Construction of a novel generator for use in HF adsorption studies

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An HF generator based on the dissociation pressure of an alkali bifluoride is described. Sodium bifluoride salt was found to yield HF pressures of the order of 0.001 to 0.3 mm in the temperature range 60 to 135°C due to the equilibrium NaHF₂ \Rightarrow HF + NaF. The HF generator allows a dry carrier gas (typically N₂) to pass through a thermoregulated chamber filled with the crystalline bifluoride and furnishes HF concentrations from 5 to 1000 ppm at flowrates up to 5 ℓ /min for periods up to one year. The HF concentrations thus generated were stable to within 1% after a 40 min warm up period. Described also is the associated control system which allows the operator to send alternately dry carrier gas with or without trace HF concentration to an external cell or analyser.

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On décrit un générateur de HF qui est basé sur la pression de dissociation d'un bifluorure alcalín. On a trouvé qu'un sel de bifluorure de sodium fournit des pressions de HF de l'ordre de 0.001 à 0.3 mm à des températures allant de 60 à 135° C dues à l'équilibre NaHF \Rightarrow HF + NaF. Le générateur de HF permet à un gaz porteur sec (N₂) de passer à travers une chambre à température constante remplie de bifluorure cristallin et fournit des concentration de HF de 5 à 1000 ppm à des vitesses d'écoulement allant jusqu'à 5 ℓ /min pour des périodes allant jusqu'à une année. Les concentrations de HF générées de cette manière sont stables à 1% après une période de réchauffement de 40 minutes. On décrit aussi un système de contrôle associé qui permet à l'opérateur d'envoyer d'une façon alternative un gaz porteur sec avec ou sans trace de concentration de HF vers une cellule extérieure ou un analyseur.

[Traduit par le journal]

Introduction

In the course of our research program on the adsorption of HF on alumina powders, we needed a reliable, precise, and inexpensive source of dilute hydrogen fluoride in an appropriate carrier gas. Although dilute gas mixtures were available at relatively low pressures on special order from commercial suppliers of compressed gases, their composition was variable and their cost prohibitive for our purposes. We have succeeded in building a simple generator based on the temperature dependent dissociation of sodium bifluoride

[1] $NaF \cdot HF \rightleftharpoons NaF + HF$

At HF/NaF mole ratios <1, where no other stoichiometric compounds except NaHF₂ and NaF have been reported, the equilibrium vapour pressure of HF should be independent of the quantity of the bifluoride or fluoride present and can be calculated from the equilibrium constant of eq. [1] as

[2]
$$\ln P_{\rm HF} (\rm atm) = \ln K_{\rm diss} = \frac{\Delta G_{\rm diss}}{RT}$$

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This system has been studied by Fisher (1), Froning *et al.* (2), and Miller (3) using, respectively, direct pressure measurements, a transpiration method (both at higher temperatures), and a room temperature effusion method. They calculated K_{diss} and hence $P_{\rm HF}$, the partial pressure of HF as a function of temperature and their results can be expressed respectively as

[3] $\log P_{\rm HF}(\text{atm}) = 6.594 - 3521/T(T \text{ in } \text{K})$

At 473-548 K

[4]
$$\log P_{\rm HF}(\text{atm}) = 5.821 - 3196/T(T \text{ in } \text{K})$$

At 310–371 K

[5] $\log P_{\rm HF}$ (atm) = 6.677 - 3940/T (T in K)

At 273 K, eqs. [3], [4], and [5] predict equilibrium values of 5.0×10^{-7} , 1.3×10^{-6} , and 1.8×10^{-8} atm. Extrapolation to 373 K also gives rise to the contradictory values 1.4×10^{-3} , 1.8×10^{-3} , 1.3×10^{-4} atm. Although it is difficult to comment on the validity of the different experimental techniques employed, it has been noted by Miller (3) that the discrepancy may be due in part to the different temperature regions investigated.

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Results reported in this study are based on concentration, not pressure measurements. In the presence of an inert carrier gas of molecular weight M_{CG} , and a total pressure P_T atm, the HF concentration may be conveniently expressed as a weight fraction:

[6] [HF] in ppm
$$\simeq \frac{M_{\rm HF}P_{\rm HF} \times 10^6}{M_{\rm HF}P_{\rm HF} + M_{\rm CG}(P_{\rm T} - P_{\rm HF})}$$

While the apparent molecular weight of hydrogen fluoride gas approaches that of H_6F_6 at very high pressures (4), a value of 20.01 g/mol was used at the low partial pressures prevailing in this present work. On the basis of eqs. [3] to [5] it could therefore be expected that HF/N_2 mixtures (5 ppm to 10%) of fixed compositions should result by passing dry nitrogen gas through a bed of NaHF₂ crystals at temperatures in the range 0 to 200°C. A prototype generator based on these thermodynamic predictions was built and, incidentally, numerical results in close agreement with Miller's work were obtained.

Experimental

(1) Reagents

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Sodium bifluoride was prepared from Analar hydrofluoric acid 48% and Baker Analyzed Reagent sodium fluoride. HF (230 ml 48%) was added to 235 g NaF dissolved in 3 ℓ of boiling doubly distilled water. The solution was allowed to digest overnight on a steam bath, allowed to cool slowly to 0°C, and then rapidly filtered. The precipitate was recrystallized from doubly distilled water in a similar manner, dried in a dry air stream and finally in a vacuum oven for 12 h at 110°C at 10 mm Hg. All manipulations were carried out using new Nalgene Labware cleaned with live steam and boiling hot distilled water.

A hexamethylenetetraamine (Baker Grade), HMTA, solution was used to absorb HF. This buffer solution was prepared by neutralizing a 1% HMTA aqueous solution to pH 5.6 with 6 *M* HCl and adding 2 ml of the surfactant Triton X-100 0.2% in order to lower its surface tension.

(2) Instrumentation

The HF generator consists of the bifluoride reactor, a temperature control system, and a control system for the switching of gas streams. It is designed to be used with an external cell where HF can react or be adsorbed and an external HF analyser where the original or the residual HF concentration can be measured. The entire generating system is constructed from commercially available hardware, SWAGELOK connections, WHITEY and NUPRO valves and metering valves, 1/4 in. and 1/8 in. copper tubing. For the sake of economy all metal parts in contact with the gas stream are copper or brass rather than more resistant metals such as monel. However, after three months of continuous use at temperatures up to 135°C no deterioration due to HF attack was noticeable.

NaHF₂ Reactor

The reactor consists of a slightly modified PICKER type 449 TP 11 *M* heat exchanger. Its 48 inner copper tubes were filled with crystalline sodium bifluoride salt. The finely divided salt retained by two copper screens and thin Teflon membranes was compacted by mechanically vibrating the entire structure. One charge of the reactor, about 850 g NaHF₂, is theoretically sufficient to furnish over two million litres of HF at a concent

tration of 100 ppm. Connections to the external system are achieved by two B-14BKM4S4 WHITEY valves which can also be closed to isolate the reactor for repairs or exchange.

Temperature Control

The temperature of the NaHF₂ reactor is controlled by circulating oil in the outer jacket of the reactor in a countercurrent direction to the gas flow in the inner tubes. The oil is heated by a 800 W element which is controlled by a Yellow Springs Instrument type 406 thermistor located at the entrance to the reactor. The temperature of the circulating oil is thus controlled to better than 0.1° C at the lower end of the reactor, i.e. the exit of the HF/N₂ gas. The thermistor constitutes part of an electrical bridge and its resistances. The out-of-balance signal controls the heating element whose power can be further adjusted with a variable transformer to yield about 50% utilisation time.

Reactant Controls

The control logic governing the gas flow is schematized in Fig. 1. A stream of carrier gas sent through the network (1 + 2) or a stream passing through the network 3 can be directed to an external cell by means of a fourway valve (S-Reactor). Subsequently either stream can be sent to the external HF analyser or to waste by means of a fourway valve (S-Analyser).

HF Analyser

The gas stream containing concentrations of the order of 10 to 500 ppm HF is contacted in an absorption tower, Fig. 2, with the HMTA absorbing solution. After degassing, the buffered solution is analysed using an Orion fluoride electrode 94-09-A in a manner not unlike that described previously (5). The 4 ml free gas volume of the tower provides a contact time of more than 0.5 s (at flow rates up to 0.5 e/min) with about 0.3 ml of liquid hold up. The volume of the capillary tubing between the tower and the electrodes was kept to 0.2 ml, and the dead space of the electrode compartment to 0.1 ml in order to obtain a response time of less than 30 s.

Results and Discussion

HF Analyser

The electrode response of the analyser was calibrated using NaF solutions 10^{-6} to 10^{-1} *M* F⁻ in the 0.05 *M* HMTA buffer. These standard solutions were drawn through the electrode compartment by a Technicon Pump at the same rate as the sample solutions, i.e. 1.52 to 1.54 ml min⁻¹. A Nernstian electrode response with a slope $-58.5 \text{ mV/log }[\text{F}^-]$ was observed over the concentration range 10^{-1} to 10^{-4} *M* but slight deviations from linearity became notice-







FIG. 2. HF adsorption tower and electrode compartment. able below $5 \times 10^{-5} M F^{-}$. Measurements of HF concentrations in the sample solutions were confined

to the range 5 × 10^{-2} to 10^{-4} *M* F⁻. Evaluation of the efficiency of the scrubbing or absorption tower ideally requires a steady source of a fixed HF concentration in an inert carrier gas and the purpose of this project was precisely to construct such a generator. By allowing the scrubbed nitrogen carrier gas to bubble through a second absorption solution for extended periods of time it was evident that over 99% of the HF was absorbed in the tower for nitrogen flow ranges below 500 ml/min. As the gas flow rate increased further and the residence time in the absorption tower was reduced to less than 0.5 s, the scrubbing efficiency decreased slightly to about 95%. The scrubbing efficiency did not depend on the F⁻ concentrations except under conditions where the F⁻ concentration in the absorbing solution exceeded the concentration of the HMTA buffer, i.e., 0.05 M.

The HF analyser (i.e. the absorption tower and electrode response) can be evaluated by varying the flow rate of the buffer solution, the flow rate of the HF/N_2 gas, or the concentration of the HF in the carrier gas. The fluoride concentration in the buffer solution should vary as

$$[F^{-}] = \frac{[ppm HF]_{N_2}}{20} \times \frac{Nitrogen flow rate}{Buffer flow rate} \times \frac{Density of N_2}{Density of HMTA} \times 10$$

where the density of the nitrogen carrier gas at the temperature of the tower (14°C) can be taken as 1.22 g/ℓ and that of the buffer solution as 1.00 g/ml. Thus, the electrode response should vary in a loga-

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rithmic fashion with the nitrogen or the buffer flow rates as well as with the HF concentrations.

The variations of electrode response with the flow rates are summarized in Fig. 3. Curve (a) refers to the results obtained by maintaining a constant flow rate and constant pressure in the HF generator, directing part of the gas to waste and allowing a variable amount to pass through the analyser with a flow rate $d_{\rm HF/N_2}$. A linear relationship is obtained with a slope $-57.8 \, {\rm mV/log}$ (flow rate) up to flow rates of $0.5 \, \ell \, {\rm min^{-1}}$. At higher flow rates a non-Nernstian response can be ascribed to a decreased scrubbing efficiency as noted above.

Curve (b) refers to the results obtained by maintaining a fixed HF/N_2 flow rate of 280 ml min⁻¹, a fixed concentration of 120 ppm HF, and varying the flow rate of the HMTA buffer from 0.2 to 2 ml min⁻¹. A linear response was obtained with a slope 64 mV/log (flow rate) somewhat greater than the theoretical value of 58.5 mV. This difference is



FIG. 3. Electrode response as a function of nitrogen gas and buffer flow rates in the absorption tower. (A), Gas flow rate in analyser, $d_{\rm HF}/N_2$ in ml min⁻¹. Flow rate in generator 1.6 ℓ min⁻¹ at 125 ppm HF buffer flow rate 1.53 ml min⁻¹. (B), Buffer flow rate in ml min⁻¹. Gas flow rate in analyser and generator 280 ml min⁻¹ at 125 ppm HF.

thought to be due to the streaming potential developed by pumping the low ionic strength HMTA buffer through Teflon tubing. A similar effect was observed when standard NaF solutions were employed. Adding an inert electrolyte such as NaCl or KCl to the buffer has been suggested (6) in order to reduce the streaming potential but may promote crystallization when the analyser is left unattended.

HF Generator

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For reasons outlined below, the pressure at the outlet of the bifluoride reactor should be maintained at a constant value if possible, and all flow restrictions with the exception of a 7 micron filter (Nupron B-4FT7-7 $C_V = 0.15$) should be placed upstream. When packed with NaHF₂ crystals the columns constitute a major restriction to the gas flow rate and will only allow a flow of about 7 ℓ /min for a 10 psi pressure drop. This gas stream (stream 1, Fig. 1) can be diluted with pure carrier gas (stream 2, Fig. 1) yielding a fixed quantity of HF in a variable amount of carrier gas, or a concentration varying according to:

[7]
$$[HF]_{1+2} = \frac{[HF]_1 \times Flow rate 1}{(Flow rate 1 + flow rate 2)}$$

The initial tests on the bifluoride reactor have been confined to studies at low flow rates 1, zero flow rate 2, and such low exit pressures that the value of $P_{\rm T}$ (eq. [6] can be assumed to equal 1 atm). The steady state values for a gas flow about 350 ml min⁻¹ in the reactor are given in Fig. 4 and compared with the predictions of Miller (3) and Fisher (1). A leastsquares fit to our data yields the expression

[8]
$$\log P_{\rm HF}(\text{atm}) = 7.205 - \frac{4013}{T}(340 \text{ to } 400 \text{ K})$$

When expressed in terms of a weight fraction in a nitrogen atmosphere eq. [8] becomes:

[9]
$$\log (\text{ppm HF}) = 13.072 - \frac{4013}{T}$$

and concentrations between 25 to 1000 ppm HF are available by choosing temperatures between 70 to 125° C.

Our numerical values are almost exactly twice those obtained by Miller (3) and some ten times smaller than those reported by Fisher (1), the latter being the most widely quoted in the literature. Using for reaction [1] the free energy function calculated by Miller (3), we obtain an enthalpy of decomposition of NaHF₂ $\Delta H^0_{298} = 18.06 \pm 0.1$ kcal/mol at 25°C. This is in excellent agreement with the theoretical value predicted by Higgins and Westrum (7) as 17.88 \pm 0.2 kcal/mol.



FIG. 4. Partial pressure of HF in the $NaHF_2$ reactor at various temperatures. Included are predictions based on eqs. [3] and [5] and our experimental results.

An appreciable pressure drop in the NaHF₂ reactor itself would affect the kinetic response, i.e. the speed with which equilibrium HF concentration is attained at the exit port. Furthermore, according to eq. [6] the pressure at the exit port determines the HF concentration although it does not affect the HF partial pressure. Any flow restriction after the HF reactor, such as the filter or an external reaction cell, will increase P_T at high flow rates and thereby reduce the HF concentration. By deliberately throttling the gas flow using a fine metering valve in place of an external reaction cell we have verified that eq. [6] is obeyed at least up to 40 psi.

The HF concentration in the carrier gas could thus be calculated from eq. [6], the temperature of the bifluoride reactor and a manometer reading at the exit port. A less cumbersome and more direct method is also available. Using the control panel and the metering valve R_0 it is possible to place an equivalent flow restriction in the by-pass of the external reaction cell. Switching the four way valve (S-Analyser) will send either stream (1 + 2) or stream 3 to the analyser without provoking any pressure changes. At all times it is thus possible to measure the HF concentrations directly in the carrier gas before or after the external cell.

The time necessary to attain steady state HF con-



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FIG. 5. Time response of the HF generator. Temperature jumps from 72°C to 91°C to 103°C to 116°C to 126°C. Nitrogen flow rate 4.7 ℓ min⁻¹, absorbant flow rate 8.4 ml min⁻¹ 2% HMTA solution.

centrations is relatively short. Typical results are illustrated in Fig. 5 for the variation of the HF analyser signal as the temperature of the NaHF₂ generator is increased in a stepwise fashion from 72 to 126° C. Since the electrode potential is proportional to log [F⁻], the logarithmic chart paper is calibrated to read directly [HF] in ppm. Even at the high nitrogen flow rates employed here (5 ℓ /min) and hence the non-negligible pressure inside the NaHF₂ generator, HF concentrations stable to within 1% are rapidly attained. The equilibration time is roughly proportional to the relative HF concentration changes or the temperature increment (about 1 min/°C). It is thus possible to change the HF concentration in the carrier gas from 20 to 1000 ppm within 1 h without changing the gas flow rates or diluting the gas in any manner.

The long term stability of the reactor was evaluated over a 48 h period. The electrode response drifted about 1 mV/day due to temperature changes in the laboratory. When the electrodes were occasionally recalibrated with standard NaF solutions, the potentials remained constant to within ± 0.2 mV.

Conclusions

The HF generator yields very stable concentrations of hydrogen fluoride gas, relatively independent of the nature, or the flow rate of the carrier gas. Unlike the effusion techniques presently employed for calibration of analytical instruments, the generator can furnish high HF concentrations at high flow rates over extended periods of time with approximately the same requirements for temperature control. Also, unlike cylinders of anhydrous HF and associated metering valves, or dilute gaseous mixtures presently used for adsorption studies, the HF generator constitutes a safe, relatively cheap source of dilute gaseous mixtures whose composition is governed by thermodynamic principles.

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