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SHORT COMMUNICATION

THE AUTOPROTOLYSIS CONSTANT OF LIQUID ANHYDROUS HYDROGEN FLUORIDE

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ABSTRACT

The autoprotolysis constant of HF $K = [H^+][F^-] = 10^{-12.5_0}$ (I = 0.1, $KSbF_6$, 0° C) has been evaluated from potentiometric titrations of solutions of H^+ with F^-. The F^- concentrations were determined with the help of an Ag electrode acting in the presence of HCl and AgCl as a F^- electrode.

The earliest estimates of the autoprotolysis constant $K = [H][F]$* of liquid anhydrous hydrogen fluoride (AHF) were based on conductivity measurements and the first results from solutions of BF_3/BF_4^- [1] gave $K \simeq 2 \cdot 10^{-10}$ (20° C). A later estimation based on the molal* conductivity of H^+ (350 $ohm^{-1}cm^{-1}kgmole^{-1}$, 0° C, [2] and F^- (273, 0° C, [3]) at infinite dilution in AHF [4] and on the specific conductivity of AHF ($< 1.0 \cdot 10^{-6}$ $ohm^{-1}cm^{-1}$, 0° C, [4]) gave $K < 2.6 \cdot 10^{-12}$ [4] as an upper limiting value. Possible variations in the assingements of values for the equivalent ionic conductances of H^+ and F^- would result in only small shifts in the pK value. The specific conductivity is even somewhat lower than $1.0 \cdot 10^{-6}$ $ohm^{-1}cm^{-1}$ (25° C) [5][6]. Under the assumption that this is actually the limiting conductivity of AHF a value of $pK \simeq 12$ to 13 would be estimated for 0° C.

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*[ ], concentrations given in mole per litre.
Density of AHF : 1.0005, 0° C.

Another method for the elucidation of K is based on the potentiometric determination of hydrogen ion concentration in solutions of fluoride ions in AHF or vice versa. Gut and Gautschi /7] used a Pd - H_2 electrode for the determination of $[H^+]$ in solutions of the near strong acid AsF_5. However the resulting value of pK = 19.3 was much too high because of oxidation of H_2 and reduction of As(V) at the indicator electrode surface, as was correctly stated by Devynck et al. [8].

These authors used an elegant method of stepwise combination of redox and pH equilibria of chloranil and its various protonated and/or reduced forms in a quinone electrode system to cover the entire pH range in AHF. Their evaluation of the ionic product of AHF from pF determinations in solutions of SbF_5, acting as a strong acid [9][10], lead to a value of pK = 13.7. That is somewhat larger than the value reached by conductivity measurements. At least three redox- and/or protonation-constants of the chloranil system enter into such a pK evaluation and systematic errors may build up to the extent of some tenths of a logarithmic unit.

The electrode system Ag/AgCl(s)/HCl can be used for the determination of fluoride ion concentrations in SbF_5 acidified AHF solutions. Such determinations are based on the equilibrium reaction (1) [11].

$$Ag^+ + F^- + HCl \longleftrightarrow AgCl(s) + HF \qquad (1)$$

$$K_1 = \frac{1}{[Ag][F][HCl]} \quad ; \quad \log K_1 = 15.55^{*} \quad (I = 0.1,\ KF,\ 0^{o}\ C)$$

If [HCl] is held at a constant concentration [Ag] and [F] are inversly proportional. This permits a calibration of the electrode potential E versus pF. With [HCl] $\simeq$ 0.05 pF - values up to pF $\simeq$ 11 can be determined without marked dissolution of AgCl ($[Ag] < 10^{-3}$). Sb(V) does not interfere since it does not oxidize Ag(0) [10] nor Cl(-I). Thus solutions of SbF_5 in AHF containing dissolved HCl and some suspended AgCl were titrated with AHF solutions of KF. The resulting titration curves (Fig.1, Table 1) are analogous to the well known potentiometric titration

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* redetermined value for I = 0.1, KF, see [11].

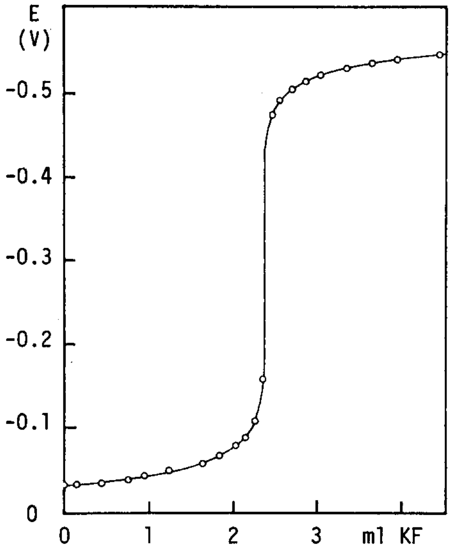

FIGURE 1. Titration curve

Composition of starting solution prepared from SbF_5, $AgSbF_6$, KCl and HF:

H^+ : 1.471 millimole
HCl : 2.108
K^+ : 2.347
SbF_6^- : 3.908
$AgCl_{(s)}$: 0.329

in 39.2 ml HF solution. I ≃ 0.1.

Titrated with:
KF : 0.6209 molar
T : 0^o C.

TABLE 1.

ml KF added	pH or pF calc.*	E (V) meas.	$E^o_{H^+}$ or $E^o_{F^-}$ (V) calc.	
0.00	1.426	-0.032	0.0453	
0.14	1.453	-0.033	0.0458	
0.44	1.519	-0.035	0.0473	
0.75	1.598	-0.039	0.0476	
0.94	1.656	-0.0435	0.0463	
1.24	1.761	-0.050	0.0454	
1.64	1.954	-0.0585	0.0474	
1.84	2.095	-0.0665	0.0470	
2.03	2.290	-0.078	0.0461	
2.14	2.461	-0.0875	0.0459	0.0464 ± 0.0008_5
2.26	2.783	-0.1085	(0.0423)	
2.34	3.348	-0.158	(0.0235)	
2.37		pF jump		
2.46	2.872	-0.473	-0.6287	
2.56	2.547	-0.490	-0.6280	
2.70	2.310	-0.503	-0.6282	
2.86	2.140	-0.513	-0.6290	
3.04	2.006	-0.520	-0.6287	
3.34	1.849	-0.528	-0.6282	
3.64	1.735	-0.534	-0.6280	
3.94	1.646	-0.538	-0.6272	
4.44	1.530	-0.5435	-0.6264	-0.6280 ± 0.0008

curves of a strong acid with a strong base. The "acid" branch of such a curve follows the relation $E = E^{o'}_{H^+} + s \log [H]$. The "alkaline" branch corresponds to $E = E^{o'}_{F^-} - s \log [F]$. $E^{o'}$ values refer to the potential of the reference electrode used. The correct dependence of E and log [F] in the equation $E = E^{o'}_{F^-} - s \log [F]$ is used by us routinely as a simple check of the proper function of the whole electrode system.

For any potential E of the indicator electrode the equation

$$E = E^{o'}_{H^+} + s \log [H] = E^{o'}_{F^-} - s \log [F]$$

holds, giving

$$\frac{E^{o'}_{H^+} - E^{o'}_{F^-}}{s} = pF + pH = pK$$

on rearrangement. The calculation of $E^{o'}_{H^+}$ needs only values of [H], obtainable from the solution composition, and the corresponding E values before the pF jump. Similarly the calculation of $E^{o'}_{F^-}$ need only values of [F] and corresponding values of E after the pF jump. The constant K_1, the amount of AgCl present and the concentration of dissolved HCl do not enter the calculation. That makes this method an extremely simple one.

Two completely independent determinations resulted in

$$pK = \frac{0.0464 - (-0.6280)}{0.0542} = 12.44_4 \pm 0.022$$

$$pK = \frac{0.0490 - (-0.6291)}{0.0542} = 12.51_1 \pm 0.045$$

giving an average of $pK_{HF} = 12.5_0 \pm 0.1$.

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