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Low Temperature Cold Trapping of Uranium Hexafluoride Containing Hydrogen Fluoride

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INTRODUCTION

The use of a freezer–sublimer system operating at low desublimation pressures to replace 10-in. nuclearly safe cold traps for low assay (<5% U-235) uranium hexafluoride (UF_6) would significantly simplify operations and is economically attractive provided the nuclear safety of the system can be assured.[1] A major requirement of such assurance is the availability of conditions guaranteeing that the nuclear safety design criterion, which requires that the H/U atomic ratio in the condensate in the freezer–sublimer always be less than 0.33 for assays up to 5%, will never be violated. The existing data[2,3,4] on the HF-UF_6 system have been analyzed and several experimental test runs have been made to establish the existence of the necessary control factors.

SUMMARY AND CONCLUSIONS

A general vapor pressure equation giving the vapor pressure of HF–UF_6 solutions as a function of temperature and mole fraction UF_6 has been developed from the data of Davis et al.[3] The precision of the data at the 95% confidence level is ± 0.1 torr at temperatures between -100°F and -121°F. The calculated vapor pressure of pure HF is 4.6 torr at -100°F and 3.1 torr at -108°F. Theoretical considerations suggest that the true value will be slightly lower. Data reported herein suggest the true value is about 0.5 torr lower than the calculated value. In experimental studies of the cold trapping operation at -108°F and at a trap pressure of 2.2 torr, only 7.3% of the HF entering the trap was retained in the trap. At a trap pressure of 4.6 torr, over 80% of the HF entering the trap was retained. Nearly all the retained HF could be removed by evacuation at -108°F with a mechanical vacuum pump for 1 to 4 h. The data obtained in this study confirms that the physical chemistry of the HF-UF_6 system previously developed accurately describes the behavior of the system and that so long as the pressure in the trap is maintained below the vapor pressure of pure HF at the trap temperatures, there is no way that sufficient HF can be trapped to give an H/U ratio of 0.33 regardless of the HF/UF_6 ratio in the feed to the trap.

Specifically, for a freezer–sublimer operating at –100°F, the trap pressure should be maintained below 3 torr to guarantee that the H/U remains well below the control value of 0.33.

ANALYSIS OF PHASE EQUILIBRIA DATA

The experimental data of Davis et al[2,3,4] have been critically reviewed to determine the consistency of the data and to establish the range of the confidence band on the vapor pressure as a function of temperature and composition when the data are extrapolated to the conditions of interest. These estimates were subsequently verified to the extent required by the experimental data reported in the next section. The method chosen to establish the consistency of the data was to plot the vapor pressure as a function of the liquid composition for the 30 experimental data points and to construct smoothed curves through the data for each of the seven temperatures at which data was taken. Thus 98 values at selected solution compositions between 0.0 and 0.1 mole fraction were read for improved equation fittings. Advantage was taken of the fact that Davis et al[3] had established that the vapor pressure of a liquid solution of a given UF_6-HF composition was adequately represented by an equation of the form

$$\ln P(cmHg) = A_{(x)} + B_{(x)}/T \tag{1}$$

where P(cmHg) is the vapor pressure at mole fraction of UF_6, X, in cmHg, $A_{(x)}$ and $B_{(x)}$ are functions of the composition only, and T is the absolute temperature in K.

An equation of this form is also preferred for the extended extrapolation of vapor pressures of pure liquids.[5] Excellent fits to the experimental data were found when A and B were expressed as fourth order polynomials in the mole fraction UF_6 in the range of mole fraction UF_6 between 0.0 and 0.1 as follows:*

$$A_{(x)} = 15.25118 + 13.88719X - 277.23934X^2 + \tag{2}$$

$$3085.46120X^3 - 12432.84269X^4$$

$$\text{and } B_{(x)} = -3203.594 - 2197.09576X + 70963.81576X^2 - \tag{3}$$

$$1043895.379X^3 + 4780826.925X^4$$

$$\text{where } X = \text{mole fraction } UF_6.$$

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*As is normal for higher order polynomial fits, equations 2 and 3 are not valid for values of X_{UF6} much greater than 0.1 and should not be used outside the compositional range of the experimental data. Examination of the solid – liquid phase diagram for HF-UF_6 shows that this range of mole fractions of UF_6 in saturated liquid HF-UF_6 solution is sufficient to cover all freezer–sublimer operations regardless of the mole fraction of UF_6 in the vapor fed to the freezer–sublimer.

The statistical information relating to the variation of the dependent variable, ℓn P(cmHg), as a function of the mole fraction, X, and the absolute temperature in K is given in Table 1.

The calculation of the 95% confidence interval at the temperature of interest employs the data in Table 1 and the t-Tables. For 30 observations with 10 required to define the system of equations, the value of t at the 95% confidence level for 20 degrees of freedom is 2.09. Within the experimental temperature range of 314.09 to 365.24 K, the limit of error in the logarithm of the vapor pressure at the 95% confidence level is

$$\begin{aligned} L_{95} &= \pm t\ \sigma_r \\ &= \pm(2.09)\ (0.006466) \\ &= \pm 0.01351. \end{aligned}$$

Table 1. Statistical information on the variance of ℓn P(cmHg) as a function of mole fraction and temperature

Item	Value
σ_r^2, variance of ℓn P(cmHg)	4.18018×10^{-5}
σ_r, standard deviation of ℓn P(cmHg)	6.466×10^{-3}
Av. 1/T, mean value of reciprocal T	2.92746×10^{-3} (T = 341.59K)
$\sum (1/T - \overline{1/T})^2$	1.94154×10^{-6}
σ_b^2, variance of the regression coefficient, B	21.5335
σ_b, standard deviation of the regression coefficient B	4.64042

Outside the experimental range of temperature*, the limit of error in the logarithm of the vapor pressure at the 95% confidence level is given by

$$L_{95} = \pm t \ \sigma_{r,i} \tag{4}$$

$$\sigma^2_{r,i} = \sigma^2_r + \left(\frac{1}{T_i} - \overline{\frac{1}{T}} \right)^2 \sigma^2_b \tag{5}$$

$$\sigma^2_b = \frac{\sigma^2_r}{\Sigma \left(\frac{1}{T} - \overline{\frac{1}{T}} \right)^2} \ . \tag{6}$$

The values of $\sigma^2_{r,i}$, $\sigma_{r,i}$, and L_{95} are given in Table 2 for a potential operating temperature for freezer-sublimers (-100°F or -73.33°C), the temperature at which the experimental study reported herein was made (-78°C, sublimation temperature for solid CO_2), the freezing point of pure HF(-83.6°C) and the eutectic temperature of the UF_6-HF system (-85.0°C). The minimum, mean and maximum values of the vapor pressure of pure HF at the 95% confidence level are given in Table 3 for these same four temperatures.

To avoid condensation of a solution phase of HF and UF_6, the total pressure in the freezer–sublimer must be maintained below the pressure at which the liquid solution can condense at the operating temperature of the freezer–sublimer. Since at a given temperature the vapor pressure of pure HF is lower than the vapor pressure of any solution of UF_6 in HF in the solution composition range of interest (the HF-UF_6 system is azeotropic with a maximum in the vapor pressure curve), the condition of non–condensation of HF is guaranteed by staying below the vapor pressure of pure HF at any selected freezer–sublimer operating temperature. Thus, employing the vapor pressure equations to estimate the maximum permissible overpressure, the operation of the principle can be demonstrated at the convenient experimental temperature of -108°F (the sublimation

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*The contribution of the term,

$$(x_i - \bar{x})^2 \frac{\sigma^2_r}{\Sigma \ (x - \bar{x})^2} \ ,$$

which would normally be included in equation 5, is neglected since the contribution to $\sigma^2_{r,i}$ is not very important when the value of x_i is within range of the experimental x-values.

temperature for solid CO_2 slush). The experimental trapping data also permit a partial assessment of the accuracy of the vapor pressure equation extrapolation in comparison to the precision which was developed in this section.

Table 2. 95% Confidence limits on the natural logarithm of the vapor pressure at four temperatures of interest

Temperature °C	Reciprocal Temp. $(K)^{-1}$	$(1/T^{-1} - \bar{1}/T)^2$	Variance of ℓn P at T_i, $\sigma^2_{r,i}$	Std. Dev. of ℓn P at T_i, $\sigma_{r,i}$	95% C.I., L_{95}
-73.33	5.00325×10^{-3}	4.30890×10^{-6}	1.34594×10^{-4}	±0.01160	±0.02425
-78.0	5.12295×10^{-3}	4.82018×10^{-6}	1.45102×10^{-4}	±0.01207	±0.02523
-83.6	5.27426×10^{-3}	5.50747×10^{-6}	1.60404×10^{-4}	±0.01267	±0.02548
-85.0	5.31350×10^{-3}	5.69319×10^{-6}	1.64403×10^{-4}	±0.01282	±0.02579

Table 3. The predicted vapor pressure of HF at four temperatures at the 95% confidence level

Temperature		Vapor Pressure, torr		
°C	°F	Minimum	Mean	Maximum
-73.33	-100	4.50	4.61	4.72
-78.0	-108	3.05	3.13	3.21
-83.6	-118	1.88	1.93	1.98
-85.0	-121	1.66	1.70	1.75

EXPERIMENTAL AND RESULTS

Experiments have been performed that demonstrate that gaseous UF_6 containing HF as an impurity can be separated from the HF by cold trapping.

In these experiments two cold traps were connected in series. The first of these was cooled by a CO_2 - isopropyl alcohol slush to a temperature of -108°F. The second trap was cooled with liquid nitrogen to -320°F. Provision was made for measuring the gas pressure between the traps over a range of 0 to 5 torr by use of a calibrated Validyne pressure transducer.

Prior to the start of each experiment, the traps were evacuated at ambient temperature, removed from the system and weighed to milligram accuracy. The traps were then put back in the system, cooled to their respective temperatures, and the experiment started.

Continuous flows of UF_6 and HF were fed to a mixing tee through separate Hastings flow-meters. From the flow rates and the elapsed time, the total amount of each constituent going to the first trap could be calculated. At the first trap the UF_6 from the mixture was trapped at -108° F. The effluent, consisting of HF which had not been trapped by the first trap, was then passed to the second trap where it was trapped at -320° F. The outlet line of the second trap was continuously pumped on by a Welch mechanical vacuum pump.

During each experiment the back pressure on the first trap measured by the pressure transducer between the traps was monitored continuously. Due to the pressure drop in the connecting lines between traps, there was always considerable back pressure on the first trap, this could be increased further by adjusting a throttle valve at the inlet of the second trap. Since the back pressure was measured between the traps rather than within the first trap; the actual back pressure within the first trap was slightly higher than that observed at the transducer. For the various experiments the observed back pressure ranged from 2.2 to 4.6 torr.

The pertinent data obtained from these experiments are listed in Table 4. As these data show, with a back pressure of 2.2 torr, only a small part of the total HF entering the first trap was retained by that trap. However, at a back pressure of 4.6 torr, over 80% was retained. The vapor pressure of HF at -108°F has been calculated to be 3.1 torr; a measured value of 3.6 torr[4] has been obtained at -112° F. From the data of Table 4 it is concluded that as long as the back pressure on the trap does not exceed 2.2 torr, or roughly 2/3 of the vapor pressure of the HF, very little of the HF going to the trap will be retained. However, when the back pressure exceeds the vapor pressure of HF, most of the HF will be trapped. The data of Table 4 also shows that pumping for a few hours on the trap after the flow of UF_6 and HF to the trap has stopped will remove most of the HF from the trap.

The traps were operated for periods of 2 to 4 h with flow rates of 42 to 56 sccm of UF_6 and 6.0 to 8.5 sccm of HF. On a trap cross sectional area basis, the UF_6 flow rate would range from 4.2 to 5.6 lb/ft^2-h.

In determining the amount of HF retained by the first trap, several techniques were used. One of these involved a material balance where the amount of HF recovered by the second trap was compared with the total amount flowing to the first trap as indicated by the flow-meter. This was further checked by determining the amount of HF removed from the first trap after extensive pumping on this trap at -108° F. In addition, this trap was further pumped on at this temperature after heating the contents of the trap to 190° F to liquefy the UF_6 and thereby free any HF trapped within the solid UF_6 crystals. Extensive use was made of a comparison of the observed vapor pressure of the trap contents with the known vapor pressure of UF_6 at -108°, 32° and 77° F. At -108° F the UF_6 vapor pressure is low enough to be negligible. At 32° F it is about 18 torr and at 77° F about 112 torr. Any time the vapor pressure of the contents of the trap was in excess of the known vapor pressure of UF_6 at any one of these temperatures, the excess pressure was assumed to be due to HF. In general, where the amount of HF retained by the trap was determined by several different techniques, the highest value found is the one reported in Table 4. Since each experiment was performed under slightly different conditions, no statistical limit of error can be calculated in the usual manner. However, the instrumentation and techniques used give confidence that the values listed in Table 4 are within ±10% of the correct value.

Table 4. **Uranium hexafluoride plus hydrogen fluoride cold trapped at -108° F**

Run No.	Run Time, hr.	Flow sccm,		HF/UF_6 Mole Ratio Entering Trap	Back Pressure, torr	Percent of HF Trapped	HF/UF_6 Mole Ratio In Trap	Remarks
		HF	UF_6					
1	2	6.2	42	0.15	2.2	0.15	0.00022	Pumped 1-1/3 h after flow stopped
2	2	5.5	54	0.10	2.2	7.25	0.00725	Trap closed off while flow in progress
3	2	5.9	54	0.12	4.6	80.58	0.0967	Trap closed off while flow in progress
						2.32	0.00278	Pumped 3 h after flow stopped
4	4	8.8	56	0.16	2.5	22.00	0.0352	Trap closed off while flow in progress
						0.86	0.00136	Pumped 3-1/2 h after flow stopped

DISCUSSION

The vapor pressure equation developed from the data of Davis et al[3] has a precision of about 0.1 torr in this temperature range. The accuracy may be slightly less because the molar heat of vaporization which is contained in the B-value will not be independent of temperature but will show a small increase with decreasing temperature reflecting the change in the molar heat capacity of the liquid relative to that of the vapor at the same temperature. An experimental value of 3.6 torr was measured at -80.3 to -80.6° C by Davis et al[4] in a system in which the HF vapor was pumped through the HF liquid at temperature. In such a system the effects of minor concentrations of impurity gases such as air are maximized* and it is not surprising that the calculated value of 2.6 torr is lower. Considering the method of measurement of the vapor pressure, the agreement is considered good with the calculated value being the more reliable estimate of the vapor pressure but

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*The data of Davis et al[4] at -80.3 and -80.6° C were obtained by condensing the vapor at that temperature in a side trap. Errors on the high side are apt to be even larger than in normal operation.

it still may be slightly high. In the work reported at -108°F in the experimental section, a significant amount of the HF was trapped at a back pressure of 2.5 torr which thus must be close to the vapor pressure of the condensate solution. The pressure calculated from the set of equations 1, 2, and 3 is 3.1 ±0.1 torr for this condition. Only 7% of the HF was trapped with a back pressure of 2.2 torr which, as calculated earlier, indicates that if a back pressure of less than two thirds of the calculated vapor pressure is maintained, condensation of HF will not be a problem at the proposed trapping temperatures.

At an operating temperature for the freezer-sublimer of -100° F, maintenance of a back pressure of less than 3.0 torr will prevent the accumulation of HF in the UF_6 desublimate and guarantee that the H/U ratio will remain below the specified value of 0.33 for material containing up to 5% U-235. It has been experimentally verified that the necessary conditions for controlling the H/U ratio in the cold traps exist.

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