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Investigation of the Chemical Reactivity of Phosgene in Uranium Hexafluoride

April 2006

L. D. Trowbridge and D. W. Simmons

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INVESTIGATION OF THE CHEMICAL REACTIVITY OF PHOSGENE IN URANIUM HEXAFLUORIDE

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SUMMARY

This report documents work aimed at determining whether phosgene ($COCl_2$) could survive the chemical environment of a UF_6 cylinder from the time of filling with liquid UF_6 many years ago to the present day. Information was obtained from the scientific literature, from thermodynamic calculations, and from limited laboratory experimentation. The conclusion derived from this work is that $COCl_2$ is more resistant to chemical reaction than expected. We have demonstrated that at least a portion could survive the short-term contact with liquid UF_6 during cylinder filling. We cannot say from the information developed whether it could survive the long-term contact at lower temperature.

In the early days of the U.S. uranium enrichment endeavor, a number of surplus cylinders were obtained from the U.S. Army's chemical weapons program. The cylinders may once have contained chlorine (Cl_2) or phosgene ($COCl_2$), and are now used to store depleted UF_6. A memo issued by the U.S. Department of Energy's Inspector General (DOE IG) questions whether residual $COCl_2$ initially present in cylinders could unfavorably affect the safety or the operability of the conversion operation [Walter 2005].

There are numerous conditions and events that can rule out the presence of $COCl_2$ in a particular UF_6 cylinder in the present day. One key question is

> *If $COCl_2$ were present when the cylinder was filled with liquid UF_6, would it survive contact with liquid UF_6 (at 64 to 90°C) during the few days required for cooling and survive contact with the solid or gas at ambient temperatures over the next 60 years?*

If the answer to this question is no, then *no* cylinder will have $COCl_2$ at the present day. This report describes scoping work addressing this question.

This question was approached from several angles. To provide a structure for data interpretation and analysis, we first established a baseline "cylinder fill-and-store scenario" that specifies physical conditions [temperature, volume, initial (worst-case) quantities of UF_6 and $COCl_2$] and an event time-line for those conditions. Data found were applied to this scenario in an attempt to answer the above question.

Next, a literature search was conducted for applicable data on reactivity, chemical stability, and solubility. Solubility data are needed because we must consider reaction in three phases, the gas phase, the liquid phase (during the filling process), and the solid phase (during later storage). In the literature search, we found information indicating that $COCl_2$ and UF_6 will have a strong thermodynamic tendency to react. We did not, however, find information on their reaction rate, and indirect information (i.e., rates of reaction of similar chemicals) was not conclusive. We found data on liquid solubility that can be extrapolated to cylinder fill conditions, but none on solid solubility.

Finally, since the literature search did not conclusively settle the question, we carried out a series of scoping experiments. These examined the rate of consumption of $COCl_2$ in the gas phase both at room temperature and at liquid-UF_6 temperature, and a single experiment investigated the reaction rate in liquid UF_6. We also examined the effects of container surface area and of the prior UF_6 exposure history of the container. This set of experiments briefly explored all phases of the cylinder fill-and-store scenario *except* the reaction rate of $COCl_2$ dissolved in solid UF_6. While we observed some reactivity in both the gas and liquid phases, the rates observed do *not* categorically rule out survival of a portion of the $COCl_2$ for the duration of the full cylinder fill-and-store scenario. Additional, considerably more extensive and longer-duration experimentation would be needed to answer the $COCl_2$ survival question. From a programmatic and practical standpoint, this suggests that factors other than reactivity must be used to demonstrate the lack of $COCl_2$ in suspect cylinders (e.g., historical records or sampling).

ABSTRACT

In the early days of the U.S. gaseous diffusion uranium enrichment enterprise, a number of surplus cylinders were obtained from the U.S. Army's chemical weapons program. These cylinders, which may once have contained chlorine (Cl_2) or phosgene ($COCl_2$), have been used to store depleted UF_6. The question was recently raised whether residual $COCl_2$ initially present in cylinders could unfavorably affect either the safety or operability of the UF_6 conversion operation planned for the near future. There are numerous conditions and events that would lead to the conclusion that no such problem exists for particular cylinders or even for all cylinders. This report discusses work on one such area, namely the chemical reactivity of phosgene in a UF_6 environment. A literature search, laboratory experimentation, and theoretical calculations were undertaken in an effort to determine whether it could categorically be demonstrated that phosgene, even if initially present in cylinders, would essentially have all reacted to more familiar products by the present day. In the end, the information developed would not support that categorical statement. Although the efforts here were limited by time and resources, potentially useful information was developed regarding the rate and products of reaction of $COCl_2$ with UF_6, surface effects on that reaction rate, and solubility of $COCl_2$ in UF_6.

1. INTRODUCTION

An issue has been raised that has impacted U.S. Department of Energy (DOE) plans for conversion of depleted UF_6 to a chemically more stable form. In the early days of uranium enrichment, a number of surplus cylinders were obtained from the U.S. Army's chemical weapons program by the U.S. enrichment facilities and have since been used to store depleted UF_6. During their tenure with the Army, these cylinders may have contained Cl_2 or $COCl_2$. A memo issued by the DOE Inspector General questions whether residual $COCl_2$ initially present in cylinders could unfavorably affect either the safety or operability of the conversion operation [Walter 2005].

Numerous conditions and events would all have to occur to permit the survival and presence of $COCl_2$ in a given UF_6 cylinder and for that cylinder to present a problem in the present day. A list (probably not exhaustive) of questions about such conditions or events is as follows:

(a) Was there significant residual $COCl_2$ in the cylinder when it was received from the Army?
(b) Was the cylinder hydrostatically tested (i.e., filled with water at pressure, then drained and dried, a process that would have removed $COCl_2$ initially present)?
(c) Was the cylinder later emptied of UF_6 (thereby simultaneously removing $COCl_2$)?
(d) If $COCl_2$ were present when the cylinder was filled with liquid UF_6, would it be chemically destroyed either at liquid UF_6 temperature (64 to 90ºC) during the few days required for cool-down after filling, or at ambient temperatures over the next 60 years?
(e) If $COCl_2$ is still present, does it (at its maximum possible concentration) impose any incremental health hazard above that of the UF_6 or other impurity gases (e.g., HF)?
(f) If $COCl_2$ is still present, does it (at its maximum possible concentration) impose any processing difficulties in the conversion process?

If any of (a) through (c) are answered in such a way as to preclude the presence of $COCl_2$ for a given cylinder, then that cylinder will present no problem. If (d) is answered "yes," then *no* cylinder will have $COCl_2$ at the present day. If (e) is answered "no," then no incremental health concerns arise for *any* cylinder; similarly, if (f) is answered "no," then no operating concerns arise for *any* cylinder.

This report describes scoping work addressing only question (d), which, paraphrased, is

Assuming $COCl_2$ was initially present in a 30A cylinder used for storing depleted UF_6 in the 1940s, can we definitively prove that $COCl_2$ would not have chemically survived to the present day?

This question was approached from several angles. To provide a structure for data interpretation and analysis, we first established a baseline "cylinder fill-and-store scenario" itemizing physical conditions [temperature, volume, initial (worst-case) quantities of UF_6 and $COCl_2$] and, as appropriate, a rough time line of the changing physical conditions. Data found are applied to this scenario in an attempt to answer the question.

Next, a literature search was conducted for applicable data on chemical stability, reaction rate, and solubility. The need for solubility data arises from the fact that we must consider reactions in three phases – the gas phase, the liquid phase (applicable during the filling process), and the solid phase (applicable during the extended storage period) – and must know what fraction of $COCl_2$ will reside in each phase. In this literature search, we found chemical stability information (thermodynamic data, that is) indicating that $COCl_2$ and UF_6 will have a strong tendency to react. We did not, however, find

information on their reaction rate; and indirect information (i.e., rates of reaction for chemically similar compounds) were inconclusive. We found data on liquid solubility that can usefully be extrapolated to cylinder fill conditions, but none on solid solubility.

Finally, since the literature search did not definitively show that $COCl_2$ would be consumed in a UF_6 environment, we carried out a series of scoping experiments. Planning for these experiments was materially assisted by observations made by United States Enrichment Corporation (USEC) personnel at the Paducah Gaseous Diffusion Plant (PGDP) in which reaction of $COCl_2$ was observed (both in the presence and absence of UF_6) during analytical calibration operations.

Our experiments examined the rate of consumption of $COCl_2$ in the gas phase both at room temperature and at liquid-UF_6 temperature. One experiment examined the rate of reaction in liquid UF_6. No experiments were conducted explicitly to measure $COCl_2$ solubility in liquid or solid UF_6, but as a by-product of one experiment, we obtained a tentative indication of its solubility in solid UF_6. We also examined the effect on $COCl_2$ consumption of container surface area and of the prior history of container exposure to UF_6.

This set of experiments cursorily explores all phases of the cylinder fill-and-store scenario *except* the rate of reaction of $COCl_2$ dissolved in solid UF_6. Given the short time frame allowed for this experimental campaign (Dec 8, 2005 to Jan 16 2006), no long-term experiments could be undertaken to explore, for example, the room temperature solid or gas-phase rates or the rate of build-up of catalytic effects of surfaces during UF_6 exposure.

This report has been prepared to document only the authors' activities related to potential $COCl_2$ contamination of UF_6 cylinders (though brief mention is made of some useful related experiments conducted at PGDP) . Many other activities were carried out by other organizations on other aspects of the residual $COCl_2$ issue.

This report will be organized in a slightly unconventional way, with separate sections covering chronologically separate tasks as they were commissioned and carried out. In each section, supporting information, discussion, and conclusions relevant to the findings of that activity will be presented. Then the overall findings as a whole will be synthesized at the conclusion of the report.

2. CYLINDER FILL-AND-STORE SCENARIO DEFINITION

In the event that none of those preliminary cylinder operations took place that would have removed $COCl_2$ (e.g., evacuation, hydro-testing, cleaning), we can define a worst-case scenario for the initial $COCl_2$ load on the following basis.

- Before use with UF_6, a valve suitable for UF_6 service would have been installed. That operation would open the cylinder to the atmosphere. The boiling point of $COCl_2$ is 8.3ºC, so if liquid were still present, it would boil off at this time, eventually leaving only gas at atmospheric pressure.

- Normally, cylinders are evacuated using air jets to remove the bulk of the gaseous contents. This would reduce the internal pressure to 5 psi (absolute) or lower. Assuming the cylinder contained nothing but $COCl_2$ vapor, the 30A cylinder [the class of cylinder in question, which has 726 L total internal volume [ORO 1977] could at this temperature (~25ºC), contain about 2.15 lb of $COCl_2$]. If the air-jet evacuation did not occur, however, the figure would triple to 6.45 lb. We will use this latter figure as a "worst-case" initial quantity of $COCl_2$ (except as otherwise stated).

- The cylinder would then be filled with liquid UF_6. The specified full load of a 30A cylinder is 4950 lb UF_6 [ORO 1977]. $COCl_2$ (if unreacted) would constitute a 1300 wt-ppm impurity in the UF_6 (divide by 3 if air-jet evacuation occurs).

- The temperature of the UF_6 during the fill must be somewhat above the 64°C melting point to avoid freezeout in piping. A range of 70 to 90°C is a reasonable assumption; we will use 80°C as a median value for the initial temperature of the liquid UF_6.

- The cylinder is left to cool prior to movement. Liquid UF_6 contracts slightly on cooling to its freezing point, then contracts a great deal more on freezing; so the void space in the cylinder will enlarge by about 250 % during the entire cooling process. The cooling and freezing process may take up to several days, during which the UF_6 slowly freezes as heat is lost.

- After cooling, the cylinder can be transported to its storage location. At that point, it will be exposed to ambient weather conditions until it is eventually retrieved. The temperature will rise and fall day to night and winter to summer. The average temperature will be about 15°C, but cylinder surface high and low temperatures might range from −15 to +50°C. This temperature variation will have the effect of evaporating and condensing (actually subliming and desubliming) UF_6 in the void space, effectively mixing the gas with a surface layer of the solid over time. Most of the mass of the UF_6, however, will reside in the bulk solid.

Table 1 lists densities for UF_6 at temperatures of interest in this scenario. Densities are computed from formulae given in a report by Anderson [Anderson 1994]. The volumes of the gas and condensed phases are also listed for the 30A cylinder at these temperatures, partitioning the statutory maximum load of 4950 lb of UF_6 between the phases per mass balance and the listed theoretical densities.

Table 1. UF_6 partition between phases in 30A cylinder fill-and-store scenario

	UF_6 densities			Volume distribution[a]		
T	Liquid	Solid	Gas	Liquid	Solid	Gas
°C	mol/L	mol/L	mol/L	L	L	L
100	9.68		0.146	659		67
80	10.05		0.088	635		91
64(liq)	10.32		0.056	618		108
64(sol)		13.81	0.056		461	265
20		14.39	0.0044		444	282

[a] The 30A cylinder's total volume is 726 L

So far, this discussion defines the condition of the UF_6 but not the condition of $COCl_2$. When liquid UF_6 enters the cylinder, there will probably be sufficient agitation and liquid circulation to allow $COCl_2$ to dissolve into the liquid to a level approaching its equilibrium solubility in the liquid UF_6. It might also react with UF_6 in the gas phase, in the liquid, or at the cylinder walls. Assuming $COCl_2$ chemically survives contact with UF_6 as the cylinder cools to the freezing point, $COCl_2$ will tend to separate to the (diminishing) liquid phase, since solubilities tend to be lower in the solid state than in the liquid state. This will raise the $COCl_2$ concentration in the liquid phase and also eventually in the gas phase. In addition, the volume of the gas phase will increase considerably as the UF_6 freezes. Both factors suggest that a larger fraction of $COCl_2$ will be in the gas phase during the decades-long storage period than was the case immediately after the cylinder was filled with liquid UF_6. This distribution between liquid and

gas (initially) and solid and gas (during storage) can be calculated if we can obtain solubility information for $COCl_2$ in liquid and solid UF_6. Such a prediction may, however, differ from reality if mixing and transport are slow compared with the time scales of the scenario – that is, if solution equilibrium is not achieved.

3. LITERATURE SEARCH

Chemical survival of (at least a significant fraction of) $COCl_2$ in the condensed phase in this scenario would require that $COCl_2$ survive contact with UF_6 in the liquid state until the liquid froze (i.e., for a few days) and with UF_6 in the solid state at the local outdoor ambient temperature for about 60 years. Similarly, chemical survival of that portion in the gaseous state requires that it survive contact with UF_6 in the gaseous state at significantly elevated temperatures for the few days while the liquid was cooling and ambient temperatures for the next 60 years. During the lengthy storage period, the solid's temperature changes will be moderated by the high heat capacity of the bulk of the solid, but the gas will likely experience larger temperature swings. Most significant, sun-exposed metal surfaces could occasionally get quite hot, perhaps as high as 50 to 60ºC during the heat of a sunny summer day.

A literature search was undertaken to determine if data existed in the scientific literature that would prove helpful in elucidating the behavior of $COCl_2$ in a UF_6 environment, in particular its chemical stability (would it survive) and solubility (if it survived, how would it distribute between the gas, liquid, and solid phases).

3.1 SOLUBILITY

One article was found on the subject of solubility: Maier and Beattie [1984] report the solubility of UF_6 at its saturation vapor pressure in liquid $COCl_2$ at cryogenic temperatures (−2 to −114ºC). In addition to the solubility data, their experiments demonstrate that the $COCl_2$-UF_6 reaction at these temperatures is not significant. They did, however, report generation of a slight solid residue at the highest temperatures studied, probably indicative of the onset of a slow reaction even at −2ºC.

The physical conditions in the Maier and Beattie study (low temperature; $COCl_2$-rich mixture) are far removed from the conditions of interest in the cylinder-fill-and-store scenario (which involves a higher-temperature UF_6-rich liquid for the fill portion of the scenario, and room-temperature, solid state UF_6 for the storage portion of the scenario). Extrapolation from their experimental conditions (−2 to −114ºC) to the conditions of interest to us (64 to 80ºC for the liquid) is somewhat speculative, but interpreting the experimental data using regular solution theory shows a degree of consistency that supports such an extrapolation. This data treatment is discussed in Appendix B. No information was found in the literature on the solubility of $COCl_2$ in solid UF_6.

3.2 CHEMICAL STABILITY

Several types of information that might be found in the literature could help us assess the chemical stability of $COCl_2$ in the cylinder environment. These fall broadly into two categories, thermodynamics and kinetics. Thermodynamics tells us the energetic stability of a system of compounds. Given a list of potential reactants and products, one can (if the appropriate thermodynamic data are available) calculate the most stable combination of compounds. This can tell us what the end-point of a reaction should be but does not tell us the rate at which it is approached. Chemical kinetics requires more detailed information on the reaction system but elucidates the rate of reaction. In its most detailed form, a lengthy system of elementary reaction steps and rates can be used to compute the consumption and formation of

reactants, reaction intermediates, and final products. Less detailed treatments may simply provide an empirical equation for the overall rate of consumption of reactants and formation of products. At the lowest level of detail, observations may simply indicate that reactions occur under specified conditions, from which we can infer only whether an observable degree of reaction took place in the time period the workers allowed for an experiment.

3.2.1. Thermodynamics

Sufficient thermodynamic information is available for the reactants (UF_6 and $COCl_2$) and potential reaction products (reduced uranium fluorides such as UF_5, Cl_2, COF_2, CF_4, COFCl) to reliably establish the chemical equilibrium state. Calculations were run using the commercial thermodynamics equilibrium package HSC [HSC 2004] using data from its internal database. The postulated reactions

$$COCl_2 + UF_6 \Longrightarrow COFCl + \tfrac{1}{2} Cl_2 + UF_5$$

and

$$COCl_2 + 2\,UF_6 \Longrightarrow COF_2 + Cl_2 + 2\,UF_5$$

are strongly thermodynamically favored (their free energies of reaction being −114 and −229 J/mole respectively at 25°C). Further reaction of COF_2 to form CF_4

$$COF_2 + 2\,UF_6 \Longrightarrow CF_4 + \tfrac{1}{2} O_2 + 2\,UF_5$$

is also favored (the free energy of reaction being −77 J/mol). While we found no information on the kinetics of the first two reactions, experience with the kinetics of fluorocarbon flame systems and experimental observations in our laboratory lead us to doubt that the third reaction will take place at a significant rate at the conditions of our cylinder scenario.

3.2.2. Reactivity Literature

Several classes of data were sought. In order of decreasing direct relevance, they were

(a) reaction of UF_6 with $COCl_2$,

(b) reaction of $COCl_2$ with other inorganic fluorides,

(c) thermal decomposition of $COCl_2$,

(d) chemical kinetics models of related systems

The reason for the first category is obvious. The reason for the second is to elucidate trends in reactivity among compounds chemically similar to UF_6. The reason for the third category is that the rate of thermal decomposition of $COCl_2$ establishes a lower limit on the reactivity, since phosgene's thermal decomposition intermediates (COCl, Cl) and products (CO) are highly likely to be quickly attacked by UF_6. The final category might, if rate data were found for a sufficiently comprehensive set of elementary reaction steps, allow us to establish a lower limit to the effective reaction rate.

Reaction of UF_6 with $COCl_2$. No direct information was found on reaction of UF_6 with $COCl_2$ other than the largely negative result in the previously mentioned solubility article [Maier and Beattie 1984],

namely that UF_6 and $COCl_2$ did not significantly react at temperatures ranging from −114 to −2°C. Some slight reaction *may* have occurred at the highest temperatures, but the degree of reaction was not quantified and it took place in $COCl_2$ solution.

Reaction of $COCl_2$ with other inorganic fluorides. Numerous inorganic fluorides are reported to react with $COCl_2$, the products generally being COF_2 or the intermediate compound COFCl. Elevated temperatures and pressures are frequently required. Significant reaction at lower temperatures frequently requires catalysts such as activated charcoal or solid transition metal halides of lower valence. A selection of the most relevant reactions follows, illustrating the range of temperatures and pressures required for significant reaction:

Heating SbF_3 with an excess of phosgene in the presence of a catalytic amount of $SbCl_5$ at 135 °C and 3.25 MPa produces primarily COFCl plus a little COF_2 [Eméleus 1948; Ryan 1996].

AsF_3 mixed with an excess of phosgene and $SbCl_5$ as a catalyst, kept in a stainless steel lecture bottle at 130 °C for 10 h and a pressure of 5.5 MPa (800 psi) reacted significantly, the major product being COFCl [Christe 1965].

$COCl_2$, COFCl, and COF_2 all form low-temperature complexes with AsF_5 and SbF_5 [Christe 1999]. The $COCl_2 – SbF_5$ solid complex, formed at −78°C, decomposes on warming to room temperature to produce COFCl and SbF_4Cl [Hoge 1999], suggesting that the formation of such complexes may enhance the reactivity of $COCl_2$.

F_2 did not react when bubbled through liquid $COCl_2$ at 6°C but frequently reacted to thermal runaway at ~ 200°C in glass. F_2 and $COCl_2$ gas passed over granulated CaF_2 at 200°C gave a product that boiled at −42 °C. Though the product was not identified at the time, this is thought to be the first reported preparation of COFCl [Humiston 1919].

An HF-$COCl_2$ liquid mixture (necessarily at high pressure) reacted to give COFCl at temperatures ranging from 80 to 150°C (the variation in the temperature of significant reactivity being due to catalytic effects) [Simons 1946]. At higher temperatures (above 425°C), various chlorofluorocarbons were formed [Haszeldine 1957].

A patent describes the preparation of COF_2 by the continuous gas flow reaction of $COCl_2$ with HF at atmospheric pressure and 50°C. The yield of the reaction is much improved in the temperature range 150 to 300°C and by the use of activated carbon as a packed bed catalyst. The excess HF and the by-product HCl are stripped from the product by NaF [Tullock 1958].

$COCl_2$ reacts with HF in the presence of liquid CH_3CN to form COF_2 at room temperature [Franz 1979].

Gaseous mixtures of $COCl_2$ and HCN in the presence of NaF react to form COF_2 and various cyanates at room temperature [Tullock 1960].

NF_3 and $COCl_2$ react readily at temperatures of 310, 360, and 400°C in a flowing gas tube to produce COFCl and COF_2, with the yield of COF_2 increasing with higher temperatures. Contact time in these experiments was short, on the order of 5 minutes [Glemser 1967].

SiF_4 reacted with $COCl_2$ at 360°C and 0.5 atm to yield COFCl with 15-s reaction time. At 420°C the yield was 42%. Higher temperatures reduced the yield due to the dissociation of the $COCl_2$ [Christe 1964].

SF_4 reacts with $COCl_2$ in the presence of TiF_4 at 250ºC to produce 90% CF_4 and 9% COF_2. No reaction occurs at 250ºC without the catalyst [Hasek 1960].

PF_5 reacts with $COCl_2$ to give CF_2Cl_2 and POF_3 between 250 and 350ºC [Haszeldine 1959].

Thermal decomposition of $COCl_2$. Numerous articles were found reporting various aspects of rates of thermal decomposition of $COCl_2$. Rates and proposed reaction mechanisms varied, but experimentally, one may generalize the collective observations and say that decomposition became significant only at temperatures of 380 – 500ºC. [Bodenstein 1924; Lord 1970; Ryan 1996].

Elementary reaction steps. The literature search also sought a collection of rates for elementary reaction steps, from which could be constructed a model of this reaction. There is an extensive literature in this area covering the realms of flame chemistry and atmospheric chemistry. This search, however, did not elucidate sufficient information to be useful in the present evaluation. Many reaction steps that would be involved in the thermal decomposition or reaction of $COCl_2$ were found (e.g., Cl + COCl). Similarly, many reaction steps for the analogous COF_2 decomposition mechanism were found (e.g., F + COF), but rates for analogous cross-reactions (e.g., F + $COCl_2$, or Cl + COF) were not found, although such reactions clearly must take place. The incompleteness of the reaction set implies that, while we could model thermal decomposition of $COCl_2$, it would not properly represent the reactions leading to the fluorination of $COCl_2$ or lead to a result substantially different from thermal decomposition rates mentioned in the previous subsection.

Discussion of literature search findings. The rates of reaction of many of the inorganic fluorides mentioned under "Thermal decomposition of $COCl_2$" are significantly faster than one would predict if the reaction mechanism began with thermal decomposition of $COCl_2$. For others, the onset of significant reaction occurs only when thermal decomposition temperatures are reached. This suggests that the $COCl_2$ + UF_6 reaction rate, either alone or catalyzed by surface deposits, *might* be significantly higher as well. However, without direct measurement, we can't say from these observations whether it will be high enough at the cylinder fill or storage conditions to destroy all traces of $COCl_2$. The fact that many of the reaction rates have a catalytic component (i.e., are accelerated by the presence of specific surfaces) can complicate the application of laboratory-determined rates to field conditions. Surface deposits in a cylinder are inevitable (iron fluorides on the steel surface, reduced uranium fluorides such as UF_5, UO_2F_2 from hydrolysis), but we find no information in the literature indicating whether these particular materials will catalytically enhance the reaction of UF_6 with $COCl_2$.

In summary, the information found in the literature does not make an ironclad case that $COCl_2$, if initially present, would have been destroyed by UF_6 in the course of the fill-and-store scenario.

4. EXPERIMENTAL

When it became clear that the question of chemical reactivity would not be laid to rest by findings from the literature search, a short-term experimental study was commissioned. Just before this study was commissioned, PGDP staff, while developing analytical standards for cylinder head-space analyses, observed reaction of $COCl_2$ in a UF_6 environment. Since their results provided some key insights into the $COCl_2$ reactivity question, a brief summary of their results, as they pertain to $COCl_2$ reactivity, is provided here.

4.1 PGDP EXPERIMENTAL SUMMARY

PGDP technical staff, in the course of running calibration spectra for analyzing cylinder head-space gases, mixed low partial pressures of UF_6 (~10 Torr) and $COCl_2$ (~ 0.5 Torr) in their infrared (IR) gas cell at room temperature (11/30/2005). They observed a decline in concentration of $COCl_2$ and a simultaneous increase in two plausible reaction products, COFCl and COF_2. A substantial fraction of the $COCl_2$ reacted in the few hours duration of the experiment [Brazell 2005a].

Following this experiment, the IR cell was evacuated and the cell was loaded with $COCl_2$ (actually, with a 0.5% $COCl_2$-in-N_2 mixture). This gas was left over the weekend of 12/2 to 12/5/2005. The following Monday, little or no $COCl_2$ remained. It had essentially all reacted to form COF_2, though a trace of COFCl was evident. Note that in this second PGDP experiment, there was *no* overt inclusion of any fluorinating agent, UF_6 or otherwise [Brazell 2005b].

A third experiment (12/6/2005) was done, duplicating the conditions of the second, but in this one, spectra were taken over a period of 90 minutes, during which time about 20% of the $COCl_2$ disappeared and was replaced with COF_2 and COFCl [Brazell 2005c].

A fourth experiment (12/7/2005) was performed, duplicating the conditions of the first $COCl_2$ + UF_6 experiment. This one was followed for 5 hours, at the end of which time about 90% of the $COCl_2$ had reacted [Brazell 2005d].

A final experiment (1/6–9/2006) followed a mixture with a higher partial pressure of $COCl_2$ and a lower partial pressure of UF_6 (about 5 Torr each) over a weekend. At the end of that time, about half the $COCl_2$ was reacted. In this experiment, unlike in the first and fourth experiments, the amount of UF_6 did not exceed what would be necessary to fully fluorinate $COCl_2$, although some UF_6 did remain at the end of the experiment [Brazell 2005e].

A summary of the conditions and results of the PGDP experiments is presented in Table 2. ORNL results (discussed in Section 4.2) are similarly listed in that table. The experimental conditions listed are duration, temperature, and initial partial pressures of reactants. Results are given as partial pressures of $COCl_2$, COFCl, and COF_2, which are used to compute average rates of $COCl_2$ loss and product gain. Rates are presented both as an absolute rate (Torr/hour) and as a relative loss or gain, referenced to the initial partial pressure of $COCl_2$. Finally, the relative rates are inverted to give an "effective lifetime" for $COCl_2$ based on $COCl_2$ loss and product gain. These lifetimes imply a first-order rate behavior that was generally only approximately valid for this system. The available data are too limited to usefully explore the rate equation behavior of this system.

Collectively, the PGDP experiments suggested a fairly rapid reaction rate for $COCl_2$ relative to the duration of the cylinder fill-and-store scenario. However, the fact that $COCl_2$ reacted *even in the absence of UF_6* suggested that this reactivity needed further investigation.

Table 2. Summary of experimental results

Expt. ID	Duration	Temp	Init $COCl_2$	Init UF_6	Final $COCl_2$	Final COFCl	Final COF_2	$COCl_2$ loss based		Rxn prod based		Exponential lifetime	
								Rate	Rate	Rate	Rate	$COCl_2$-loss	Prod-gain
	(Hours)	° C	(Torr)	(Torr)	(Torr)	(Torr)	(Torr)	(Torr/h)	(Fr/h)	(Torr/h)	(Fr/h)	(Days)	(Days)
PGDP 1	2	23	0.421	16	0.101	0.354	0.085	1.6E-1	3.8E-1	2.2E-1	5.2E-1	0.11	0.08
PGDP 2	64	23	0.629	0	<0.01	0.08	1.9	< 1.0E-2	< 1.5E-2	3E-2	5E-2	< 3	< 1
PGDP 3	1.7	23	2.80	0	2.184	0.147	0.460	3.6E-1	1.3E-1	3.6E-1	1.3E-1	0.32	0.33
PGDP 4	4.7	23	0.208	22	0.025	0.250	0.081	3.9E-2	1.9E-1	7.0E-2	3.4E-1	0.22	0.12
PGDP 5	66	23	5.05	5	2.37	n/r	n/r	4.1E-2	8.0E-3	n/c	n/c	5.18	n/c
ORNL 1	16	25	5.18	0	5.10	0.030	0.016	5.0E-3	9.7E-4	2.9E-3	5.5E-4	43	76
ORNL 2	88	25	~ 8	0	~ 8	n/d	n/d	n/c	n/c	< 1.5E-4	< 2 E-5	n/c	> 2100
ORNL 3	20	25	4.7	53	4.695	n/d	n/d	2.5E-4	5.3E-5	< 0.7E-4	< 1.5E-4	783	> 280
ORNL 4	20	77	5.55	58	5.51	0.022	[0.025]?	2.0E-3	3.6E-4	1.1E-3	2.0E-4	116	208
ORNL 5 *	16	77	8.31	52.6	8.31	0.025	n/d	n/c	n/c	1.6E-3	1.9E-4	n/c	222
5, cont'd	86	77	8.31	52.6	8.17	0.038	n/d	1.6E-3	2.0E-4	4.4E-4	5.3E-5	213	781
ORNL 6 *	21	77	9.68	0	8.46	0.139	0.499	5.8E-2	6.0E-3	3.0E-2	3.1E-3	6.9	13
Liquid-phase			(mmole)	(mmole)	(mmole)	(mmole)	(mmole)	(mmole)	(Fr/h)	(mmole/h)	(Fr/h)	(Days)	(Days)
ORNL 7 *	17.25	77	0.294	19.232	0.342	0.0075	0.0005	-2.7E-3	-9.3E-3	4.6E-4	1.6E-3	n/c	26

Notes:
* IR cell included Monel screen, increasing superficial surface area about 5× relative to earlier experiments.
n/d = not detected
n/r = not reported
n/c = not calculated (lack of data or data precision prevents meaningful calculation of this value)

4.2 ORNL EXPERIMENTS

4.2.1 Apparatus

The ORNL $COCl_2$ + UF_6 gas-phase and liquid-phase experiments were done in a modified section of an existing UF_6 test loop located in Bldg. 4501. The test loop has been used for a variety of similar experiments in the recent past. The PGDP observations had shown fluorination of $COCl_2$ *alone* taking place in a previously fluorinated but otherwise apparently empty experimental system [Brazell 2005b,c]. We did not know precisely what reactant or catalyst might be involved, but we reasoned that extensive prior use in a fluorinating environment was likely responsible. We therefore created a modified section to our UF_6 test loop which consisted entirely of new or acid-cleaned components (Fig.1).

The new section consisted of a Monel 10-cm pathlength IR cell with ZnSe windows sealed by Krytox-coated Viton gaskets, and a stainless flex-hose leading to a regulator and supply of $COCl_2$. The IR cell was also connected to the existing loop and UF_6 supply via a (previously used) flex hose. A new MKS 628B capacitance manometer (pressure sensor) was located immediately at the IR cell; it also could be isolated from the IR cell. The IR cell itself had isolation valves located immediately at the cell to avoid long runs of tubing that could present a diffusion mixing problem. Contrary to our customary practice, we deliberately did *not* fluorine-passivate this new hardware.

Most of the experiments performed (1 to 6) involved only gas phase reactants. The last (7) attempted to examine the possibility of reaction in the liquid phase. For this experiment, additional equipment was added to the hardware listed earlier. A "P-10 tube," which is a small sample container commonly used for liquid UF_6 sampling, was utilized as a reaction chamber. This modified P-10 tube assembly consisted of a Kel-F plastic tube fabricated to replicate the sealing dimensions of a ½-in Swagelok VCR gland, sealed by VCR stainless steel nuts. The assembly we used had a Swagelok "p-nut" valve welded on the connecting VCR nut to allow isolation of the minimum possible volume during UF_6 liquefaction. All components were new. The total internal volume of the P-10 tube was measured to be 6.37 cc by gas expansion from a known volume. During UF_6 and $COCl_2$ loading, and later during gas sampling after the experiment, the P-10 tube was connected to the $COCl_2$ inlet line. During the period while the tube was heated to above the UF_6 melting point, it was disconnected, capped, and located in a secondary containment enclosure.

The main instrumentation used in these experiments consists of a Bomem Michelson MB-104 Fourier Transform Infrared (FTIR) spectrometer, the MKS capacitance manometer, and several thermocouples. The pressure and temperature sensors were connected to a data acquisition system. The FTIR was operated at 4 cm^{-1} resolution and could take spectra manually or periodically during times of unattended operation. Most of the gases involved or potentially involved in this reaction system (e.g., $COCl_2$, COFCl, COF_2, CO_2 CCl_4, CF_4, and UF_6) have known IR spectra, allowing us to quantify (with varying accuracy) the partial pressure of these gases. $COCl_2$, UF_6, and HF reference spectra were taken in our FTIR as part of this effort or in the recent past and should give fairly accurate estimates of partial pressure. Band strengths for most of the other compounds derive from information obtained from earlier work here or in literature references. Band strengths for COFCl used here were derived from mass balance calculations based on one of the PGDP experiments (See Appendix A for a more detailed explanation). O_2 and Cl_2 are IR-inactive (that is, transparent in the IR spectrum), so they cannot be detected by FTIR.

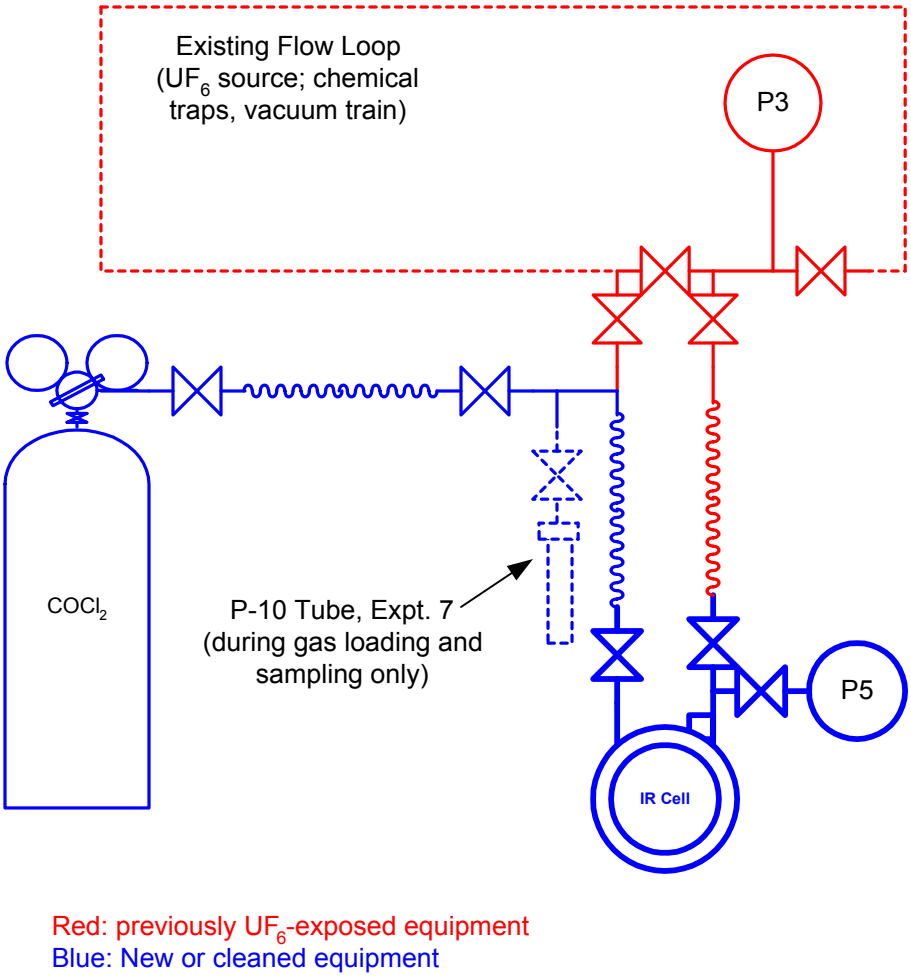

Fig. 1. Test loop modifications for $COCl_2$ / UF_6 experiments.

4.2.2 Methods and Results

Experiments performed as part of this effort were all of a scoping nature, each designed to answer a specific question. There was essentially no duplication, so it is not possible to comment on reproducibility of the results. For the sake of coherence, each experiment will be discussed separately, giving operational details and then results and interpretation. Since the results of one experiment led to or strongly influenced the design of the next, this will also show the chronology of the study's findings.

Experiment 1, phosgene stability in test loop. The purpose of this test was to determine whether $COCl_2$ would be stable in the presence of components previously exposed to UF_6 and other fluorinating agents and reaction products in the existing ORNL test loop.

The IR cell was held at 25ºC for this test. Phosgene gas (99+%, Linde, Inc.) was loaded into the IR cell and into both flex hoses adjacent to the cell to a pressure of 5.2 Torr. The cell isolation valves were left open. Pressure gauge P5 was not yet installed; the system pressure was read by sensor P3. The IR outlet hose and tubing had a prior history of UF_6, F_2 and ClF_3 use; the remainder of the hardware did not. Overnight (16 h) the system was static, but the pressure rose from 5.7 to10.4 Torr. This rise was later found to be due to a valve seat leak adding N_2 or He to the IR outlet line from another (inert-gas-pressurized) section of the test loop. There was no means to force gas mixing, so any reaction in the previously used section would be seen only after the products had diffused to the IR cell or been slowly forced toward the cell by the inert leak. Spectra were taken periodically overnight. $COCl_2$ diminished only slightly, the net loss being < 0.1 Torr. Whether this is due to reaction or the flushing action of the leak is uncertain.

Product gases appeared at trace levels. COFCl was seen clearly via its 1093 cm^{-1} band, though at a very low level, ~ 30 microns Hg at the end of the run. COF_2 *may* have also been present (~ 20 microns Hg, but its peak was very weak and the signal-to-noise ratio poor). CO_2 definitely was seen, but at a level that seems not directly related to gaseous $COCl_2$ (~ 0.9 Torr, neglecting pressure broadening, which should not be strong at 5 to10 Torr total pressure). More CO_2 appeared than could be accounted for by the < 0.1 Torr loss of $COCl_2$.

Conclusion, Expt 1: Some $COCl_2$ reaction was seen in this partly-cleaned, partly UF_6-exposed system. Based on the rate of appearance of reaction products, the "lifetime" of $COCl_2$ would be about 76 days, a reaction rate much slower than observed in the similar PGDP experiments.

Experiment 2, phosgene stability in new components of test loop. The purpose of this test was to determine if $COCl_2$ (alone) was stable in the new and clean section of the test loop.

The IR cell was again held at 25ºC for this test. Only the cell and nearby new or cleaned hardware were involved during the 4-day exposure. $COCl_2$ was added to the (evacuated) IR cell and to the inlet and outlet lines. Then (because a leak from the atmosphere had not yet been ruled out), N_2 was added to raise the pressure to approximately one atmosphere. Thus, although 7.6 Torr was initially present in the starting volume, most of that $COCl_2$ was flushed by this fill technique into the smaller IR-cell and inlet line volume. After filling with N_2, the IR cell outlet isolation valve was shut but the inlet line isolation valve was left open.

Initial spectra showed much less than the expected concentration of $COCl_2$ (most of it having been flushed out of the IR cell to the far end of the IR inlet line). Spectra taken unattended over the New Year Holiday weekend (4 days) showed the $COCl_2$ partial pressure slowly rising to approximately the expected (compressed) initial value. This experiment proved to be a demonstration of the slow rate of diffusion of

gases in long tubes, but it also sufficed as a stability test for $COCl_2$. $COCl_2$ stability could not be precisely quantified from $COCl_2$ loss because even after 4 days, diffusion mixing was not complete. No reaction products (COF_2 or COFCl) appeared, however.

CO_2 again appear and grew during the experiment, but at levels that are unlikely to be directly related to $COCl_2$ reaction.

Conclusion, Expt 2: $COCl_2$ was stable in the new/clean section of our system, showing no reaction to form COFCl or COF_2.

Experiment 3, phosgene + UF_6. The purpose of this experiment was to observe the reaction rate of gaseous $COCl_2$ and UF_6. (as in the two PGDP experiments), but in a system with no history of prior exposure to UF_6 or other fluorinating agents.

The IR cell was held at 25ºC for this test. About 4.7 Torr $COCl_2$ was loaded into the IR cell and the nearby pressure gauge (P5). The gas was held for approximately 1 hour to see if $COCl_2$ reacted in the absence of UF_6. No changes in the IR spectra were seen.

UF_6 was added to the cell (53 Torr additional), which was valved in such a way that the $COCl_2$ would all remain in the IR cell during the fill process. The P5-gauge isolation valve shut after about 1 minute (because the pressure gauge is internally heated to 100ºC, and we did not want that hot zone to confuse the intended room-temperature experiment).

The gases were held in the IR cell at this condition for 20 h, during which time IR spectra were periodically taken. Over this period of time, UF_6 declined somewhat (to be expected in a non-passivated system), but $COCl_2$ did not, nor did the expected products, COFCl or COF_2, appear. The detection limits for the product species in these spectra were approximately 0.002 Torr for COFCl and 0.004 Torr for COF_2. CO_2 and HF both grew during the 20-h hold period. HF is a plausible product of UF_6 reacting with H_2O. H_2O plausibly might be present as an initial adsorption layer on materials of construction or might have permeated the Viton gaskets sealing the IR windows. The CO_2 source was, again, unknown.

About 20 h into the exposure, the P5-gauge isolation valve was opened. Over the next half-hour, gases in that (~6 cc) volume were able to mix by diffusion with gases in the IR cell (~55 cc). If $COCl_2$ had fully reacted in the (hotter) pressure gauge region, we should have seen a drop of about 10%. We did not see any drop in $COCl_2$, nor did we see any COFCl or COF_2. UF_6 dropped slightly, indicating higher consumption in the warmer gauge region.

Conclusion, Expt 3: No reaction was observable in the clean/new (SS, Monel, ZnSe) system at 25ºC. Based on reaction product detection limits, the $COCl_2$ consumption rate is less than 0.03%/h under these conditions.

Experiment 4, phosgene + UF_6, higher temperature. The purpose of this experiment was to observe the gas-phase reaction rate at a temperature approximating that which the cylinder would experience during filling with liquid UF_6.

At the end of 1 day at 25ºC (Experiment 3), no reaction of $COCl_2$ was observed in the $UF_6/COCl_2$ mixture. A new mixture was not made; rather, the existing one was heated up for this experiment. The IR cell was heat-traced and its temperature controlled by a thermocouple taped to the cell wall and insulated from the heat tape. The temperature was controlled at 77 ±1ºC. This temperature emulates the temperature of a cylinder during filling with liquid UF_6 (although no liquid was involved in this

experiment). Heat-up took about 1.5 h, after which the cell remained at operating temperature for another 20 h.

Toward the end of the run, absorption bands began growing in the 1100 – 1300 cm^{-1} region of the IR spectrum. These closely matched a reference spectrum of Fomblin® oil. A thin layer of Krytox® grease (chemically very similar to Fomblin) had originally coated the Viton O-rings that sealed the IR windows. This apparently flowed or wicked onto the IR windows. This interference is not directly relevant to the reactions we are trying to observe, but tended to obscure certain peaks of interest in later spectra.

$COCl_2$ bands decreased in intensity and changed shape with the increased temperature. Most of this change was due to gas expansion, but some was due to redistribution of molecular energy level populations. After the experiment, a second IR calibration series was done for $COCl_2$ at 77ºC. It is this second calibration that was used in the data analysis for this experiment. We already had a 75ºC calibration series for UF_6. For COFCl and COF_2, room temperature peak strength calibration factors were adjusted only for ideal gas density changes and thus may be less accurate.

There was no clear loss of $COCl_2$ during this experiment. Taking starting vs ending spectra at face value, perhaps 1% was lost at most, but the difference between initial and final spectrum peak heights is not statistically significant. UF_6 loss continued, as expected.

No obvious indication of product bands was seen in the raw spectra, but spectral subtraction was applied to null out first the Krytox bands, then the $COCl_2$ band at 1833 cm^{-1}. The resulting spectrum contained a *hint* of a peak at 1885 cm^{-1}, (one of the strong bands of COFCl). The signal-to-noise ratio was poor (~2:1), and artifacts can appear at band edge locations during subtraction (1885 is in the band edge region of the 1833 cm^{-1} $COCl_2$ peak). There was an even more tentative hint of a peak in the COF_2 region. Taking these possible bands at face value, we deduced final partial pressures of 0.022 Torr COFCl and 0.025 Torr COF_2. The apparent loss of $COCl_2$ is consistent with this gain of products, but all may be statistical fluctuations.

Conclusion, Expt 4: In this 77ºC experiment, there is a very tentative indication of trace reaction products of $COCl_2$ at the limit of detection. Again, the rate (~0.02%/h) is orders of magnitude lower than in the corresponding PGDP room-temperature experiments.

Experiment 5, phosgene + UF_6, 77ºC, higher surface area. In this experiment, a fine Monel screen was added to the IR cell to increase the surface area of the system significantly. The intent was to test the possibility that reaction of $COCl_2$ with UF_6 is catalyzed by the UF_6-exposed material of construction surfaces (or perhaps by UF_5 or similar deposits formed by passivation of the metal surfaces). Except for the addition of the screen, this experiment duplicated the conditions of Experiment 4 (77ºC, similar partial pressures).

The Monel mesh used contained a rectangular grid of 200 wires per inch, each wire being 0.0021 inches in diameter. The effect on the superficial surface area (i.e., not considering microscopic roughness, which was not known) of the internal exposed surfaces of the IR cell and nearby tubes and valves would be to increase it from 100 cm^2 (10 cm^2 of which was due to the ZnSe IR windows) to 525 cm^2.

The cell was heated to and controlled at 77ºC. $COCl_2$ was introduced to the evacuated cell to a pressure of 8.3 Torr, following which UF_6 was added, increasing the pressure to 60.6 Torr. The gases were isolated in the IR cell (plus P5 pressure gauge region) overnight (17 h). The total pressure the next morning was essentially unchanged (60.8 Torr measured), but IR spectra revealed that UF_6 declined from its initial value of 52.6 Torr to 38.6 Torr, while HF increased to 14 Torr. $COCl_2$ was essentially

unchanged at 8.27 Torr. COFCl was detectible at a partial pressure of 0.025 Torr. This experiment was allowed to continue over the following weekend, at the end of which (at 89 h total duration) $COCl_2$ was down only slightly to 8.16 Torr (a total loss of 0.11 Torr). UF_6 had fallen to 26.5 Torr and HF had risen to 22 Torr. COFCl had grown only slightly to 0.038 Torr. COF_2 was not detectible; our estimate of its detection limit in these spectra is 0.012 Torr.

Conclusion, Expt 5: Though it was more definitively identified in this experiment, the rate of growth of the COFCl for the first 16 h is not significantly different from that observed in experiment 4 (conducted at the same temperature but without the increased surface area afforded by the Monel screen). This rate of apparent $COCl_2$ reaction is not sufficient to consume $COCl_2$ during the time the UF_6 is at or near the melting point in the 30A cylinder fill scenario. Of course, most of the UF_6 and $COCl_2$ (if it were present) would likely be in the liquid phase in a filled cylinder, not the gas phase.

Experiment 6, phosgene (alone), 77°C, higher surface area. The purpose of this experiment was to see if the previous 6 days of UF_6 exposure had changed the ability of $COCl_2$ to remain stable in the system.

Following the previous experiments, the IR cell was evacuated. $COCl_2$ alone was then put into the IR cell and P5 region, all originally clean areas that had now accumulated about 6 days exposure to UF_6 in experiments 3 through 5. This gas mixture was left overnight at 77°C. The high-surface-area Monel screen was still present in the cell. Over the previous 6 days of experimentation, the system had consumed a significant amount of UF_6 (thus depositing reduced fluorides such as UF_5 and oxyfluorides such as UO_2F_2). Recall that it was the observation of such "blank" reactivity at PGDP that had led us to testing reactivity in clean/new hardware.

Overnight, $COCl_2$ declined about 17% (from 10.1 to 8.4 Torr, a loss of 1.7 Torr). We observed growth of COFCl (0.14 Torr) and COF_2 (0.50 Torr). Other species seen were CO_2 (0.18 Torr) and SiF_4 (0.05 Torr) There is a possibility that a trace of CCl_4 was present (if so, at 0.04 Torr), but the observation is questionable. $COCl_2$ can disproportionate to CCl_4 and CO_2 at high temperature (on the order of 500°C) [Fink 1933], but it is hard to imagine it doing so at the conditions of this experiment. Absent were any of the simple fluorocarbons (CF_4, C_2F_6 or C_3F_8) or chlorofluorocarbons (C_XF_{4-X}).

The loss of $COCl_2$ significantly exceeded the appearance of plausible reaction products, even considering the uncertainty in calibration factors for the reaction products. Other loss routes include reaction to form non-volatile species or dissolution into the Viton gasket material or its Krytox coating.

Conclusion, Expt 6: The rate of growth of the reaction products COFCl and COF_2 is about 20 times the rate seen in the corresponding first day of experiment 5 ($COCl_2$ + UF_6). This reaction rate is lower than those observed in the PGDP FTIR analytical system, but the rate trend in this apparatus after less than a week's exposure to UF_6 seems to be approaching that in the PGDP system.

Experiment 7, phosgene + UF_6 , 77°C, liquid phase. This experiment attempted to duplicate the UF_6 liquid phase environment. Based on the (extrapolated) $COCl_2$ / UF_6 solubility relationships deduced from literature information (see Appendix B), most (> 99%) $COCl_2$ will, if completely mixed with liquid UF_6 during the filling process, be found in the liquid phase rather than the gaseous phase.

The apparatus for this experiment was described in Section 4.2.1. UF_6 was loaded into the P-10 tube by evacuating the tube, chilling the bottom with liquid N_2, and freezing a known quantity of UF_6 (quantified by partial pressure drop from a known volume). $COCl_2$ loading was done similarly. During this process, excess $COCl_2$ was inadvertently frozen into the tube. Most of the excess was removed by successive gas

removals, similar to post-experiment sampling (described below). Successive batches of gas were removed into a known volume, including the IR cell. For each batch, one or more spectra were taken. The amounts of $COCl_2$ and UF_6 removed were tracked and the process repeated until the computed remaining $COCl_2$ was near the target composition.

The net quantities loaded into the P-10 tube were computed from IR spectra to be 6.77 gm UF_6 and 29 mg $COCl_2$. The net weight gain of the P-10 tube, however, was 7.6 gm, essentially all of which must be due to UF_6. The average $COCl_2$ concentration is 1.5 mol %. This is about 3.2 times the 0.465 mol % derived for the scenario in which a 30A cylinder scenario containing one atmosphere of $COCl_2$ gas is filled to its statutory limit with liquid UF_6.

For these quantities loaded into the P-10 tube, we compute that at 80ºC, using densities for UF_6 liquid and gas from Anderson [1994], there will be 1.87 cc of liquid and 4.50 cc of gas. Later observation of the liquid level through the translucent P-10 tube was consistent with this prediction. Figure 2 shows the liquid mixture in the P-10 tube. If $COCl_2$ dissolves to equilibrium in the liquid UF_6, then our solubility extrapolation predicts that about 87% will be in the liquid UF_6 phase in the P-10 tube, with its gas phase partial pressure being 192 Torr. We had, however, no direct measure of pressure in the P-10 tube.

After loading, the P-10 tube was mounted into a secondary containment box itself in the radiochemical hood containing the test loop. Two thermocouples were mounted on the tube, one on the plastic body and one on the stainless steel VCR nut at the top of the tube. The P-10 tube was heat traced, with the heater controlled by an Omega CN9000A temperature controller, which was controlled by the body-mounted thermocouple. The secondary enclosure was sealed and power was applied to the heat tape. Within about 15 minutes, the solid UF_6 was seen to melt and within 30 minutes the tube was at the target temperature of 80ºC. It was held at this temperature for the next 17.25 h, the temperature being recorded overnight by the data acquisition system.

The tube was then cooled, allowing the UF_6 to freeze. Once at room temperature, it was re-connected to the IR inlet line. Gas samples were taken batch-wise by (1) evacuating the IR cell, pressure gauge region, and inlet line (total volume, 112 cc); (2) isolating that evacuated section at the IR outlet valve; (3) opening the P-10 valve, and expanding gas from it into the 112-cc volume; (4) shutting the P-10 tube valve, and (5) recording an IR spectrum.

This process was repeated some 18 times before all the volatile material in the P-10 tube was removed. After the first three sampling operations, larger expansion volumes were used to speed up the process, using valves further downstream from the IR cell. The next two samples taken were of 186 cc and the next 12 samples were of 596 cc. The final sample was again 112 cc, at which point the pressure behavior made it clear that no more solid remained in the P-10 tube to evaporate. The P-10 tube was sealed over the following weekend, and then re-sampled. Some gas had evolved (the post-weekend pressure was estimated to be 41 Torr prior to expansion). Its composition was high in carbonyl species, closely resembling the composition of the initial gas batch.

Typically, on initial opening of the P-10 valve, the pressure would rise suddenly, and then rise more slowly for a few minutes. This is common in solid UF_6 transfer operations: the initial gas expansion lowers the pressure below the UF_6 vapor pressure. Additional UF_6 evaporates (technically, sublimes), but this cools the UF_6 solid surface, lowering the (local) vapor pressure. As heat migrates to that surface, additional UF_6 can evaporate. During later batch sampling operations, this second rise became slower and slower. The P-10 tube was warmed by a heat gun to speed up evaporation of the remaining solid in later batches.

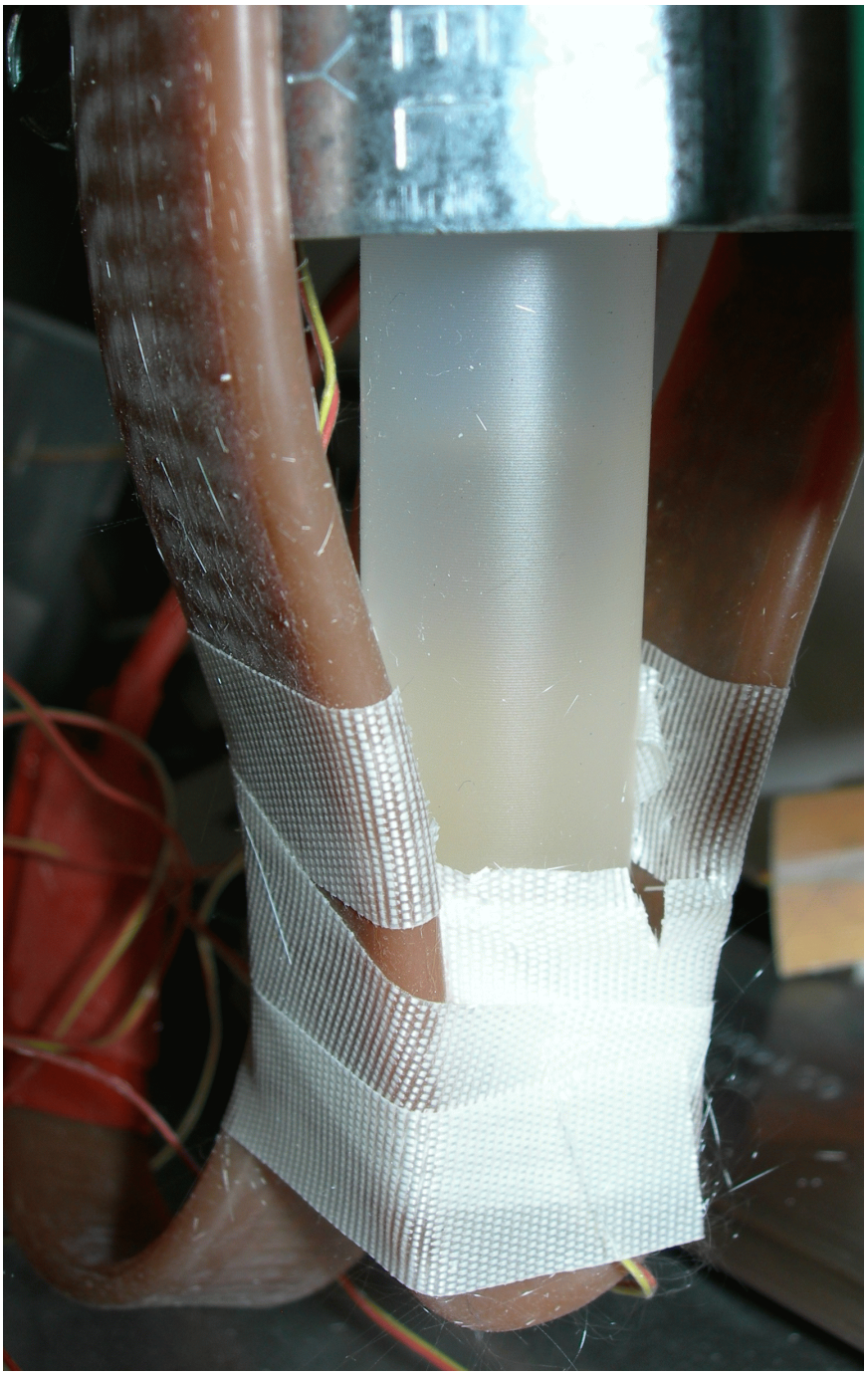

Fig. 2. P-10 tube with liquid $UF_6/COCl_2$ mixture, Expt. 7. Liquid level can be discerned about one tube diameter below bottom edge of the steel clamp.

The gas compositions deduced from the IR spectra are plotted vs percent of total gas removed in Fig. 3. The $COCl_2$ concentration was 64 mol % in the first sample and then fell sharply over the next several samples until it stabilized at a level of 0.05 mol %, after which it slowly rose in succeeding samples to 0.2 mol %. Finally, in the last sample (of much lower total pressure than earlier samples), its concentration again rose. UF_6 was relatively low in the initial sample (20%) but quickly rose to 99% and remained at that level until the final samples, in which it fell to 20%. COFCl was present at 1% in the initial sample but quickly fell below the detection limit in later samples. COF_2 was present in the initial spectrum at 0.1% but was not detectible again until the post-weekend gas sample. CO_2 appeared in the spectra at a level of about 1% throughout the entire sampling process. HF was 10% of the initial sample but fell below the limits of detection within a few samples.

The spectral data were combined with pressure and temperature data to compute the quantities of each gaseous compound removed in each batch sample, and they were summed over all batches to arrive at a mass balance estimate for each gas in this experiment. Because the gas from a single batch was not mixed, composition differences (e.g., between gas still in the inlet line and gas that has reached the IR cell) will result in a certain degree of inaccuracy in this mass balance. With that in mind, however, the computed results for this experiment are shown in Table 3.

Table 3. Experiment 7 mass balance, per IR. Units = micromoles

	UF_6	$COCl_2$	COFCl	COF_2	HF	CO_2
Initial	19232	294	0	0	n/a	n/a
Final	17700	342	7.47	0.52	54	280
Recovery[a]	92%	116%	2.54%	0.18%	n/a	n/a

[a] "Recovery" for carbonyl product species is referenced to initial $COCl_2$ quantity

The apparent increase in $COCl_2$ is probably due to the unmixed-sample problem mentioned, although the initial loading of both UF_6 and $COCl_2$ suffers from some uncertainty because of the inadvertent addition and later removal of excess $COCl_2$.

We cannont definitively determine whether the reaction took place in the gas phase as opposed to the liquid phase, since at least 13% of the original phosgene is expected to reside in the gas phase (based on mass balance calculations using solubility data discussed in Appendix B). It is likely, however, that most reaction took place in the liquid phase with its much higher UF_6 density. Reaction of about 2.7% of the $COCl_2$ (based on reaction product appearance) over the span of 17.25 h yields an average fractional loss rate of 0.16%/h, about eight times larger than either the 77°C gas-phase $COCl_2$ + UF_6 rate in our system (expts. 4 and 5), but a little lower than the no-UF_6 rate in Expt. 6 (which, however, had a much lower partial pressure of $COCl_2$).

There are some ancillary implications to these data as well. The less important factor is that a moderate fraction of the total recovered carbonyl species and HF (3% of total $COCl_2$, 8% of COFCl, 9% of COF_2 and 7% of HF) appeared only after 3 days in which the P-10, previously evacuated after the experiment, had modestly re-pressurized by (we speculate) evolution of gases dissolved into the Kel-F body of the tube. Most of the recovered material (83% of $COCl_2$, 92% of COFCl, 91% of COF_2 and 90% of HF) appeared in the first sample taken (3 days earlier). Considering the system volume ratios, the first gas sample taken should represent the gas present over the solid UF_6 – in fact it must have been slightly diluted by some evaporating UF_6.

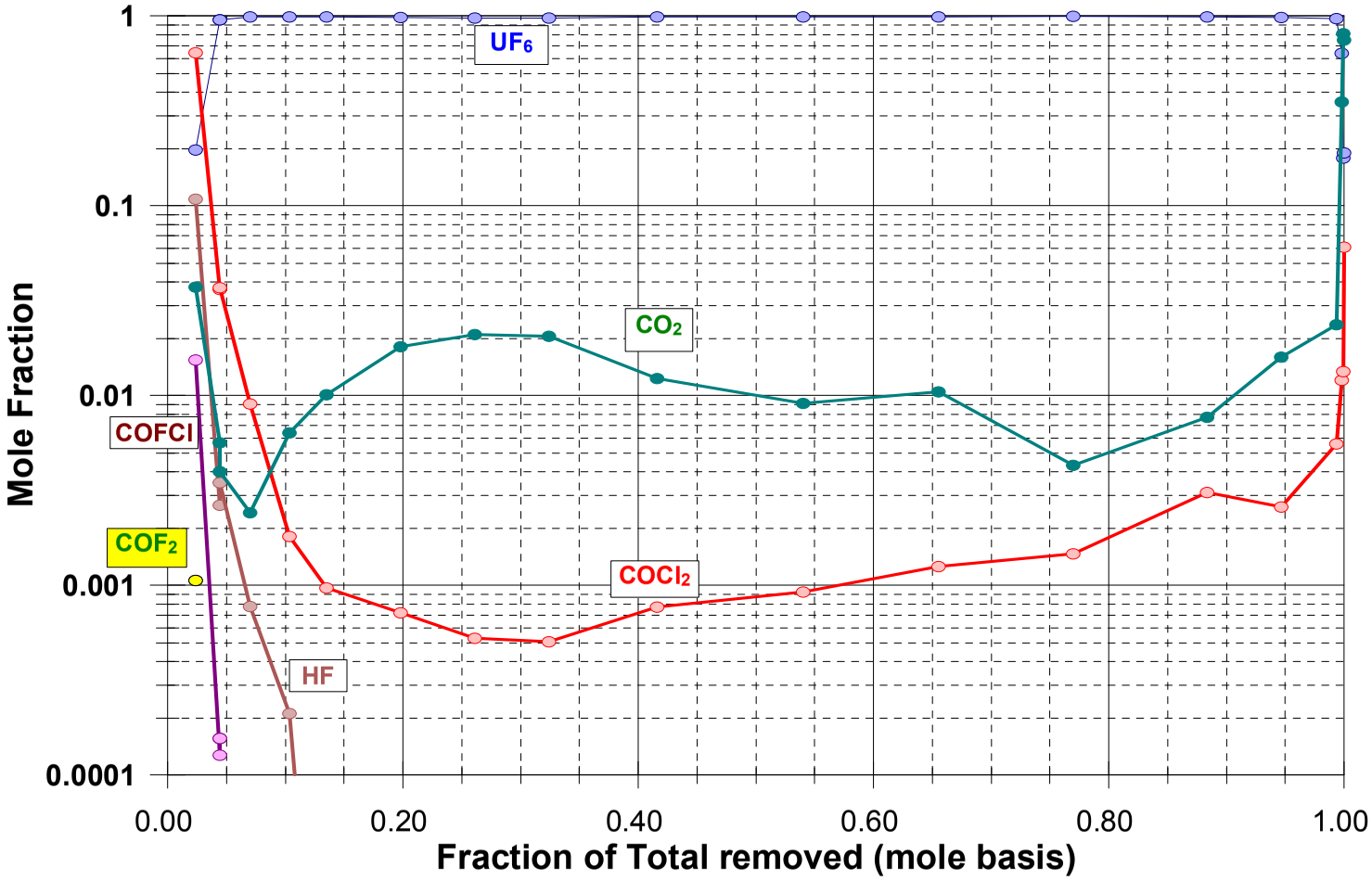

Fig. 3. Experiment 7, $COCl_2$ + UF_6 (liquid) at 78°C. Each point represents the gas composition of a sample taken at room temperature after the end of the experiment. Sampling continued until the reactor contents were exhausted (see text for more complete description).

The more important ancillary observation is that during most of the sampling, the $COCl_2$ level was between 0.05 and 0.2 mol %. These levels are one to two orders of magnitude higher than what could evolve from the Kel-F over the time interval between sample withdrawals (based on the post-experiment gas evolution rate). Thus, the majority of the $COCl_2$ seen in the middle samples represents the concentration of $COCl_2$ in the evaporating solid UF_6. We estimate this (apparent) $COCl_2$ solubility in solid UF_6 to be about 100 times lower than the predicted solubility in the liquid. Considering the uncertainties in composition measurement and liquid solubility extrapolations, this ratio may be uncertain by a factor of 4. Although tentative, this observation provides us the only information we have on the solubility of $COCl_2$ in solid UF_6.

Since there was no pressure gauge reading the P-10 tube while it was hot, we had no direct or indirect measure of the degree to which $COCl_2$ was dissolved in the UF_6 liquid. It is clear, however, that after cooling, little of the $COCl_2$ remained in the solid. It either separated out during the freezing process or never fully dissolved in the liquid initially. If no $COCl_2$ initially dissolved in the liquid UF_6, its partial pressure in the gas phase would have been about 1400 Torr. In contrast, if it fully dissolved to equilibrium (see Appendix B), we compute that the $COCl_2$ partial pressure would have been 192 Torr. There thus would have been a considerable driving force toward dissolving $COCl_2$ into the UF_6 liquid phase. We do not know the binary diffusion coefficient for $COCl_2$ and UF_6 in the liquid state, but values for pairs of species of similar molecular dimensions and chemical character span only a limited range [Weast 1984] of values. We carried out a simple numerical simulation of diffusion of $COCl_2$ into UF_6 liquid. The results suggest that at even at the lowest plausible values for their (liquid-phase) binary diffusion coefficient, dissolved $COCl_2$ should have reached at least 80% of its equilibrium value in the time allotted for experiment 7.

Conclusion, Expt 7: The effective reaction rate of $COCl_2$ in liquid UF_6 appears higher than that in the gas phase, but is too low to definitively demonstrate that $COCl_2$ would have been essentially entirely destroyed during the few days that the cylinder temperature was above the UF_6 melting point.

4.3 Discussion

It initially appeared (from the first PGDP serendipitous experiments) that $COCl_2$ and UF_6 reacted fairly rapidly at room temperature in the gas phase. Soon, however, $COCl_2$ fluorination in the absence of gaseous fluorinating agents was observed. This led to the ORNL experiments being designed with new or cleaned hardware. In that hardware, little or no reaction was observed in the gas phase, even at more elevated temperatures.

As mentioned in the literature search section of this report, products typically observed when $COCl_2$ reacts with inorganic fluorides are COFCl and COF_2. Only at temperatures much higher than would be experienced in the cylinder scenario were other products reported (e.g., CF_4, CO_2, chlorofluorocarbons). Our observations are consistent with this. We (and PGDP) observed COFCl and COF_2, and when experimental uncertainties permitted, there generally was a good correspondence between $COCl_2$ losses and COFCl and COF_2 gains.

We also, however, observed CO_2 in many of our experiments. While this could have been a reaction product of $COCl_2$, the quantities observed tended not to correspond to $COCl_2$ loss. Further, there was no obvious evidence of a reaction product containing Cl though Cl_2 is a thermodynamically viable product and is not detectable by FTIR. A seriously complicating factor is that our FTIR is not perfectly buffered against CO_2 from the air – a small concentration change in CO_2 in the (long) IR beam path *outside* the IR cell will appear as a large change if it is assumed the CO_2 is entirely *inside* the cell. The question of the source of CO_2 that frequently seemed to appear in our experiments is unresolved, but this simply could

not be investigated in the time available.

Results from both PGDP and ORNL are summarized in Table 2. In that table, experimental conditions are listed, followed by $COCl_2$ loss rates both in absolute terms (e.g. Torr/h) and fractional terms (fraction of initial quantity per hour). $COCl_2$ loss rates are computed two ways, first from observed reduction in $COCl_2$ from start to finish of the experiment and second from the appearance of reaction products COFCl and COF_2. The second mode assumes that these are the only products of $COCl_2$ fluorination, an assumption not guaranteed by thermodynamics but made plausible by literature search results and not contradicted by any of our observations. Finally, the fractional loss rates are inverted to yield an apparent "lifetime" for $COCl_2$. Mathematically, this suggests that the loss rate follows first-order kinetics, but we do not mean to imply that this is the case. There are not sufficient data to establish reaction mechanisms, reaction orders, or kinetic equations. We present these "lifetimes" to allow for more intuitive comparison of experiments with one another and with the timescale of the cylinder fill-and-store scenario.

The ORNL results are superficially at considerable variance from the PGDP experiments. PGDP experiments 1 and 4 show $COCl_2$ apparent lifetimes in UF_6 of a few hours, whereas the closest corresponding ORNL experiment, ORNL 3, shows a lifetime of at least a year. ORNL experiments 4 and 5, run at liquid-UF_6 temperature (both without and with increased surface area) show lifetimes of hundreds of days.

What is the difference between the ORNL and PGDP experiments? It is obvious from the ORNL experiments that $COCl_2$ and UF_6 in the gas phase do not, *per se*, react rapidly at room temperature or indeed at 77°C. Hypotheses we have considered to explain the differences between PGDP and ORNL results fall into two categories: (1) another reactant was present in the PGDP system or (2) some material or system impurity catalyzes reaction of $COCl_2$. "Other reactants" might be reduced uranium fluoride or oxyfluoride deposits resulting from passivation of hardware surfaces, metal fluoride films (e.g., CuF_2 or NiF_2) formed on surfaces of materials of construction during system passivation, or more exotic deposits remaining from previous work in the system. Another possibility is adsorbed but unreacted passivation agents (e.g., ClF_3) that might remain in limited (monolayer or less) quantity after pre-experiment system passivation. A possibility that falls into category (2) is the fact that the PGDP system used AgCl windows, whereas ours uses ZnSe.

We have not resolved the question of the source of accumulating reactivity in "used" systems, but after only a week of UF_6 experiments in our own (initially new and deliberately unpassivated hardware), $COCl_2$ reactivity in the otherwise empty system began to manifest itself. It never reached the level seen at PGDP, but the PGDP system, having been used in the analytical services organization, presumably had a lengthy history of gas analyses of UF_6. The observation of increasing latent empty-system reactivity in our own experimental system tends to rule out several of the possibilities – e.g., the exotic historical deposit postulate, the residual passivation agent, or IR window material differences. We also note that the $COCl_2$ fluorination rate absent UF_6 was considerably higher than its immediately prior fluorination rate when UF_6 *was* present. This suggests that the presence of UF_6 may actually impede the reaction somewhat (though not eliminate it). A final factor worth noting is that both the PGDP and ORNL experimental systems are constructed of materials that are especially well-suited for UF_6 service (Monel, nickel, or stainless steel), whereas the 30A cylinders are constructed of steel, a material adequately resistant but subject to slightly higher corrosion rates. If this question were to be further investigated, longer-term tests would be desirable, as would tests in steel containers more closely matching the actual cylinder wall material.

HF appears as a common reaction product in our experimental system, especially when the system is

deliberately not passivated with F_2 or ClF_3 prior to use. Given the extremely small degree of reaction observed, we cannot logically rule out the possibility that HF rather than UF_6 is the reactant, but we regard this as unlikely given the much more favorable thermodynamics of UF_6 as a fluorinating agent.

4.3.1 Application of Experimental and Theoretical Results to Cylinder Fill-and-store Scenario

The baseline scenario postulates a cylinder containing 1 atm of gaseous $COCl_2$, to which about 4950 lb of liquid UF_6 is added. The cylinder cools until the UF_6 solidifies (a process taking a few days at most), then is stored at outdoor ambient temperature for decades.

During the initial cylinder fill, it is likely that there would be considerable agitation. Therfore, we can reasonably assume that $COCl_2$ will dissolve into the liquid to a level approaching its equilibrium solubility, which would put 99% or more of the $COCl_2$ into the liquid phase (see Appendix B). During the day or so during which the cylinder cools and freezes, the reaction rate we observed in the liquid would lead to reaction of 3 to 10% of the $COCl_2$., largely producing COFCl. The portion in the gas phase (only a fraction of a percent of the total $COCl_2$ if solution equilibrium was achieved) would be only 0.5 to 2% converted to products in the same time frame at the gas-phase rates observed.

During the freezing of the UF_6, $COCl_2$ will tend to separate to the remaining (but diminishing) liquid phase and ultimately to the gas phase. We have no way of knowing how close this separation will come to achieving equilibrium and only a tentative idea of the equilibrium solid solubility of $COCl_2$ in solid UF_6. Over the range of probable solid solubilities mentioned in Appendix B, mass balance dictates that 10 to 65% of the (surviving) $COCl_2$ will remain in the solid *if solution equilibrium is reached*, and more will remain if some $COCl_2$ is trapped at supersaturated levels during the freezing process.

Ambient temperatures over the many decades of storage would generally be in the range of 0 to 35°C (with occasional wider extremes, especially on sun-exposed surfaces), with the average temperature (day/night/summer/winter) being about 15°C. We saw no reaction products in 20 h at room temperature in our laboratory experiment but we do note that longer accumulated exposure to UF_6 appears to increase the apparent reactivity of $COCl_2$, producing COFCl initially and ultimately COF_2. Sixty years of exposure would very likely suffice to react all $COCl_2$ in the head space to COF_2, although we cannot claim to have definitively demonstrated this. Temperature changes will add UF_6 to and remove it from the head space, so there will be mass transfer of dissolved $COCl_2$ from near-surface solid regions.

We have, however, no prediction regarding the rate of reaction of that portion of $COCl_2$ trapped deep in the solid mass of UF_6. The diffusion rate of $COCl_2$ through solid UF_6 is not known but is likely very low, so transport to the head space or to metal surfaces is not assured. We have only a very approximate indication of the solubility of $COCl_2$ in the solid, but the fraction dissolved or trapped in the solid mass could easily be a substantial fraction of the $COCl_2$ initially present in the cylinder.

5. CONCLUSION

The various activities described here were undertaken to determine if sufficient information could be developed to conclusively demonstrate that $COCl_2$, were it initially present in a UF_6 cylinder filled some 60 years ago, could have survived to the present day unreacted.

Thermodynamically, there is a strong tendency for reaction to take place, but information derived from the literature could not demonstrate that UF_6 or compounds chemically similar to it would necessarily react with $COCl_2$ rapidly enough to guarantee its destruction. Experimental efforts at PGDP and ORNL

were undertaken to develop further information.

While we observed some reactivity in both gas-phase and liquid-phase experiments, the rate was too low at liquid-UF_6 temperatures for a definitive claim of complete $COCl_2$ reaction during that phase of the scenario. At room temperature (representative of the 60-year storage period), the consumption was too low to detect in the gas phase, and no solid-phase experiments were conducted. Our observations (and those of PGDP), however, indicated that containers exposed to UF_6 slowly developed a propensity to promote reaction of $COCl_2$. This suggests that head space surfaces might develop this propensity and that $COCl_2$ in the head space would therefore not survive lengthy storage. We cannot, however, quantify that effect from data so far developed. Finally, no rate information was developed for reaction of $COCl_2$ dissolved in solid UF_6.

Liquid solubility found in the literature search (extrapolated to liquid UF_6 conditions) and a tentative experimental observation of the solubility of $COCl_2$ in solid UF_6 allow us to estimate (with considerable uncertainty) the partition of $COCl_2$ between phases during the different stages of the cylinder fill-and-store scenario.

Taken in total, from the information we have developed, we ***cannot say definitively*** that all (or even a large majority) of any $COCl_2$ initially present in a cylinder would have been consumed over the history of the scenario we have outlined. We have not, however, proven that $COCl_2$ *would* survive. Missing or incomplete information includes the following:

- Experimental determination of solubility of $COCl_2$ in liquid UF_6 at cylinder "fill" conditions.
- Experimental determination of $COCl_2$ solubility in solid UF_6.
- Reaction rate of $COCl_2$ in solid UF_6.
- Diffusion rate of $COCl_2$ in solid UF_6.
- Surface effects on the reaction rate, in particular the effect of steel as a surface and elucidation of the mechanism of the observed increase in reactivity with increased exposure to UF_6.
- Temperature dependence of the gas-phase and gas-surface reaction rates.

Experimental investigation of these topics could definitively answer the question of $COCl_2$ survival, but it would require a considerably larger effort than was possible in this campaign and would include some fairly long-term experiments. From a programmatic standpoint, it is more prudent to "clear" suspect cylinders by other means, for example, by reference to historical records of events that would have removed all $COCl_2$ from each cylinder or by cylinder sampling. This course of action was undertaken in parallel with our investigation of the chemical reactivity question.

REFERENCES

Anderson, J. C., C. P. Kerr, and W. R. Williams 1994. *Correlation of the Thermophysical Properties of Uranium Hexafluoride over a Wide Range of Temperature and Pressure,* ORNL/ENG/TM-51, Oak Ridge National Laboratory, Oak Ridge, TN, August.

Bodenstein, M., and H. Plaut 1924. "Bildung und Zerfall von Phosgen in der Wärme," *Z. Phys. Chem.* **110**, 399.

Brazell, Tom, 2005a. Paducah Gaseous Diffusion Plant/U.S. Enrichment Corporation. Private communication to L. D. Trowbridge, Oak Ridge National Laboratory, December 1, 2005.

Brazell, Tom, 2005b. Paducah Gaseous Diffusion Plant/U.S. Enrichment Corporation. E-mail to L. D. Trowbridge, Oak Ridge National Laboratory, 11:39, December 5, 2005.

Brazell, Tom, 2005c. Paducah Gaseous Diffusion Plant/U.S. Enrichment Corporation. E-mail to L. D. Trowbridge, Oak Ridge National Laboratory, 14:18, December 6, 2005.

Brazell, Tom, 2005d. Paducah Gaseous Diffusion Plant/U.S. Enrichment Corporation. E-mail to L. D. Trowbridge, Oak Ridge National Laboratory, 15:24, December 7, 2005.

Brazell, Tom, 2005e. Paducah Gaseous Diffusion Plant/U.S. Enrichment Corporation. E-mail to L. D. Trowbridge, Oak Ridge National Laboratory, 8:23, January 9, 2006.

Christe, K. O., and A. E. Pavlath 1964. "Silicon Tetrafluoride, a New Fluorinating Agent," *J. Org. Chem*. **29**, 3007.

Christe, K. O., and A. E. Pavlath 1965. "The Chemistry of Carbonyl Chloride Fluoride. I. The Ring Opening of Cyclic Ethers with Carbonyl Chloride Fluoride," *J. Org. Chem*. **30**, 1639.

Christe, K. O., et al. 1999. "Characterization of Oxygen Coordinated Adducts of $COCl_2$ COClF COF_2 w AsF_5 and SbF_5," *Inorg. Chem.* **38**, 3143.

Emeléus, H. J., and J. F. Wood 1948. "The Preparation and Reactions of Carbonyl and Sulphuryl Fluorides and Chlorofluorides," *J. Chem. Soc.*, 2183.

Fink, C. G., and C. F. Bonilla 1933. "Study of Reactions of CCl_4 Synthesis," *J. Phys. Chem* **37**, 1135.

Glemser, O., and U. Biermann 1967. "Über Reaktionen des Stickstofftrifluorids mit einigen Oxychloriden und Oxyfluoriden der Nichtmetalle," *Chem. Ber.* **100**, 1082.

Hasek, W. R., W. C. Smith, and V.A. Englehardt 1960. "The Chemistry of Sulfur Tetrafluoride. II. The Fluorination of Organic Carbonyl Compounds," *J. A. C. S.* **82**, 543.

Haszeldine, R. N., and H. Iserson 1957. "Aliphatic Halogen Compounds: Conversion of Carbonyl Halides into Tetrahalomethanes," *J. A. C. S.* **79**, 5801.

Haszeldine, R. N., and H. Iserson 1959. "Preparation of Tetrahalomethanes," U.S. Patent 2,907,798.

Hoge, B., and K. O. Christe 1999. "A Convenient Synthesis of Carbonyl Chloride Fluoride," *J. Fluor. Chem.* **94**, 107.

HSC 2004. *HSC Chemistry ver 5.0 Chemical Reaction and Equilibrium Software***,** Outokumpu Research Oy, P.O. Box 60 FIN–28101, Pori, Finland.

Humiston, B. 1919. "Action of Fluorine on Organic Compounds," *J. Phys. Chem*. **23**, 572.

Lord, A., and H. O. Pritchard 1970. "Thermodynamics of Phosgene Formation from Carbon Monoxide and Chlorine, *J. Chem. Thermodynamics* **2**, 187.

Maier, W. B., and W. H. Beattie 1984. "Solubility of Uranium Hexafluoride in Some Low-Temperature Solvents," *J. Chem. Eng. Data* **29**, 190.

ORO 1977. *Uranium Hexafluoride: Handling Procedures and Container Criteria*, ORO-651, Rev. 4, Oak Ridge Operations Office, Energy Research and Development Administration, Oak Ridge, TN, April.

Ryan, T. A., C. Ryan, E. A. Seddon, K. R. Seddon 1996. in R. J. H. Clark, ed., *Phosgene and Related Carbonyl Halides, Monograph 24, Topics in Inorganic and General Chemistry*, Elsevier, Amsterdam.

Simons, J. H., D. F. Herman, and W. H. Pearlson 1946. "Carbonyl Chlorofluoride," *J. A. C. S.* **68**, 1672.

Tullock, C. W. and D. D. Coffman 1960. "Synthesis of Fluorides by Metathesis with NaF," *J. Org. Chem* **25**, 2016.

Tullock, C. W., 1958. "Preparation of Carbonyl Fluoride," U.S. Patent 2,836,622.

Walter, A. K., 2005. "Management Alert on 'Uranium Hexafluoride (UF_6) Storage' (S05IS017)," memorandum to manager, U.S. Department of Energy, Oak Ridge Operations, September 30.

Weast, R. C., ed. 1984. *CRC Handbook of Chemistry and Physics,* 65th ed., CRC Press, Boca Raton, FL.

APPENDIX A

INFRARED SPECTRAL CALIBRATION

APPENDIX A. INFRARED SPECTRAL CALIBRATION

The primary analytical tool in our experiments is a Fourier transform infrared spectrometer. Infrared active gases (i.e., those with absorption bands at IR frequencies) can be approximately quantified by measuring the intensity of characteristic bands. The accuracy of quantification for specific compounds depends on the source of calibration data and to a lesser degree on other physical conditions of the sample spectrum. The Beer's Law extinction coefficient (sometimes termed "k-factor," the peak height-to-partial pressure ratio of a specific band) should be derived from reference spectra taken at conditions similar to those of the sample spectra. Calibration spectra are taken at several partial pressures, ideally, though not always, spanning the partial pressures of the samples later analyzed using the calibration. A linear fit of partial pressure vs peak height (measured in absorbence units) yields the k-factor for the compound. The detection limit for a given compound and peak will be determined by the largest peak height that could *not* be discerned in the sample spectrum. This is somewhat subjective, and may depend on noise level in the spectrum and the presence of interfering bands overlapping the band of interest.

HF is particularly subject to an effect termed "pressure-broadening". Briefly stated, HF peaks will appear stronger in dilute concentration spectra than they would in a spectrum of the same partial pressure of pure HF. The degree of apparent exaggeration is dependent on the partial pressure and the identity of diluents. Our reported HF partial pressures were calculated taking this into effect, using techniques and data presented by D. F. Smith [1965]. In the pressure regime of interest here, UF_6 and $COCl_2$ do not seem to be particularly subject to this phenomenon.

For UF_6 and $COCl_2$ we have taken calibration spectra in our own system (a 10-cm gas cell in our Bomem Michelson MB-104 FTIR) with the gas cell held at the temperatures of the experiments. Thus, IR calibration factors for these compounds are quite good. The accuracy of partial pressure results is estimated at better than ±5% of measured value. For COF_2 , we do not have such spectra but use peak calibration factors deriving from spectra taken in the past on other types of instruments. Applied to this work, the accuracy is estimated at ± 15% of the calculated partial pressure except when degraded by signal-to-noise considerations at very low partial pressures. For COFCl, quantification is tentative. Nielsen [1952] displayed a spectrum of COFCl which is useful for identifying the peak positions, but not for quantifying their strengths to better than about an factor of 4. In general, we use the bands at 1883 cm^{-1} and 1093 cm^{-1} to quantify this species. Unfortunately, we do not have a ready reference for COFCl. The k-factors used here derive from mass balance calculations in the third PGDP experiment [Brazell 2005c] taken as $COCl_2$ apparently reacted with wall deposits. We assumed that $COCl_2$ reacted to form either COFCl or COF_2 (and nothing else), applied the "known" factors for $COCl_2$ and COF_2, and computed a factor for COFCl that minimized the carbonyl mass balance discrepancy in that experiment's several spectra. The factor determined produced a carbonyl mass balance that varied by no more than 1% in any spectrum in that run. This factor for the 1883 cm^{-1} peak, which we use throughout this document, is 3.77 Torr/AU at 24°C (and 4.46 at 77°C, adjusting only for gas density change with temperature). This is by no means exact – values as low as 2 or as high as 6 could be considered admissible. One "AU", or "absorbence unit," is defined as the reduction in IR beam intensity (at the specific frequency of interest) by a factor of 10.

K-factors used for gas quantification are listed in Table A-1. The values for $COCl_2$ agree reasonably well with those obtained at PGDP and with a reference spectrum of dilute $COCl_2$ in air provided to us by Jack Dermagian of Argonne National Laboratory [2005].

Table A-1. IR Peak strengths (k-factors) used in this document

	Freq (cm^{-1})	**k** (23°C) Torr/AU	**k** (77°C) Torr/AU
$COCl_2$	858	2.95	3.81
	1833	4.99	6.42
COFCl	1883	3.77	4.46[a]
	1093	3.00	3.54[a]
COF_2	1955	10.6	12.6[a]
CF_4	1281	4.99	6.42
UF_6	1157	210	260
	625	1.06	1.25[a]

[a] 77°C value calculated adjusting only for ideal gas density change.

References.

Brazell, Tom, 2005. Paducah Gaseous Diffusion Plant/U.S. Enrichment Corporation. E-mail to L. D. Trowbridge, Oak Ridge National Laboratory, 14:18, December 6, 2005.

Dermagian, Jack, 2005. Argonne National Laboratory. E-mail to L. D. Trowbridge, Oak Ridge National Laboratory, 15:23, November 22, 2005.

Smith, D. F., 1965. *Infrared Spectra Analysis for Hydrogen Fluoride*, K-1275, Oak Ridge Gaseous Diffusion Plant, Union Carbide Nuclear Corp, Oak Ridge, TN, April.

Nielson, A. H., et al. 1952. "Infrared and Raman Spectra of F_2CO, FClCO and Cl_2CO," *J. C. P.* **20**(4), 596.

APPENDIX B

SOLUBILITY OF $COCl_2$ IN UF_6

APPENDIX B. SOLUBILITY OF $COCl_2$ IN UF_6

Should $COCl_2$ survive immediate contact with UF_6, then the solubility of $COCl_2$ in both liquid and solid UF_6 becomes important in determining the distribution of available $COCl_2$ between the gas and the condensed states. Reaction rates are likely to be considerably different in the gas phase, liquid phase, and solid phase. Similarly, diffusion to potentially catalytic surfaces (cylinder walls) will be relatively fast in the gas phase, slow in the liquid phase, and possibly negligible in the solid phase.

As mentioned in the literature search section, Maier and Beattie [1984] discussed experiments in which a small quantity of UF_6 was dissolved (from its solid form) into liquid $COCl_2$ at temperatures ranging from 159 to 271K. The conditions of the experiment are very far removed from those of the cylinder-filling scenario in terms of concentration, temperature, and duration. That aside, it was noted in their article that the data behavior was fairly well represented by a "regular solution" model and indeed not very far from an ideal solution.

A regular solution model is typically appropriate for molecules without specific strong interactions (for example, acid-base association, complex formation, ionic interactions, or strong hydrogen bonding) [Lewis 1961]. The $COCl_2 - UF_6$ pair appears to meet this criterion. The stability of a regular solution can be characterized by a simple excess free energy term

$$dG_{xs}/RT = R_0 X_A X_B$$

where R is the gas constant, T is absolute temperature, X_I is mole fraction of species I, and R_0 is a parameter related to the difference in energy of interaction between like and unlike molecular pairs. This excess free energy term is added to the free energy for an ideal solution to modify the equilibrium between gas and liquid solution.

For a regular solution, R_0 typically is nearly constant (that is, it is not a function of concentration), although it may vary modestly with temperature. Since we have, from Maier and Beattie, data on solubility at one extreme of concentration, we investigated the degree to which those data were well represented by this regular solution model. A local adaptation of the public-domain computer program SOLGASMIX [Trowbridge 1995] was used for this purpose. Using that program, we determined, for each data point in Maier and Beattie's article [1984], a value of R_0 that exactly reproduced the liquid solubility reported. These values are plotted in Fig. B-1 . As can be seen, these values are approximately constant across the temperature range of the experimental data, averaging 1740 J/mol. An *ideal* solution would, by definition, have $R_0 = 0$. For our particular scenario, we need a value for R_0 at temperatures from 64°C to perhaps 80°C. Shown in Fig. B-1 are three extrapolated lines, one a simple average (R_0 = constant), a second in which R_0 is fit as a linear function of T, and a third in which it is fit as a parabolic function of T. Extrapolated values for R_0 at 80°C are listed in Table B-1 for an ideal solution, for the constant value (taken as the simple average of the derived values for R_0), for the linear fit in T, and for the parabolic fit in T. In addition, extrapolated 90% confidence bands are listed for the linear extrapolation. Calculations were done using SOLGASMIX to determine the predicted partition of $COCl_2$ between gas and liquid phases at 80°C for these various values of the excess free energy parameter. The results are listed in Table B-1. The average mole fraction used for these calculations was 0.1 mol % $COCl_2$, and the relative liquid and gaseous volumes were roughly representative of a full 30A cylinder.

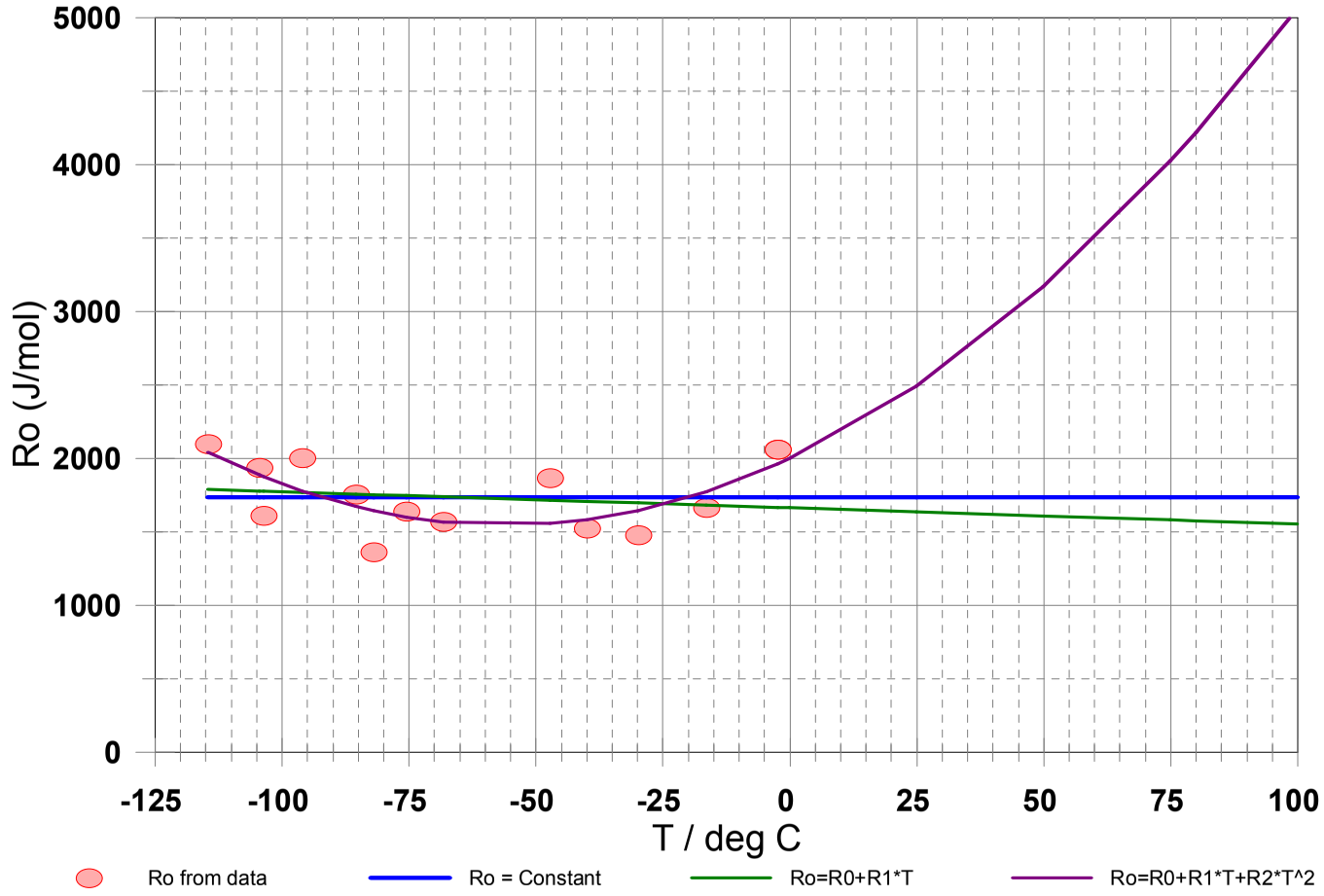

Fig. B-1. Extrapolation of regular solution excess free energy parameter R_0 for the system $COCl_2$ + UF_6.
Points show values derived from literature experimental data [Maier 1984]. Lines show regression fit of those points as a simple average (i.e., constant value), as a linear fit, and as a parabolic curve-fit.

Table B-1. Calculated partition between gas and liquid phases for different extrapolated values of the regular solution excess free energy parameter R_0. The average $COCl_2$ concentration is 0.1 mol %, and gas-to-liquid volume ratio is that of a nearly-full 30A cylinder

R_0 (J/mole)	P(bar) $COCl_2$	P(bar) UF_6	$COCl_2$ X (mol %) in gas	$COCl_2$ X (mol %) in liq.	% of total $COCl_2$ in liq.	Activity ratio P / X	Basis of extrpolation
0	0.0077	1.88166	0.41%	0.0992%	99.6%	7.8	Ideal solution
949	0.0107	1.88166	0.56%	0.0988%	99.5%	10.8	Linear fit, neg. 90%. c.i.
1578	0.0132	1.88167	0.69%	0.0985%	99.3%	13.3	Linear fit
1739	0.0139	1.88167	0.73%	0.0984%	99.3%	14.1	Simple average R_0
2208	0.0162	1.88168	0.85%	0.0981%	99.2%	16.5	Linear fit, pos. 90% c.i.
4219	0.0315	1.88171	1.65%	0.0962%	98.4%	32.8	Parabolic fit of R_0

It is worth noting that although the gas phase concentration of $COCl_2$ varies more than a factor of 4 between an ideal solution ($R_0 = 0$, almost surely too low a value) and the parabolic extrapolation (almost surely too high a value), the concentration in the liquid hardly varies at all. Since nearly all the UF_6 mass is in the liquid state, 99% or more of the total mass of $COCl_2$ will be in the liquid state – that is, if the initially gaseous $COCl_2$ and liquid UF_6 are sufficiently mixed to reach solution equilibrium. Without experimental data in the general realm of the cylinder-fill scenario, we will not know how accurate such a model is in our specific chemical system, although such models have worked well for similar chemical systems [Lewis 1961; Trowbridge 1995].

Solubility in the liquid (i.e., during cylinder fill) is not a particularly good guide to solubility in the solid phase (i.e., the condition that will apply during the 60 years following freezing). Dissolved gases also may not reach solution equilibrium with the gas during freezing because of slow transport between and within phases. We found no data in the literature on solid solubility of $COCl_2$ in UF_6, but one of our reactivity experiments gave a tentative indication of this solid solubility.

In brief, during the final reactivity experiment, a mix of UF_6 and $COCl_2$ (which had been present first as liquid but later was cooled to room temperature and frozen) was removed from the small reaction vessel by incrementally expanding "batches" of gas to the IR cell, each batch being analyzed by IR to give the composition. The initial batch was predominantly $COCl_2$, but within a few batches the $COCl_2$ composition fell to a fairly constant 0.05 mol % and then slowly and steadily rose as more batches were removed until it reached 0.2 mol % near the end of the removal process (see Fig 2). It is plausible that the range of 0.05 to 0.2 mol % represents the solubility of $COCl_2$ in solid UF_6 in equilibrium with the partial pressure of $COCl_2$ prevailing at room temperature (although one could also argue "at the freezing point of UF_6, 64°C").

Using the quantities of UF_6 and $COCl_2$ loaded into the expt. 7 vessel, the vessel volume, and literature densities for liquid and solid UF_6, thermodynamic calculations were run simulating the room temperature endpoint of this experiment. The temperature-independent value for R_0 (1740 J/mole) was used as the excess free energy parameter for the liquid state, and the solid was defined as a (solid) regular solution of

UF_6 and $COCl_2$ (using thermodynamic parameters for liquid $COCl_2$). R_0 for this solid solution was varied until the $COCl_2$ concentration in the solid duplicated values in the range of concentrations observed (specifically, 0.05 mol %, 0.1 mol % and 0.2 mol %). The R_0 values for the solid solution that matched these conditions were 18,150 J/mol, 16,500 J/mol and 14,700 J/mol, respectively. On the basis of this single, serendipitously derived data point with many potential uncontrolled variables, we cannot with confidence assert that this model of solubility is valid or that these values encompass the full range of uncertainty. The apparent solid solubility values they predict, however, are plausible, in line with expectation, and (perhaps most important) all that we have to work with.

As tentative as the solubility information may be, we can use it to simulate the solubility behavior of $COCl_2$ in the cylinder scenario. We used the median values for both the liquid (1740 J/mol) and solid solubility (16,500 J/mol) R_0 values to simulate a 30A cylinder filled to its limit of 4950 lb (6384 g-mol) UF_6 and containing the 2.15 lb (9.89 g-mol) of $COCl_2$ from the "air-jet-evacuated" scenario. These calculations were done for several characteristic temperatures: 80ºC (temperature when filled with liquid UF_6), 65ºC (cooled to just above the point at which solid UF_6 appears), 59.7ºC (the temperature at which the last of the liquid freezes), and 20ºC (nominal ambient temperature). Selected results from these calculations are displayed in Table B-2.

Table B-2. **Solubility simulation of 30A cylinder**

Condition		Filled	Cooled	All frozen	Room T
T	ºC	80	65.0	59.7	20
$P(COCl_2)$	mm Hg	16	12	566	458
$P(UF_6)$	mm Hg	1410	916	709	64
Gas vol.	L	91	108	270	290
Gas	mole $COCl_2$	0.067	0.061	7.372	7.014
Liq	mole $COCl_2$	9.823	9.829	0	0
Sol	mole $COCl_2$	0	0	2.518	2.876
% of total $COCl_2$ in gas		0.68%	0.62%	74.54%	70.92%

Features to note in this table are the increasing free volume as UF_6 cools and then freezes, and the percentage of total $COCl_2$ present in the gas volume of the cylinder. The percentage present in the gas phase does not vary much with temperature except for during the transition between liquid and solid. These calculations predict that much, but not all, of the $COCl_2$ should separate to the gas as freezing progresses.

Similar calculations were run for the room-temperature final state for the other "low" and "high" values of the solid-solubility R_0, yielding values for percent-of-total-$COCl_2$ in the gas phase of 54% and 83%. Three additional calculations were also run for the case in which the cylinder was not air-jet evacuated prior to filling with UF_6, i.e., with an initial load of 6.46 lb (29.7 g-mol) of $COCl_2$. In all three cases, sufficient $COCl_2$ was present that a small volume of $COCl_2$-rich liquid remained after freezing (0.3 to 1.3 L containing about 75 mol % $COCl_2$). The percentage of total $COCl_2$ present in the gas phase *plus* in this (easily evaporated) liquid phase ranged from 58 to 90%; the rest would be sequestered in the solid and thus not readily accessed by, for example, head space sampling. It should be noted that none of these calculations takes into account loss of $COCl_2$ due to reaction with UF_6.

The implication of these computational results is that a significant fraction of all $COCl_2$ would be in the gas space and would be detectible by gas analysis, assuming it survived chemical reaction and assuming that solution equilibrium were approached. The balance, however, also a significant fraction, would be sequestered in the solid, even at the lowest solubility scenarios considered. Since we were unable to develop any information on the reaction rate of $COCl_2$ trapped in solid UF_6, at a minimum we must conclude that this fraction *might* survive to the present day.

References.

Lewis, G. N., M. Randall, K. S. Pitzer, and L. Brewer 1961. *Thermodynamics*, 2nd ed., McGraw-Hill, New York, 282.

Maier, W. B., and W. H. Beattie 1984. "Solubility of Uranium Hexafluoride in Some Low-Temperature Solvents," *J. Chem. Eng. Data* **29**, 190.

Trowbridge, L. D. and J. M. Leitnaker 1995. *A Spreadsheet-Coupled SOLGAS—A Computerized Thermodynamic Equilibrium Calculation Tool*, K/ETO-140 Rev.1, Lockheed Martin Energy Systems, K-25 Site, Oak Ridge, TN, September.

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