405	260.0816	1957461	5.629453	-13615.2	-37.7038	1667.496
	(2L)	110.3913	-23262.3	-8.29405	405.3063	1.6E+07	5.629453	-59291.1	-38.1548	1813.541
ClF2OAsF6	(Est)	100.1909	-23396.9	-8.29405	283.29	2013448	6.143898	-12268.7	-41.1494	1831.803
	(3L)(a)	100.1909	-20253.3	-8.29405	283.29	1647115	6.143898	-14520.8	-41.1494	1831.544
H3OAsF6	(3L)	101.8475	-30388.3	-6.94983	116.6242	2562009	2.466142	-7054.7	-16.5172	635.827
SF3AsF6	(3L)	96.24361	-21033.1	-8.29405	284.7084	1978747	6.135107	-15345.4	-41.0905	1740.569
	(2L)	90.4098	-18768.8	-8.29405	297.8586	930537.8	6.135107	-16616.9	-42.7457	2383.15

Notes (2L) Derived from (P,T) data and estimated Cp via 2nd Law method
 (3L) Derived from (P,T) data and estimated S and Cp via 3rd Law method
 (Est) Derived from thermodynamic values estimated from trends among similar complexes
 (a) Equation for Kp is an upper limit
 (X) No reports of the existence of this complex were found in the literature reviewed

Table 3: Recommended values for thermodynamic properties of complexes

	dHf ±	s(dHf)		S ±	s(S)		Cp ±	s(Cp)
2 ClF*BF ₃	-1335350 ±	5892	[3L]	193.882 ±	13.450	[A]	157.431 ±	21.550 [S]
ClF ₃ *BF ₃	-1391338 ±	747	[2L]	204.305 ±	2.617	[2L]	173.053 ±	22.698 [S]
ClF ₅ *BF ₃	-1430710 ±	8581	[N]	247.590 ±	23.069	[E]	182.668 ±	18.428 [S]
ClF ₃ O*BF ₃	-1430809 ±	7461	[3L][M]	190.295 ±	17.131	[A]	163.291 ±	17.761 [S]
ClO ₂ F*BF ₃	-1260621 ±	592	[2L][K]	229.865 ±	2.072	[2L][K]	142.039 ±	17.091 [S]
H ₃ OF*BF ₃	-1831262 ±	4367	[3L][F]	160.771 ±	14.602	[E]	137.044 ±	3.734 [S]
SF ₄ *BF ₃	-2003598 ±	542	[2L]	247.231 ±	1.824	[2L]	162.944 ±	17.750 [S]
2 ClF*PF ₅	-1796287 ±	8538	[N]	251.447 ±	16.794	[E]	205.211 ±	23.077 [S]
ClF ₃ *PF ₅	-1832382 ±	4828	[3L][K]	246.019 ±	22.148	[A][K]	220.833 ±	24.263 [S]
ClF ₅ *PF ₅	-1896587 ±	10072	[N]	305.156 ±	28.433	[E]	230.448 ±	20.405 [S]
ClF ₃ O*PF ₅	-1879090 ±	6717	[3L]	248.042 ±	22.528	[E]	211.071 ±	19.636 [S]
ClO ₂ F*PF ₅	-1713524 ±	1496	[2L]	269.720 ±	5.411	[2L]	189.819 ±	18.839 [S]
H ₃ OF*PF ₅	-2301882 ±	8481	[N]	218.337 ±	19.830	[E]	184.824 ±	11.721 [S]
SF ₄ *PF ₅	-2454252 ±	1456	[2L]	288.234 ±	5.079	[2L]	210.724 ±	19.623 [S]
2 ClF*AsF ₅	-1471278 ±	2448	[2L]	280.591 ±	9.999	[2L]	237.185 ±	23.882 [S]
ClF ₃ *AsF ₅	-1533838 ±	9698	[3L]	250.717 ±	22.571	[A]	252.806 ±	25.101 [S]
ClF ₅ *AsF ₅	-1576519 ±	917	[2L]	297.243 ±	3.298	[2L]	262.421 ±	21.447 [S]
ClF ₃ O*AsF ₅	-1559022 ±	10072	[3L][M]	256.086 ±	23.054	[A]	243.045 ±	20.609 [S]
ClO ₂ F*AsF ₅	-1399872 ±	10059	[3L]	253.885 ±	22.856	[A]	221.793 ±	19.727 [S]
H ₃ OF*AsF ₅	-1986556 ±	12886	[3L]	226.199 ±	20.364	[A]	216.798 ±	13.057 [S]
SF ₄ *AsF ₅	-2135404 ±	1947	[2L]	333.185 ±	5.758	[2L]	242.698 ±	20.594 [S]

Source Notes:

- [2L] This work - 2nd Law/3 parameter Kp equation
- [3L] This work - 3rd Law/3 parameter Kp equation
- [M] Combination of Interpolation as modified by "upper limit" information from literature stability reports
- [K] Narrow temperature range; 2L entropy > 1 sigma from density correlation estimate.
- [F] Complex melts in vicinity of data, a factor ignored in this analysis
- [N] Interpolation from dHf for various related complexes
- [A] density correlation/literature XRD density; value used in component density optimization
- [E] derived from one or more steps in arithmetic "chain" from density correlation
- [S] Est as sum of Cp for solid components

EXAMPLES OF USE OF DEVELOPED PARAMETERS

To illustrate the use of the information developed here, two sample scenarios will be considered. In the first, we will pose the following situation:

Scenario 1:

A gas mixture from a cleanup treatment at 35°C contains a partial pressure of ClO_2F of 30 Torr. We would like to answer the question, "What partial pressure of AsF_5 could lead to the formation of deposits of ClO_2AsF_6 ?"

$$T = 35^\circ\text{C} = 308.15 \text{ K}$$

The using the formula developed for K_p (Equation A-14, using the recommended parameters in Table 2) for the dissociation of the complex ClO_2AsF_6 , we calculate

$$K_p = 6.331 \times 10^{-6}$$

where

$$K_p = P(\text{ClO}_2\text{F}) P(\text{AsF}_5)$$

where the pressures units implicitly are bar. The partial pressure of ClO_2F was specified as 30 Torr, which converts to 0.03999 bar. Dividing, we obtain the estimate for the equilibrium partial pressure of AsF_5 over the complex as 0.0001583 bar, or 0.119 Torr. A partial pressure for AsF_5 below this value would lead to decomposition of the complex; above this value, to formation of the complex. These are, of course, conclusions about the equilibrium of the system, and cannot address the question of the rate at which the system would approach equilibrium.

We might also want to know how certain this estimate is. This question can be answered using the methods described in the "Error Propagation..." section of Appendix A in conjunction with the uncertainty data provided along with the K_p coefficients in Table 2.

From Table 2, we select the values for the elements of the covariance matrix (See Eqn A-23) for this particular $\ln K_p$ equation:

$$\text{Covar} = \begin{vmatrix} 260.08157 & -13615.19 & -37.70381 \\ -13615.19 & 1957461.3 & 1667.4965 \\ -37.70381 & 1667.4965 & 5.6294534 \end{vmatrix}$$

and the corresponding temperature function matrix (see Equation A-24) is

$$F(T) = \begin{vmatrix} 1 & 0.0032452 & 5.7305867 \\ 0.0032452 & 1.053 \times 10^{-5} & 0.0185967 \\ 5.7305867 & 0.0185967 & 32.839624 \end{vmatrix}$$

The estimated variance of $\ln K_p$ is given by summing the products of corresponding terms of the $F(T)$ and the covariance matrices; the result in this case is:

$$\sigma^2(\ln K_p) = 7.088$$

The estimated standard deviation of $\ln K_p$ is the square root of this, namely

$$\sigma(\ln K_p) = 2.662$$

This translates into a multiplier for K_p of

$$e^{\pm\sigma(\ln K_p)} = e^{\pm 2.662} = 14.33 \pm 1$$

where the notation 14.33 ± 1 means that the predicted value for K_p would be multiplied or divided by 14.33 to obtain the upper and lower bounds on the uncertainty (at the one standard deviation level). In this case, that implies that the equilibrium pressure of AsF_5 could be 14 times higher or lower than the predicted value based on the uncertainty in the K_p parameters. That may not be very accurate, but such are the consequences of relying on uncertain information.

Scenario 2:

In scenario 2, we postulate a gas mixture at one half atmosphere containing 30 Torr ClF , 20 Torr each ClF_3 and ClO_2F , 1000 ppm AsF_5 , the balance of the gas consisting of chemically inert species. The question posed is: "At what temperatures can complexes form from this gas mixture and which complexes form?" This involves a more complicated system, so to solve it, we resort to use of a computational thermodynamics program (SOLGAS) which can determine the equilibrium in complex systems. The program must be provided with the appropriate information, namely: (1) species information for each gaseous component mentioned above; (2) species information for the three complexes Cl_2FAsF_6 , ClF_2AsF_6 and ClO_2AsF_6 ; (3) the indicated pressure and (4) starting gas composition. Having done this, a number of runs were made at temperatures ranging from 0 to 150°C . The results are depicted graphically in Figure 2. At temperatures below 40°C , this particular gas mixture is predicted to form the complex ClO_2AsF_6 ; above this temperature, none of the three complexes is predicted to form.

Since AsF_5 is in short supply in this mixture relative to the chlorine fluorides, only that complex which is predicted to be the most stable forms. ClO_2AsF_6 was predicted to be slightly more stable than the ClF_3 complex (see Figure 1, which shows its dissociation pressure slightly lower), but the uncertainties in the K_p equation parameters make this by no means certain.

Figure 2 - Predicted complex formation in conjectural cleanup off-gas mixture

CONCLUSIONS

By examination of available literature data on the stability of complexes of AsF_5 , PF_5 and BF_3 and use of a variety of property estimation techniques, thermodynamic data has been estimated for several series of such materials. Since the bases of the data for several species are quite uncertain, the thermodynamic properties derived therefrom are also fairly uncertain. For that reason, quantitative estimates of the uncertainty have been developed along with the "best estimate" values for each quantity. "Best" estimate does not necessarily mean "good" -- in applying some of the results, predicted dissociation pressures can be uncertain by large multiples. More accurate prediction of behavior would require more accurate experimental information on the systems in question.

From the information developed, a tentative picture of the formation and behavior of the complexes of AsF_5 and related compounds begins to emerge. At moderate temperatures, low partial pressures of AsF_5 combined with either ClF_3 or ClO_2F could result in the formation of solid complexes. Solid deposits will tend to form and remain where the temperature is lowest, and will slowly dissociate and migrate away if either constituent gas were removed. Both complexes fume in moist air and react explosively with liquid water. $\text{ClF}_3 \cdot \text{AsF}_5$, if exposed to moisture from humid air, will first form the $\text{ClO}_2\text{F} \cdot \text{AsF}_5$ complex. Further reaction, however, may convert ClF_3 to ClO_3F (which forms no stable AsF_5 complex) or form $(\text{ClF})_2 \cdot \text{AsF}_5$ which is relatively unstable and would more readily dissociate than its precursors. However, there is a class of complexes (including $\text{H}_2\text{OF} \cdot \text{AsF}_6$ and $\text{H}_3\text{O} \cdot \text{AsF}_6$) whose members are even more stable to dissociation than are the ClF_3 and ClO_2F complexes. Thus, hydrolysis of the original complexes might also lead to the formation of the solid species H_3OAsF_6 , while ClF or ClO_3F would be lost as gases. Hydrolysis generates significant quantities of HF , and since the vapor pressure of $\text{HF-H}_2\text{O}$ solutions is significantly lower than that of water or HF alone, condensation of a liquid solution might occur during this process. This scenario is tentative at this point, but does explain many of the events that have been observed in certain auxiliary systems at both diffusion plants.

Appendix A

Thermodynamic Property Derivation Methods Used in this Report

The mathematical form of vapor pressure or dissociation pressure equations can be obtained from considerations of free energy change for the process under consideration:

has a free energy change given by

$$\Delta G_{\text{rxn}}^0(T) = \Delta G_{\text{f,products}}^0(T) - \Delta G_{\text{f,reactants}}^0(T) \quad (\text{A-2})$$

where "rxn" should be taken to indicate vaporization, sublimation, or dissociation, as appropriate to the particular case under consideration, $\Delta G_{\text{f,products}}^0(T)$ and $\Delta G_{\text{f,reactants}}^0(T)$ represents the sum of free energies of formation at temperature "T" of the products and reactants of the reaction under consideration. Throughout this report, the "reactant" will be a complex (e.g. $\text{ClF}_3 \cdot \text{BF}_3(\text{s})$) and the "products" will be its dissociation products (e.g. $\text{ClF}_3(\text{g})$ and $\text{BF}_3(\text{g})$). $\Delta G_{\text{rxn}}^0(T)$ for such a process is given by

$$\Delta G_{\text{rxn}}^0(T) = -R T \ln K_p \quad (\text{A-3})$$

and K_p is given to a good accuracy by the product of the partial pressures (expressed in the current standard units of bar) of the gaseous species. For the simple case of evaporation or sublimation:

and

This form is also valid for dissociation in which one product remains as a condensed phase:

For more the complicated dissociation reactions discussed in this report, the following apply:

K_p in principle is a measurable parameter. Commonly, pressure measurements over pure condensed phases can be interpreted per the reaction equation to deduce K_p . For example, in the two-component complex depicted in equation A-6, a measured dissociation pressure, P_{dis} , would be interpreted as consisting of 50% $P(A)$ and 50% $P(B)$. Thus

$$K_p = P(A)P(B) = (P_{\text{dis}}/2)(P_{\text{dis}}/2) = P_{\text{dis}}^2/4 \quad (\text{A-6a})$$

Similarly, for the processes depicted in (A-7) and (A-8), if a dissociation pressure is available, then

$$K_p = P^2(A)P(B) = (2P_{\text{dis}}/3)(P_{\text{dis}}/3) = \frac{4}{27} P_{\text{dis}}^3 \quad (\text{A-7a})$$

$$K_p = P(A)P(B)P(C) = (P_{\text{dis}}/3)(P_{\text{dis}}/3)(P_{\text{dis}}/3) = \frac{1}{27} P_{\text{dis}}^3 \quad (\text{A-8a})$$

So long as the reaction equations are written correctly (i.e. there are no additional species present which have been neglected, such as gas phase dimers or complex species, or solution effects), and so long as the pressure measured is due only to the species under consideration (i.e. no inert diluents or decomposition products of, e.g. wall reactions), the equations for K_p given in this report can be converted to dissociation pressures per the above.

An equation developed for K_p is appropriate to cases in which the gases are not present in the stoichiometric ratio depicted by the reaction equation, but a dissociation pressure equation explicitly assumes proper stoichiometry.

The functional form of the vapor or dissociation pressure equation is implicit in equation (A-3) when one notes that

$$\Delta G_{\text{rxn}}^0(T) = \Delta H_{\text{rxn}}^0(T) - T \Delta S_{\text{rxn}}^0(T) \quad (\text{A-9})$$

Combining (A-2) and (A-9) we get

$$\ln K_p(T) = -\Delta H_{\text{rxn}}^0(T) / RT + \Delta S_{\text{rxn}}^0(T) / R \quad (\text{A-10})$$

A functional form to which vapor pressure and dissociation pressure data are often fit is

$$\log P = A + B/T \quad (\text{A-11})$$

Comparing (A-10) and (A-11) we can see that the "A" parameter is related to the entropy change of the process and the "B" parameter is related to the enthalpy change. If ΔH_{rxn}^0 and ΔS_{rxn}^0 values are derived directly from the parameters in an equation of the form shown in (A-11), then it should be recognized that their values are most appropriate to the average

temperature in the data set from which the parameters were determined.

Since ΔH_{rxn}^0 and ΔS_{rxn}^0 vary with temperature, use of vapor or dissociation pressure data to deduce these parameters at standard conditions (i.e. 1 bar and 25°C) should take account of this temperature dependence to the extent the data and known or estimable thermodynamic properties warrant. The variation of enthalpy with temperature is given by:

$$\Delta H_{\text{rxn}}^0(T_2) - \Delta H_{\text{rxn}}^0(T_1) = \int_{T_1}^{T_2} \Delta C_{P,\text{rxn}}(T) dT \quad (\text{A-12})$$

where $\Delta C_{P,\text{rxn}}(T)$ is the difference in the constant pressure heat capacities of the products and reactants, analogous to the free energy difference shown in (A-2). The corresponding adjustment for entropy is

$$\Delta S_{\text{rxn}}^0(T_2) - \Delta S_{\text{rxn}}^0(T_1) = \int_{T_1}^{T_2} \Delta C_{P,\text{rxn}}(T)/T dT \quad (\text{A-13})$$

The values of ΔH_{rxn}^0 and ΔS_{rxn}^0 are not very sensitive to the precise value of $\Delta C_{P,\text{rxn}}(T)$ and temperature dependent changes in C_p tend to cancel. Since many of the thermodynamic parameters used in the analyses in this report are estimated and therefore of necessity somewhat uncertain, we will use the approximation that $\Delta C_{P,\text{rxn}}$ is a constant. Under this approximation, the integrals in equations (A-12) and (A-13) become

$$\Delta H_{\text{rxn}}^0(T_2) - \Delta H_{\text{rxn}}^0(T_1) = \Delta C_{P,\text{rxn}} (T_2 - T_1) \quad (\text{A-12a})$$

and

$$\Delta S_{\text{rxn}}^0(T_2) - \Delta S_{\text{rxn}}^0(T_1) = \Delta C_{P,\text{rxn}} \ln (T_2 / T_1) \quad (\text{A-13a})$$

The reason for dwelling on this temperature adjustment is that we often have or wish to derive values for enthalpy and entropy of formation at the standard reference temperature of 298.15K (25°C). Identifying T_1 with T and T_2 with 298.15, and combining equations (A-10), (A-12a), and (A-13a), we obtain an equation of the form

$$\ln K_p(T) = A + B/T + C \ln T \quad (\text{A-14})$$

where the parameters A, B, and C are to be identified with:

$$A = [\Delta S_{\text{rxn}}^0(298.15) - (1 + \ln 298.15) \Delta C_{P,\text{rxn}}] / R \quad (\text{A-14a})$$

$$B = - [\Delta H_{\text{rxn}}^0(298.15) - 298.15 \Delta C_{P,\text{rxn}}] / R \quad (\text{A-14b})$$

$$C = \Delta C_{P,\text{rxn}} / R \quad (\text{A-14c})$$

If one were to determine values for A, B, and C, for example by fitting pressure vs. temperature data to the above equation, then values for $\Delta H_{\text{rxn}}^{\circ}(298.15)$, $\Delta S_{\text{rxn}}^{\circ}(298.15)$, and $\Delta C_{\text{P,rxn}}$ can be determined by inverting the above equations, namely:

$$\Delta H_{\text{rxn}}^{\circ}(298.15) = -B R + 298.15 \Delta C_{\text{P,rxn}} \quad (\text{A-15a})$$

$$\Delta S_{\text{rxn}}^{\circ}(298.15) = A R + (1 + \ln 298.15) \Delta C_{\text{P,rxn}} \quad (\text{A-15b})$$

$$\Delta C_{\text{P,rxn}} = C R \quad (\text{A-15c})$$

While inclusion of the "C" term in the above equation can avoid fairly significant errors in the calculated value of $\Delta H_{\text{rxn}}^{\circ}(298.15)$ when extrapolating over a considerable temperature range, when fitting pressure data over the fairly narrow range typical of experimental studies, the results are fairly insensitive to its value. Conversely, fitting typical vapor pressure data directly to the above equation generally will result in a determination of C which provides a very unreliable estimate of $\Delta C_{\text{P,rxn}}$. In the various systems examined in this report, $\Delta C_{\text{P,rxn}}$ seems to be more accurately estimated *a priori*. We will therefore estimate $\Delta C_{\text{P,rxn}}$ in all cases. The reader is referred to Appendix B for an explanation of the methods used to perform this estimate.

Fixing the value of C, one is left with two parameters (A and B) to determine, one related to the entropy and one related to the enthalpy of the process under consideration. One can simply perform a linear regression on the rearranged equation

$$\ln K_{\text{p}}(T) - C \ln T = A + B/T \quad (\text{A-15})$$

and determine values for A and B, from which values for $\Delta H_{\text{rxn}}^{\circ}(298.15)$ and $\Delta S_{\text{rxn}}^{\circ}(298.15)$ can be determined per Eqns. (A-15a and A-15b). Such a method is sometimes known as the "2nd Law" method for determining enthalpy and entropy⁴⁵. The application of this method and the interpretation of results is fairly straightforward, but there are a few pitfalls. If the available pressure-temperature data cover a fairly narrow temperature range, or if there are systematic errors in the experimental data (for example, instrument calibration problems or the undetected presence of inert diluents), then the fitted parameters can have significant error. Error in A and B (and hence in $\Delta H_{\text{rxn}}^{\circ}(298.15)$ and $\Delta S_{\text{rxn}}^{\circ}(298.15)$) will be correlated, of course, in such a way that the experimental data are well-reproduced by the equation in the temperature range of the data. Use of the parameters outside this range, or use of the derived thermodynamic properties for other purposes, however, could lead to significant error.

An alternative method of data treatment is termed the "3rd Law" method. In this method, an independent value or estimate for entropy is used to determine parameter A, leaving only B (and $\Delta H_{\text{rxn}}^{\circ}(298.15)$) to be deduced from the pressure data. This method gets its name from the fact that generally the entropy estimates come from application of the third law of thermodynamics to the chemical species in the system, calculating the absolute entropy of each by integrating C_{p}/T from 0 K to the temperature of interest, or performing some theoretical equivalent treatment. It is often found, however, that even estimation methods for entropy

can be more accurate than values determined from the 2nd Law method⁴⁶.

In deciding between the two methods, one should carefully examine the uncertainty in the derived parameters based on both the statistics and the uncertainty in estimation methods used. In this report, both methods will be applied to literature data and recommended thermodynamic values will be based on a consideration of the uncertainty in the results.

There are cases, including those of most relevance to the problem at hand, in which only very limited pressure data are available -- one or two points only -- so no meaningful temperature dependence can be obtained via the 2nd Law method. Under such circumstances, the 3rd Law method allows the only means of predicting temperature dependence of dissociation pressures for such complexes.

Methods used for estimating $\Delta S_{rxn}^0(298.15)$ are discussed in Appendix B.

It should be noted that the above 2nd Law/3rd Law discussion applies as well to the case in which pressure-temperature data are fit to the more traditional "Arrhenius" form (Eqns A-10 and A-11), since these forms are simply variations on the three-parameter K_p equation in which C (and hence $\Delta C_{P,rxn}$) is taken to be zero.

Error Correlation and Propagation

The regression fitting of the experimental data is done per methods outlined in Meyer⁴⁷ and in Green and Margerison⁴⁸. Regression fitting of experimental data to determine one or more parameters yields not only information about those derived parameters, but also about their uncertainty. In fitting vapor pressure or dissociation pressure data to equations of the form

$$Y = A + B/T \quad (A-16)$$

the statistical estimate of the standard deviations of the fit parameters A and B are often given, e.g.

$$A \pm \sigma_A \quad \text{and} \quad B \pm \sigma_B \quad (A-17)$$

σ_A and σ_B can be used to generate estimates of the uncertainty of derived values, in this case of ΔH_{vap}^0 and ΔS_{vap}^0 . Rarely is the covariance σ_{AB} given, but parameters derived from fitting vapor pressure and dissociation pressure data are almost invariably highly correlated. The expected uncertainty in the dependent variable ("Y" above, which might be identified with "log P" or with " $\ln K_p - C \ln T$ ") at any given value of T will be

$$\sigma_Y^2 = \sigma_A^2 + \sigma_B^2/T^2 + 2\sigma_{AB} \quad (A-18)$$

The third term will generally cancel much of the contribution from the first and second for data sets of the type dealt with in this report. Ignoring the covariance may result in vastly

exaggerating the uncertainty of a predicted value of "Y", which is to say K_p , for the complexes considered in this report. For this reason, the covariance matrix for the linear regression is calculated along with the best fit parameter values.

We are using (on a trial basis) several equations and methods to fit the data. If we were to fit experimental data to determine all three parameters A, B, and C in equation (A-14) then the full covariance matrix could have terms for all elements of the matrix:

$$\text{Covar}_r = \begin{vmatrix} \sigma_{r,A}^2 & \sigma_{r,AB} & \sigma_{r,AC} \\ \sigma_{r,AB} & \sigma_{r,B}^2 & \sigma_{r,BC} \\ \sigma_{r,AC} & \sigma_{r,BC} & \sigma_{r,C}^2 \end{vmatrix} \quad (\text{A-19})$$

where we have used the subscript "r" to indicate that this matrix refers to the regression of the data, and does not contain contributions related to uncertainty in fixed parameters. Since, however, we have chosen to specify the value for C rather than fit it, all terms in the matrix with a subscript "C" will be zero. When using the 3rd law method, we also specify an estimated value for the entropy of all species, and hence of the parameter A. Only the $\sigma_{r,B}^2$ term of Covar_r will be non-zero in this case.

In addition to the statistical uncertainty determined in the data regression process, we must also consider the sometimes considerable uncertainty in the independently estimated values of ΔS_{rxn}^0 and $\Delta C_{p,rxn}$.

In the above data regression treatments, one or more parameters (S^0 and C_p for the complex) are externally specified (with an associated estimate of their standard deviation) prior to fitting the K_p equation and determining the remainder of the parameters. The error in these external parameters will affect the uncertainty in the results, but the values of the external parameters are correlated to those of the fitted parameters, so we cannot use the standard sort of "propagation of (uncorrelated) error" formulae to determine the overall uncertainties. Instead, a sensitivity analysis was carried out by varying the externally specified parameters systematically by plus and minus their estimated standard deviation. The computed standard deviation of this simple distribution is identical to the specified value of that standard deviation.

All possible permutations of each uncertain parameter variation were used, and the resulting fitted parameter values (A, B, and C in the K_p equation, and $\Delta H_{rxn}^0(298.15)$ and $\Delta S_{rxn}^0(298.15)$) derived therefrom) were recorded. For the thermodynamic properties, the standard deviation due to the sensitivity analysis was computed and combined with the statistical standard deviation computed at 298.15K to yield the listed estimate of the overall standard deviation for that parameter. For the A, B, and C parameters of the K_p equation, the list of calculated values was used to calculate the elements of a covariance matrix

$$\text{Covar}_s = \begin{vmatrix} \sigma_{s,A}^2 & \sigma_{s,AB} & \sigma_{s,AC} \\ \sigma_{s,AB} & \sigma_{s,B}^2 & \sigma_{s,BC} \\ \sigma_{s,AC} & \sigma_{s,BC} & \sigma_{s,C}^2 \end{vmatrix} \quad (\text{A-20})$$

per the formula:

$$\sigma_{s,PQ} = \langle PQ \rangle - \langle P \rangle \langle Q \rangle \quad (\text{A-21})$$

(where P and Q are two of the variables A, B, and C; if P = Q then the notation for σ_{PQ} changes, per convention, to σ_P^2 , and where the notation " $\langle Q \rangle$ " is meant to indicate the average value of the parameter Q among the list of values calculated during the several sensitivity runs. The subscript "s" indicates that this covariance matrix derives from the "sensitivity" analysis.

The two covariance matrices are combined by termwise addition, e.g.

$$\sigma_{PQ} = \sigma_{t,PQ} + \sigma_{s,PQ} \quad (\text{A-22})$$

which implicitly assumes that the various terms are uncorrelated to give the combined covariance matrix "Covar":

$$\text{Covar} = \begin{vmatrix} \sigma_A^2 & \sigma_{AB} & \sigma_{AC} \\ \sigma_{AB} & \sigma_B^2 & \sigma_{BC} \\ \sigma_{AC} & \sigma_{BC} & \sigma_C^2 \end{vmatrix} \quad (\text{A-23})$$

Not included are any uncertainties in accepted literature values for those thermodynamic properties for which such information is available. Only an estimate of the standard deviation of estimated thermodynamic values are included in the sensitivity analysis. Literature uncertainties in, say, $\Delta H_f^\circ(298.15)$ of chemically related compounds are often highly correlated (i.e. tracing back to the same uncertainty in some basic but uncertain value).

In the main text, only the basic equations for K_p the various complexes are presented, but in the Table 2 at the end of the main body of the report, values for all elements of the covariance matrix is given for each compound.

Use of the covariance matrix to predict the uncertainty in a calculated value for K_p will now be illustrated.

The appropriate method for use of the covariance, listed algebraically (for a two dimensional matrix) in equation (A-18), can perhaps more clearly be expressed in matrix form. For a three-term equation such as we are using, define a function matrix F(T) as:

$$F(T) = \begin{vmatrix} f_A^2 & f_A f_B & f_A f_C \\ f_A f_B & f_B^2 & f_B f_C \\ f_A f_C & f_B f_C & f_C^2 \end{vmatrix} \quad (\text{A-24})$$

where the functions f_A etc. are the functions in equation A-14 associated with each fitted

parameter, i.e. $f_A = 1$, $f_B = 1/T$ and $f_C = \ln T$. Thus, the $F(T)$ matrix has the value:

$$F(T) = \begin{vmatrix} 1 & 1/T & \ln T \\ 1/T & 1/T^2 & (\ln T)/T \\ \ln T & (\ln T)/T & (\ln T)^2 \end{vmatrix} \quad (A-25)$$

The estimate of the variance of $\ln K_p$ (i.e. the "dependent variable" of the fitting process in equation A-14) is given by the dot product of the function matrix and the covariance matrix:

$$\sigma^2(\ln K_p(T)) = F(T) \cdot \text{Covar} \quad (A-26)$$

In algebraic terms, this is:

$$\sigma^2(\ln K_p(T)) = \sum_{P,Q} f_P f_Q \sigma_{PQ} \quad (A-27)$$

To illustrate the use of the covariance matrix, consider the following case: During the fitting process for the dissociation pressure of $\text{ClF}_3^* \text{AsF}_5$ (for which very little data were available), the fit statistics for the 2nd Law method (applied to the 3 parameter equation for $\ln K_p$) yielded a regression covariance matrix of:

$$\text{Covar}_T = \begin{vmatrix} 797.76312 & -240391.1 & 0 \\ -240391.1 & 72534377 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (A-28)$$

The sensitivity analysis run varying the estimated value of C_p for the complex by its estimated standard deviation yielded (per Equation A-21) a covariance matrix of:

$$\text{Covar}_S = \begin{vmatrix} 412.01608 & -18735.81 & -61.27992 \\ -18735.81 & 851982.6 & 2786.6119 \\ -61.27992 & 2786.6119 & 9.1142775 \end{vmatrix} \quad (A-29)$$

Summing the corresponding terms, we get the combined covariance matrix:

$$\text{Covar} = \begin{vmatrix} 1209.7792 & -259126.9 & -61.27992 \\ -259126.9 & 73386359 & 2786.6119 \\ -61.27992 & 2786.6119 & 9.1142775 \end{vmatrix} \quad (A-30)$$

At a temperature of 298.15 K, the matrix $F(T)$ is:

$$F(T) = \begin{vmatrix} 1 & 0.003354 & 5.6975967 \\ 0.003354 & 1.125 \times 10^{-5} & 0.0191098 \\ 5.6975967 & 0.0191098 & 32.462608 \end{vmatrix} \quad (A-31)$$

The dot product of these matrices gives

$$\begin{aligned} \sigma^2(\ln K_p(T)) &= 1.1820802 \\ \text{or} \quad \sigma(\ln K_p(T)) &= 1.0872351 \end{aligned} \tag{A-32}$$

implying that one standard deviation implies that K_p may vary by $e^{\pm 1.09}$ times its nominal value, which is to say it may range from the predicted value times 3 to the predicted value divided by 3 (at a confidence level corresponding to one standard deviation). (This is just an example -- the 2nd Law treatment did not produce the values recommended for ClF_2AsF_6).

Appendix B

Property Estimation Methods Used in this Report

To predict the equilibrium behavior of chemical species outside the very specific physical conditions of experiments, thermodynamic data is needed; for the sorts of behavior under consideration in this report, a complete set of such data for a particular chemical species would consist of ΔH_f° and S° (both at the reference temperature and pressure) and, to allow evaluation of changes in these two values with temperature, C_p° . Other sets of variables (from which these could be derived) would serve as well. While it is generally desirable to utilize thermodynamic data based on experimental data, this is not always available. In such cases estimation is the only alternative. In some cases, experimentally derived values are sufficiently uncertain that estimates may provide better values. This appendix will outline the estimation methods used in this report.

Entropy Estimate from Density Correlation

Mallouk^{49,50}, in an examination of some 40 inorganic fluorides (including a few complexes very similar to those under consideration, namely KBF_4 , KPF_6 , SF_3BF_4 and SF_3PF_6), observed a strong correlation between the standard entropy of the solid and its molecular volume. The correlation was:

$$S^\circ(298.15) \{ \text{cal/mol K} \} = 0.42 V_M \{ \text{\AA}^3 \}. \quad (\text{B-1})$$

V_M is the volume of one "formula" of the compound. The volume is ideally determined from the X-ray crystallographic structure of the crystal. While Mallouk does not specify an estimated uncertainty for this correlation, based on examination of a plot in that report, it appears that an estimate will be accurate to approximately 9% of its value (i.e., $\pm 9\%$ represents one standard deviation).

Where crystal densities are known or can be estimated for the complexes under consideration here, this correlation is used to estimate their $S^\circ(298.15)$.

Molecular Volume Estimates

X-ray structure-determined molecular volumes are available for most of the complexes that are of most immediate apparent importance, but in a few cases, needed values are unavailable. It was observed that, to a close approximation, the known molecular volumes of complexes could be decomposed into contributions from the anion and cation components, i.e.

$$V_M = V_C + V_A \quad (\text{B-2})$$

where " V_M ", " V_C ", and " V_A " denote the total molecular volume, cation-producing species, and the anion-producing species contributions to molecular volumes.

A linear optimization procedure (inherent in Borland, Int'l's Quattro Pro spreadsheet software package) was used to find that set of molecular volume contribution values for the cation (C) and anion (A) species which minimized the error:

$$\text{Error} = \left[\sum_A \sum_C (V_M - V_C - V_A)^2 \right]^{1/2} \quad (\text{B-3})$$

where the sum is over those combinations of A and C for which known values for the complex AC's molecular volume are available. Table B-1 lists the literature values of the molecular volumes of the complex species used in generating this set of volume contributions, along with the contributions for the cation and anion components of the complexes. In this table, the cation and anion components of a complex are listed as their corresponding neutral molecule; e.g. the " ClF_3 " entry might more properly (but less recognizably) be identified as " ClF_2^+ ", and the " BF_3 " entry as " BF_4^- ".

Table B-1: Literature Molecular Volumes in $\text{\AA}^3$ used in estimating anion and cation volume contributions (in italics).

		BF_3	PF_5	AsF_5	SbF_5
	component	44.772	77.530	82.005	97.999
ClF_3	61.122	105.000 [b]	140.000 [c]	142.674 [a]	
ClF_3O	63.620	108.289 [c]		145.728 [c]	
ClO_2F	65.274	112.869 [d]	142.785 [d]	144.476 [a]	
SF_4	80.708	122.700 [b]	161.733 [d]	162.000 [b]	
NaF	29.204	73.836 [g]			127.343 [g]
KF	36.163	83.400 [e]	114.600 [e]	114.900 [e]	134.060 [h]
O_2F	42.797	86.200 [e]		131.900 [e]	
H_3OF	46.679			128.721 [f]	144.640 [f]

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From the anion and cation volume contributions estimated above the few missing values can be estimated by adding the component contributions. For example,

$$\begin{aligned} V_{\text{ClF}_3\text{O} \cdot \text{PF}_5}(\text{est}) &= V_{\text{ClF}_3\text{O}} + V_{\text{PF}_5} \\ &= 63.62 + 77.53 \text{ \AA}^3 \\ &= 141.15 \text{ \AA}^3 \end{aligned}$$

The number of decimal places listed is certainly not an indication of the expected accuracy of the estimate: the average error for the above correlation was 1% of the predicted value.

Molecular volume data for a complex could be used in the above derivation if there were at least one additional data entry for each of its cation and anion species. In Table B-1 this requirement manifests itself in the need for each column and row to have at least two data entries. In addition, there are molecular volumes for a number of other complexes, for which that datum is the only available one for either the cation or anion. In the event that we have an estimate for either the cation or anion volume contribution, we can derive the contribution for the missing value via, for example:

$$\underset{\text{unknown}}{V_C} = \underset{\text{known}}{V_M} - \underset{\text{known}}{V_A} \quad (\text{B-4})$$

These secondary values can in turn be used to generate estimates (per equation B-2) for any complex for which both V_C and V_A have been estimated.

With each stage of this process, the estimated error (assuming it is uncorrelated) would grow from 1 to $\sqrt{2}$ to $\sqrt{3}$ times the original "1% of value" estimate of error. This would be combined with the error in the original X-Ray diffraction-determined molecular volumes which are not generally quoted, but seem to be about 0.05% based on number of digits reported for cell dimensions. Our particular application for these molecular volume estimates will be to use them with the Mallouk correlation to estimate $S^0(298.15)$. Since for that correlation we have estimated an error of 9%, the variable error estimates in molecular volume (again, if uncorrelated) will have make no significant difference in the overall estimate of the uncertainty of $S^0(298.15)$, since, per standard methods for propagation of errors we estimate

$$\sigma = (9\%^2 + 1.7\%^2)^{1/2} = 9.2\% \quad (\text{B-5})$$

In a few cases, the molecular volume of a series of complexes is not known, but values or estimates can be made for a closely related series. For example volumes were not found for any ClF_5 complexes, but values are available for one ClF_7 and several ClF_3 complexes. Christie in several papers made the comment that the effective volume of an F^- seemed to be about 17 to 18 cubic Angstroms in such complexes. For such cases, then, the molecular volume will be estimated by adding or subtracting $17.5 \text{ \AA}^3/\text{F}^-$ from the known complex's molecular volume.

Table B-2 - Molecular Volumes (cubic Angstroms) and estimated uncertainties
(expressed as a percentage of the listed value).

	BF3				PF5				AsF5			
CIF3	105.000	±	0.21%	[a]	140.000	±	0.21%	[a]	142.674	±	0.21%	[a]
CIF5	140.894	±	2.41%	[b]	173.652	±	2.41%	[b]	178.127	±	2.41%	[b]
"CIF7"	175.087	±	1.24%	[b]	207.845	±	1.24%	[b]	212.320	±	0.21%	[a]
CIF3O	108.289	±	0.21%	[a]	141.151	±	1.22%	[b]	145.728	±	0.21%	[a]
CIO2F	112.869	±	0.21%	[a]	142.785	±	0.21%	[a]	144.476	±	0.21%	[a]
SF4	122.700	±	0.21%	[a]	161.733	±	0.21%	[a]	162.000	±	0.21%	[a]
O2F	86.200	±	0.21%	[a]	120.328	±	1.22%	[b]	131.900	±	0.21%	[a]
H3OF	91.451	±	1.22%	[b]	124.209	±	1.22%	[b]	128.721	±	0.21%	[a]

[a] Literature value

[b] Sum of component contribution estimates

Entropy Estimate from atom substitution rule of thumb⁵¹

If a solid compound differs from another only in the substitution of an atom of "A" for an atom "B", if the entropy of one solid compound is known, and if the intermolecular forces are likely similar, then one can estimate the entropy of the unknown from that of the known per:

$$S(\text{unknown}) = S(\text{known}) + \frac{3}{2} n R \ln M(\text{B})/M(\text{A})$$

where $M(\text{A})$ and $M(\text{B})$ are the masses of atoms A and B. This method was used only for assisting in estimating the entropy contribution for " Cl_2F^+ " by reference to the contribution (estimated by other means) from " ClF_2^+ ".

Heat Capacity Estimate from Apparent Component Contribution in Similar Salts

The contribution to the heat capacity of one of the constituents of a complex may be estimated from its apparent contribution of that component in another complex for which the heat capacities are known. For example, the C_p of BF_3 in a "salt" may be estimated as

$$C_p(\text{BF}_{3,\text{salt}}) = C_p(\text{KBF}_4) - C_p(\text{KF}).$$

When data for several such compounds can be found, an average contribution and estimated uncertainty can be deduced.

Heat Capacity for Components of Salt

The heat capacity of a solid complex may be estimated from the sum of the heat capacities of the solid constituents. This may require extrapolation from the temperature region in which the constituents are stable to the temperature of interest. Care should be taken that the resulting estimate does not greatly exceed reasonable values for solids (e.g. as embodied in, say, the rule of DuLong and Petit).

Heat Capacity of Solid from Average ΔC_p trends

Heat capacity for a solid can be estimated from a known value for the gas phase by adding the average value of $\Delta C_{p,g-s}$. Examination of the difference in literature values for the heat capacity of the gas and condensed phases of some 17 compounds similar to those under consideration in this report (inorganic, non-hydrogen containing, number of atoms > 3) gave an average value for

$$\Delta C_{p,g-s} = C_{p,g} - C_{p,s} = -23.851 \pm 14.563 \text{ J/mol K}$$

This is not very accurate, but seems to give a better representation for solids with significant covalent character than does the rule of DuLong and Petit, below.

Heat Capacity from "Rule of DuLong and Petit"⁵²

For solids, particularly ones that are mainly atomic or ionic in nature, a common estimate of the heat capacity is

$$C_p = n \text{ times } 6 \text{ to } 6.3$$

where n is the number of atoms in the chemical formula and R is the gas constant, and C_p is in cal/mole K.

Appendix C - The thermodynamic values of component species, used as basis for various complex calculations, are listed in Table C-1.

Table C-1: Data and Sources used for "monomeric" species used in estimation of properties of complexes.

		$\Delta H^\circ_f \pm \sigma(\Delta H^\circ_f)$ Source			$S^\circ \pm \sigma(S^\circ)$ Source			$C_p \pm \sigma(C_p)$ Source		
BF ₃	gas	-1135621	---	[a]	254.355	---	[a]	52.791	---	[a]
	"salt"				78.677	7.113	[c]	61.540	3.692	[f]
PF ₅	gas	-1594409	---	[a]	300.810	---	[a]	84.722	---	[a]
	"salt"				136.243	12.318	[c]	109.320	6.559	[f]
AsF ₅	gas	-1236749	---	[b]	323.381	---	[b]	96.183	---	[b]
	"salt"				144.106	13.029	[c]	141.294	---	[b][e]
2 ClF	gas	-100584	---	[a]	435.876	---	[a]	65.005	---	[a]
	"salt"				115.204	11.415	[k][c]	95.891	19.178	[o]
ClF ₃	gas	-158866	---	[a]	281.600	---	[a]	63.915	---	[a]
	"salt"				107.408	9.711	[c]	111.513	20.000	[p][e]
ClF ₅	gas	-236436	---	[a]	310.739	---	[a]	97.277	---	[a]
	"salt"				168.913	15.671	[j][c]	121.128	14.563	[d][e]
ClF ₃ O	gas	-148300	---	[m]	303.870	---	[l]	77.901	---	[l]
	"salt"				111.799	10.108	[c]	101.751	14.563	[d][e]
ClO ₂ F	gas	-25270	---	[n]	278.374	---	[l]	56.648	---	[l]
	"salt"				114.705	10.371	[c]	80.499	14.563	[d][e]
"H ₃ OF"	gas	-514372	---	[a][h]	362.614	---	[a][h]	62.830	---	[a][h]
	"salt"				82.094	7.422	[c]	75.504	1.133	[g]
SF ₄	gas	-763162	---	[a]	299.644	---	[a]	77.553	---	[a]
	"salt"				141.827	12.823	[c]	101.404	14.563	[d][e]

Notes "----" Literature value is assumed to be accurate for purposes of error analysis in this report

[a] JANAF 86⁵³

[b] Barber and Leitnaker⁵⁴

[c] Anion or cation component contribution to entropy estimated from optimization of many densities for related complexes

[d] Estimated from average ΔC_p between gas and solid for molecules with > 3 atoms

[e] "Salt" contribution estimated from value for pure solid compound.

[f] "Salt" contribution of MF_x from KF*MF_x (BF₃ or PF₅) - from NBS 82⁵⁵

[g] "Salt" contribution of HF in sodium and potassium bifluoride and of H₂O in sodium and potassium hydroxide

[h] Sum of HF and H₂O values from JANAF 86

[j] molecular volume increased or decreased from that of a similar compound per "typical" volume of F⁻ in these species.

[k] Entropy adjusted for mass effect from that of a related compound.

[l] Statistical mechanics analysis of Christie spectroscopy data^{56,57}

[m] Secondary reference by Christie to unpublished work of Kalman⁵⁸

[n] derived from experimental data of Gatti⁵⁹

[o] Average of DuLong & Petit rule and general dCp trend - value is for 2 ClF (not ClF)

[p] Grisard⁶⁰ (extrapolated experimental data)

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