Ammonium Bifluoride Equivalency to Hydrofluoric Acid in the Presence of Strong Acids for Metal Pretreatment Jon Barrows, MSF

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Hydrofluoric acid is a Bronsted-Lowry weak acid that dissociates according to the following chemical equilibrium:

 $HF \rightleftharpoons H^+ + F^-$

In the presence of a fully dissociating strong acid such as nitric acid or sulfuric acid, the equilibrium is shifted to the right according to Le Chatelier's principal. In metal finishing solutions for the pretreatment of metals, the strong acid is in such abundance that the weak hydrofluoric acid can be considered to be fully dissociated into its ions according to the equation:

 $HF \longrightarrow H^+ + F^-$

There is a side reaction that occurs between dissociated fluoride ions that leads to the formation of bifluoride ions according to the following equilibrium:

$$F^- + F^- \rightleftharpoons F_2^{-2}$$

Similarly, ammonium bifluoride is a Bronsted-Lowry weak acid that dissociates in strongly acidic aqueous solutions according to the following chemical equilibria:

1) NH₄HF₂ \longrightarrow NH₄⁺ + HF + F⁻ HF \longrightarrow H⁺ + F⁻ 2) NH₄HF₂ \longrightarrow NH₄⁺ + H⁺ + F₂⁻² F₂⁻² \rightleftharpoons F⁻ + F⁻

As shown above, the difference between hydrofluoric acid and ammonium bifluoride in the net chemical dissociations in strongly acidic solutions is only the presence of the ammonium ion. Since ammonium ions do not participate in any subsequent activity with metals, the two chemicals can be seen as identical in metal pretreatment solutions provided that the ammonium bifluoride chemical concentrations are corrected stoichiometrically to hydrofluoric acid concentration based on equivalent fluoride ion as it has been done in the table below.

Fluoride Equivalencies				
HF (48% w/w technical)	HF (70% w/w technical)	HF	F [.]	NH₄HF₂
1% by volume	0.633% by volume	5.57 g/L	5.29 g/L	7.94 g/L
1.58% by volume	1% by volume	8.806 g/L	8.36 g/L	12.55 g/L
0.180 % by volume	0.114% by volume	1.00 g/L	0.95 g/L	1.43 g/L
0.189% by volume	0.120% by volume	1.05 g/L	1.00 g/L	1.50 g/L
0.126% by volume	0.080% by volume	0.701 g/L	0.666 g/L	1.00 g/L