Oxalic Acid Bonus

Oxalic acid (H_2A) $pK_{a_1} = 1.23$, $pK_{a_2} = 4.19$

$H_2A \rightleftharpoons H^+ + HA^-$ $K_{a_1} = 10^{-1.23} = 5.88_8 \times 10^{-2}$

$HA^- \rightleftharpoons H^+ + A^{2-}$ $K_{a_2} = 10^{-4.19} = 6.45_6 \times 10^{-5}$

Since $K_{a_2} \ll K_{a_1}$, assume only K_{a_1} contributes significantly to pH

	H_2A	$\rightleftharpoons H^+$	$+ HA^-$
I	0.10	0	0
C	$-x$	$+x$	$+x$
E	$0.10-x$	x	x

$$K_{a_1} = \frac{[H^+][HA^-]}{[H_2A]} = \frac{x^2}{0.10-x}$$

$$\therefore x^2 + K_{a_1}x - 0.10K_{a_1} = 0$$

$$x = 0.0527_5, \ -0.116$$

$$\therefore x = [H^+] = 0.0527_5 \text{ M}, \quad pH = 1.27_8$$

Systematic Approach (including autoprotolysis of water)

mass balance:

$$0.10\text{ M} = [H_2A] + [HA^-] + [A^{2-}]$$

Charge Balance:

$$[H^+] = [HA^-] + 2[A^{2-}] + [OH^-]$$

Equilibrium Constants

$$K_{a_1} = \frac{[H^+][HA^-]}{[H_2A]} \qquad K_{a_2} = \frac{[H^+][A^{2-}]}{[HA^-]} \qquad K_w = [H^+][OH^-]$$

Goal: get everything in terms of $[H^+]$

$$[H_2A] = \frac{[H^+][HA^-]}{Ka_1} \qquad [A^{2-}] = \frac{Ka_2[HA^-]}{[H^+]}$$

mass balance

$$0.10\,M = \frac{[H^+][HA^-]}{Ka_1} + [HA^-] + \frac{Ka_2[HA^-]}{[H^+]}$$

$$\therefore \; [HA^-] = \frac{0.10\,M}{[H^+]/Ka_1 + 1 + Ka_2/[H^+]}$$

Charge Balance

$$[H^+] = [HA^-] + 2\left(\frac{Ka_2[HA^-]}{[H^+]}\right) + \frac{Kw}{[H^+]}$$

$\therefore$ "guess" $[H^+]$, calculate $[HA^-]$ + new $[H^+]$

— repeat until $[H^+]$ does not change

After executing the calculation, we get to convergence and a $[H^+] = 0.0528_{13}\,M$ or $pH = 1.27_8$

	A	B	C	D	E	F
1		K_{a1}	0.058884366		Final $[H^+]$ =	0.052813
2		K_{a2}	6.45654E-05		pH =	1.277
3		K_w	1E-14			
4						
5						
6	Iteration	$[H^+]$	$[HA^-]$			
7	1	0.1000000	0.0370523			
8	2	0.0371001	0.0612824			
9	3	0.0614957	0.0488903			
10	4	0.0489929	0.0545453			
11	5	0.0546891	0.0518152			
12	6	0.0519376	0.0530991			
13	7	0.0532312	0.0524877		B8 = +C7+($C$2*C7/B7)+($C$3/B7)	
14	8	0.0526150	0.0527772		C8 = =0.1/((B7/$C$1)+1+($C$2/B7))	
15	9	0.0529067	0.0526398			
16	10	0.0527682	0.0527049			
17	11	0.0528339	0.0526740			
18	12	0.0528027	0.0526887			
19	13	0.0528175	0.0526817			
20	14	0.0528105	0.0526850			
21	15	0.0528138	0.0526834			
22	16	0.0528122	0.0526842			
23	17	0.0528130	0.0526838			
24	18	0.0528126	0.0526840			
25	19	0.0528128	0.0526839			
26	20	0.0528127	0.0526839			
27	21	0.0528128	0.0526839			
28	22	0.0528127	0.0526839			
29	23	0.0528128	0.0526839			
30	24	0.0528128	0.0526839			
31	25	0.0528128	0.0526839			
32	26	0.0528128	0.0526839			
33	27	0.0528128	0.0526839			
34	28	0.0528128	0.0526839			
35	29	0.0528128	0.0526839			
36	30	0.0528128	0.0526839			
37	31	0.0528128	0.0526839			
38	32	0.0528128	0.0526839			
39	33	0.0528128	0.0526839			
40	34	0.0528128	0.0526839			
41	35	0.0528128	0.0526839			
42	36	0.0528128	0.0526839			
43	37	0.0528128	0.0526839			
44	38	0.0528128	0.0526839			
45	39	0.0528128	0.0526839			
46	40	0.0528128	0.0526839			
47	41	0.0528128	0.0526839			

$$[HA^-] = \frac{0.10}{\frac{[H^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[H^+]}}$$

$$[H^+] = [HA^-] + 2\left(\frac{K_{a2}[HA^-]}{[H^+]}\right) + \frac{K_w}{[H^+]}$$