Calculating the pH of a solution of a weak dibasic species + strong acid past V_{e_2}

When B = nicotine, BH_2^{2+} is a strong enough acid ($K_1 = 7.0_8 \times 10^{-4}$) that its hydrolysis significantly affects pH. Quantify as follows:

	BH_2^{2+}	$\rightleftharpoons$	BH^+	+	H^+	(reverse of 2nd titration rxn)
I	F'		0		F''	← set by titrant
C	$-x$		$+x$		$+x$	
E	$F'-x$		x		$F''+x$	

i.e. the "initial conditions" are setting by assuming the effect of $V_t = 21.0\,mL$ is 100% stoichiometric:

$$F' = (0.100\,M)\left(\frac{10.00\,\cancel{mL}}{(10.00+21.00)\,\cancel{mL}}\right) = \underline{0.0322_6\,M}$$

and $F'' = \underline{0.0032_3\,M}$ (conc. of excess titrant, from previous calc.)

However, not all of the BH_2^{2+} will stay protonated. Solving for x will tell us how much BH_2^{2+} "reverts" to BH^+

$$K_1 = \frac{[BH^+][H^+]}{[BH_2^{2+}]} = \frac{x(0.0032_3 + x)}{0.0322_6 - x} = 7.0_8 \times 10^{-4}$$

$$x^2 + 0.0032_3 x = -7.0_8 \times 10^{-4} x + 2.2_8 \times 10^{-5}$$

$$x^2 + 0.0039_4 x - 2.28 \times 10^{-5} = 0$$

Using TI-83 Plus Solver,

$x = 0.0032\,M$

$\therefore$ at $V_t = 21.0\,mL$,

$$[H^+] = \underbrace{0.0032_3\,M}_{\text{excess titrant}} + \underbrace{0.0032\,M}_{BH_2^{2+}\text{ that hydrolyses}} = 0.0064_3\,M$$

$\Downarrow$

$\boxed{pH = 2.19}$

(makes sense)

- Only 50% of H^+ from excess titrant!
- Still avoided systematic treatment