Properties of anhydrous hydrogen fluoride in the temperature range from 140 K to 190 K

S M Gubanov
National Research Tomsk State University, Tomsk, 634050 Russia
Sgubanov@yandex.ru

Abstract. This paper presents the analysis of the known empirical formulas on the pressure of the saturated vapors of hydrogen fluoride depending on the temperature. The possibility of using the formulas to determine the vapor pressure under the low temperatures is assessed. The calculation error of the pressure value depending on temperature outside the interval are determined.

1. Introduction
The separation technology of uranium isotopes includes the purification of the final product from light impurities, which is mostly hydrogen fluoride (HF). The purification is usually carried out by the desublimation of HF from the gas mixture stream into cooled containers using the special equipment. The main purpose of the desublimation plants is to eliminate the emission of the harmful substances into the atmosphere. Hydrogen fluoride formed during the production process is recovered from the gas mixture. The rest of the components of the mixtures are filtered and neutralized according to the sanitary standards before being discharged into the atmosphere. The properties of the anhydrous HF are: melting point - 190 K, boiling point - 292.5 K, and density - 0.99 g/cm$^3$. It dissolves well in water but is flammable and explosive. The average daily maximum permissible concentration in the air of the settlements is 0.005 mg/m$^3$. The critical concentration value is 8 mg/m$^3$.

The condensation-evaporation section is designed to condense the UF$_6$ residues and to purify the process stream from the light and harmful impurities. Fig. 1 shows the schematic diagram of the gas mixture separation process. The temperature level of 253 K is used to condense the bulk of the UF$_6$. The desublimation unit is thermostated at $T = 193$ K by air, and at $T = 77$ K - by liquid nitrogen (Fig. 1).

At the last stage, HF desublimation takes place in special containers cooled by liquid nitrogen. This cooling method is expensive and labor intensive. The main purpose of the desublimation plants is to eliminate the emission of the harmful substances into the atmosphere.

The developed chiller BXM-0,54/0,6 [1] allows cooling containers at the last stage of the desublimation by air in the temperature range of 130 K÷140 K [2]. To estimate the amount of uncondensed HF, it is necessary to measure the pressure of the saturated vapor in this temperature range. The empirical formulas known in the scientific literature [3-5] were obtained by direct measurements at a higher temperature, which is above the melting point of hydrogen fluoride. Such measurements for the temperature range from 140 K to 190 K were performed in [5].

The aim of this study is to determine the residual amount of HF in the process stream after the desublimation at the last stage when the tanks are cooled by cold air at the temperature of 130 K ÷ 140 K.
2. Formulation of the problem

After the development and establishment of the BXM-0,54/0,6 serial production [1], the HF desublimation section was switched to air cooling, which is less energy-intensive [2]. To determine the amount of HF passing through the section of its desublimation, it is necessary to determine the pressure of its saturated vapor at the temperature of the cold air in BXM-0,54/0,6.

The formulas given in [3-5] have not given a satisfactory result of the vapor pressure. The temperature ranges in which formulas [3-5] are reliable are higher than those realized in the air chiller. Formula [3] has been obtained in the temperature range from 192 K to 320 K, formula [4] - in the range from 273 K to 378 K, and formula [5] - from 293 K to 473 K. The pressure values in the temperature range from 140 K up to 190 K is not correct due to the extrapolation of the dependences to the temperature values in which measurements have not been carried out.

3. Solution

One of the first data on the saturated vapor pressure of HF at low temperatures was published in 1924 by J. Simons [3]. In the experiments, hydrogen fluoride was frozen by the liquid air (at 90 K) with subsequent heating. The measurement data were processed as the dependence of the vapor pressure on the melting point in the temperature range from 192 K to 320 K:

$$\log(P) = 7.37 - 1315 / T,$$

where $P$ is the pressure, mm Hg.

In 1953, an article was published [4]. The vapor pressure of HF was measured in the temperature range from 273 K to 378 K:

$$\log(P) = 8.38036 - 1952.55 / (62.37 + T)$$

where $P$ is the pressure, mm Hg.

Paper [5] provides data on the saturated vapor pressure of HF at high pressures in the temperature range from 293 K to 473 K. The obtained formula is:

$$\ln(P / 1000) = 25.5266 - 3267.53 / T - 1.82355 \cdot \ln(T) + 7.0719 \cdot 10^{-6} T^2$$

where $P$ is the pressure, kPa.

Formulas (1) - (3) determine the saturated vapor pressure of HF above the surface of the liquid anhydrous HF. The authors in [7] conducted the analysis on the influence of the HF molecules...
association on the value of the saturated vapor pressure. It was noted that the degree of the molecule association increases with decreasing temperature.

The formulas (1) - (3) are limited by three factors, which do not allow determining the saturated vapor pressure of HF at the temperatures below 190 K (HF solidification temperature): 1) in the formulas (1) - (3), the association of HF molecules with decreasing temperature is not taken into account; 2) formulas (1) - (3) were derived for the saturated vapor pressure above the liquid surface; 3) the extrapolation operation of the formulas to the temperature values outside the measurement interval is not a correct mathematical operation.

The theoretical temperature dependence of the saturated vapor pressure has the form:

$$P = A \exp\left(-\frac{L}{RT}\right),$$  \hspace{1cm} (4)

where $L$ is the phase-transition heat, $R$ is the universal gas constant, and $A$ is the constant.

It is known that during the sublimation and desublimation, the heat of the phase transition differs from the one during the evaporation and condensation. Therefore, the use of the formulas (1) - (3) to determine the pressure of saturated vapor over a solid HF surface is fundamentally impossible.

To determine the pressure of the saturated HF vapor over its solid surface, we have carried out the measurements on the specially designed stand [6]. The obtained formula to determine the dependence of the HF saturated vapor pressure on the pressure in the temperature range of 140K ÷ 190K is:

$$P = 1.4879 \cdot 10^{11} \exp\left(-3911.2 / T\right),$$  \hspace{1cm} (5)

where $P$ is the pressure, Pa.

Fig. 2 shows the calculation result of the HF saturated vapor pressure by the formulas from [3-6] in the temperature range of their derivation. It is noteworthy that the slope of the lines 1, 2, 3 is practically the same, but the slope of the line 4 is different. This indicates that the value of the phase transition heat in the formula (5) differs from the value determined by the formulas (1) - (3).

Fig. 3 shows the calculation results on the HF saturated vapor pressure according to the formulas from [3-6] in the temperature range from 140 K to 160 K. According to the figure, the saturated vapor pressure calculated by the formulas [3-5] significantly overestimates the values obtained from the experiments and approximated by the formula (5) [6].

The authors in [8] present the mathematical model and the calculation results on the HF desublimation on the inner walls of the tank. The calculation results according to the model [8] are plotted in Figs. 4, 5. Fig. 4 shows the distribution of the HF concentrations in the air along the height of the tank when it is cooled by the BXM at the temperature of 113 K, with the 6th level of the molecule association. During the residence time of the mixture in the tank, it cools down to the chiller temperature, having passed about the half of the tank height (Fig. 5). At the same distance, the saturated vapor pressure HF takes on the pressure value corresponding to the wall temperature.

We have estimated the HF mass concentration in the flow outgoing from the tank. The absolute pressure of the mixture is 50 Pa. The partial HF pressure is 45 Pa, and air - 5 Pa. When the mixture flow cools down to the temperature of 140 K, the partial HF pressure according to the formula (5) is 0.1067 Pa. The ratio of the partial pressures of HF and air and the ratio of the number of HF molecules to the number of air molecules are:

$$\frac{P_{HF}}{P_b} = \frac{n_{HF}}{n_b} = 0.00213,$$

where $P$ is the partial pressure, and $n$ is the molecule number per unit volume. Indexes are $HF$ is hydrogen fluoride and $b$ - air.

The mass concentration of HF in the gas mixture has the value:

$$\frac{\rho_{HF}}{\rho_b} = \frac{n_{HF} \mu_{HF} m}{n_b \mu_b} = 0.00213 \frac{19 \cdot 6}{29} = 0.00837 \frac{k_2(HF)}{k_2(b)},$$

where $\mu$ is the molar mass, $\rho$ is the density, and $m$ is the molecule association level.
Based on the obtained data, it is possible to estimate the required capacity of the chemical HF absorber that meets the technology requirements.

4. Conclusion
We have presented the analysis of the known empirical formulas on the temperature dependence of the pressure of the HF saturated vapors and its application at the low temperatures outside the empirical temperature range. The paper provides data on the calculation error of the HF saturated vapor pressure for the case of temperatures going beyond the range of the formulas’ derivation. We have also determined the HF mass concentration in the outgoing flow of the gas mixture from the desublimation tank by the empirical formula for the pressure of saturated vapor over the HF solid surface.
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