a) $[H^+]$ in 0.0253 M butanoic acid

Equilibria: $\frac{[H^+][CH_3CH_2CH_2COO^-]}{[CH_3CH_2CH_2COOH]} = \frac{1.52\times10^{-5}}{f_1^2}$, $[H^+][OH^-] = \frac{1.00\times10^{-14}}{f_1^2}$

Charge balance: $[H^+] = [OH^-] + [CH_3CH_2CH_2COO^-]$

Mass balance: $0.0253 = [CH_3CH_2CH_2COOH] + [CH_3CH_2CH_2COO^-]$

Ionic Strength: $I = \frac{1}{2}\{[H^+] + [OH^-] + [CH_3CH_2CH_2COO^-]\}$

Since concentrations are unknown, use I = 0.0 and f_1 = 1.00 as an estimate. Substitute into the K_a expression,

$$K_a = \frac{[H^+][CH_3CH_2CH_2COO^-]}{[CH_3CH_2CH_2COOH]} = \frac{[H^+]([H^+]-[OH^-])}{0.0253-([H^+]-[OH^-])} = \frac{[H^+]([H^+]-\cancel{[OH^-]})}{0.0253-\cancel{[H^+]}+\cancel{[OH^-]}}$$

to find $[H^+] = [CH_3CH_2CH_2COO^-] = 6.20\times10^{-4}$. $[OH^-] \approx 10^{-11}$ so the acid assumption is good but the weak assumption (0.0253 – 0.00062 = 0.0253) is not great. Use the quadratic formula

$$[H^+]^2 + Ka\,[H^+] - Ka\,(0.0253) = 0;\ [H^+] = \frac{-Ka + \sqrt{Ka^2 + 4(0.0253)Ka}}{2} = 6.13\times10^{-4}.$$

I = 6.13×10^{-4} so f_1 = 0.972 and a better K_a is $\frac{1.52\times10^{-5}}{(0.972)^2} = 1.61\times10^{-5}$. Repeating the problem with this new value gives $\boxed{[H^+] = 6.30\times10^{-4}}$ and f_1 = 0.972 and we are finished. The pH = –log ($f_1[H^+]$) = 3.213

b) $[H^+]$ in 0.0253 M trimethylamine

Equilibria: $\frac{[H^+][(CH_3)_3N]}{[(CH_3)_3NH^+]} = 1.59\times10^{-10}$, $[H^+][OH^-] = \frac{1.00\times10^{-14}}{f_1^2}$

Charge balance: $[(CH_3)_3NH^+] + [H^+] = [OH^-]$

Mass balance: $0.0253 = [(CH_3)_3NH^+] + [(CH_3)_3N]$

Ionic Strength: $I = \frac{1}{2}\{[H^+] + [OH^-] + [(CH_3)_3NH^+]\}$

For an initial estimate since the concentrations are unknown, use I = 0.0 and f_1 = 1.00. Substitute into the K_a expression,

$$K_a = \frac{[H^+][(CH_3)_3N]}{[(CH_3)_3NH^+]} = \frac{\cancel{[H^+]}(0.0253-([OH^-]-[H^+])}{[OH^-]-[H^+]}\,\frac{K_w}{\cancel{[H^+]}[OH^-]} = \frac{0.0253+\cancel{[H^+]}-\cancel{[OH^-]}}{[OH^-]-\cancel{[H^+]}}\,\frac{K_w}{[OH^-]}$$

to find $[OH^-] = [(CH_3)_3NH^+] = 1.26\times10^{-3}$ so $[H^+] \approx 10^{-11}$ and the base assumption is good but the weak assumption (0.0253 – 0.00126 = 0.0253) is not good. Use the quadratic formula

$$[OH^-]^2 + [OH^-]\frac{Kw}{Ka} - (0.0253)\frac{Kw}{Ka} = 0;\ [OH^-] = \frac{-\frac{Kw}{Ka} + \sqrt{(\frac{Kw}{Ka})^2 + 4(0.0253)\frac{Kw}{Ka}}}{2} = 1.23\times10^{-3}.$$

I = 1.23×10^{-3} so $f_1 = 0.961$ and a better K_w is $\frac{1.00\times10^{-14}}{(0.961)^2} = 1.08\times10^{-14}$.

Repeating the problem with this new value gives $[OH^-] = 1.28\times10^{-3}$ and $f_1 = 0.961$ so we are finished. $\boxed{[H^+] = 8.44\times10^{-12}}$. The pH = –log ($f_1$[H⁺]) = 11.091

c) $[H^+]$ in 0.0253 M lithium chloroacetate

Equilibria: $\frac{[H^+][ClCH_2COO^-]}{[ClCH_2COOH]} = \frac{1.36\times10^{-3}}{f_1^2}$, $[H^+]\,[OH^-] = \frac{1.00\times10^{-14}}{f_1^2}$

Charge balance: $[Li^+] + [H^+] = [ClCH_2COO^-] + [OH^-]$;

Mass balance: $0.0253 = [ClCH_2COOH] + [ClCH_2COO^-]$

$0.0253 = [Li^+]$

Ionic Strength: $I = \frac{1}{2}\{[H^+] + [OH^-] + [Li^+] + [ClCH_2COO^-]$

For an initial estimate use I = 0.0253 and $f_1 = 0.859$ so $K_w = \frac{1.00\times10^{-14}}{(0.859)^2} =$

1.36×10^{-14} and $K_a = \frac{1.36\times10^{-3}}{(0.859)^2} = 1.84\times10^{-3}$. Substitute into the K_a expression,

$$K_a = \frac{[H^+][ClCH_2COO^-]}{[ClCH_2COOH]} = \frac{\cancel{[H^+]}(0.0253 + [H^+] - [OH^-])}{\cancel{0.0253} - (\cancel{0.0253} + [H^+] - [OH^-])}\frac{K_w}{\cancel{[H^+]}[OH^-]} = \frac{(0.0253 + \cancel{[H^+]} - \cancel{[OH^-]})}{([OH^-] - \cancel{[H^+]})}\frac{K_w}{[OH^-]}$$

to find $[OH^-] = 4.32\times10^{-7}$ so $[H^+] = 3.14\times10^{-8}$ and the weak assumption is good. The base assumption ($4.32\times10^{-7} - 3.14\times10^{-8} = 4.32\times10^{-7}$) is not good.

$$K_a = \frac{(0.0253)}{([OH^-] - \frac{K_w}{[OH^-]})}\frac{K_w}{[OH^-]} = \frac{0.0253\,K_w}{[OH^-]^2 - K_w};\ 0.0253\,K_w = K_a[OH^-]^2 - K_aK_w$$

$[OH^-] = 4.48\times10^{-7}$ and $\boxed{[H^+] = 3.04\times10^{-8}}$. The pH = –log ($f_1$[H⁺]) = 7.583

d) $[H^+]$ in 0.0253 M cyclohexylammonium bromide, $(CH_2)_5CHNH_3Br$

Equilibria: $\frac{[H^+][(CH_2)_5CHNH_2]}{[(CH_2)_5CHNH_3^+]} = 2.71 \times 10^{-11}$, $[H^+][OH^-] = \frac{1.00\times10^{-14}}{f_1^2}$

Charge balance: $[(CH_2)_5CHNH_3^+] + [H^+] = [OH^-] + [Br^-]$

Mass balance: $0.0253 = [(CH_2)_5CHNH_3^+] + [(CH_2)_5CHNH_2]$

$0.0253 = [Br^-]$

Ionic Strength: $I = \frac{1}{2}\{[H^+] + [OH^-] + [(CH_2)_5CHNH_3^+]\}$

For an initial estimate use I = 0.0253 and f_1 = 0.859 so $K_w = \frac{1.00\times10^{-14}}{(0.859)^2} =$ 1.36×10^{-14}. Substitute into the K_a expression,

$$K_a = \frac{[H^+][(CH_2)_5CHNH_2]}{[(CH_2)_5CHNH_3^+]} = \frac{\cancel{[H^+]}(0.0253-([OH^-]-[H^+]))}{[OH^-]-[H^+]}\frac{K_w}{\cancel{[H^+]}[OH^-]} = \frac{0.0253+\cancel{[H^+]}-\cancel{[OH^-]}}{[OH^-]-\cancel{[H^+]}}\frac{K_w}{[OH^-]}$$

to find $[OH^-] = 1.27\times10^{-5}$ so $\boxed{[H^+] = 1.07\times10^{-9}}$ and the assumptions are good.
The pH = –log ($f_1[H^+]$) = 9.037

e) $[H^+]$ in 0.0253 M sodium hypochlorite, NaOCl

Equilibria: $\frac{[H^+][OCl^-]}{[HOCl]} = \frac{3.0\times10^{-8}}{f_1^2}$, $[H^+][OH^-] = \frac{1.00\times10^{-14}}{f_1^2}$

Charge balance: $[Na^+] + [H^+] = [OCl^-] + [OH^-]$

Mass balance: $0.0253 = [HOCl] + [OCl^-]$;

$0.0253 = [Na^+]$

Ionic Strength: $I = \frac{1}{2}\{[Na^+] + [H^+] + [OCl^-] + [OH^-]\}$

For an initial estimate use I = 0.0253 and f_1 = 0.859 so $K_w = \frac{1.00\times10^{-14}}{(0.859)^2} =$ 1.36×10^{-14} and $K_a = \frac{3.0\times10^{-8}}{(0.859)^2} = 4.07\times10^{-8}$. Substitute into the K_a expression,

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]} = \frac{\cancel{[H^+]}(0.0253+[H^+]-[OH^-])}{\cancel{0.0253}-(\cancel{0.0253}+[H^+]-[OH^-])}\frac{K_w}{\cancel{[H^+]}[OH^-]} = \frac{0.0253+\cancel{[H^+]}-\cancel{[OH^-]}}{[OH^-]-\cancel{[H^+]}}\frac{K_w}{[OH^-]}$$

to find $[OH^-] = 9.19\times10^{-5}$ so $\boxed{[H^+] = 1.48\times10^{-10}}$ and the assumptions are good.
The pH = –log ($f_1[H^+]$) = 9.896

f) $[Ag^+]$ from Ag_2CrO_4 in 0.0253 M KNO_3

Equilibria: $[Ag^+]^2\ [CrO4^{-2}] = \dfrac{1.2\times10^{-12}}{(f_{Ag^+})^2 f_{CrO4^{-2}}}$

Charge balance: $[K^+] + [Ag^+] = [NO_3^-] + 2[CrO_4^{-2}]$ (assume $[H^+] = [OH^-]$)

Mass balance: $[K^+] = 0.0253$

$[NO_3^-] = 0.0253$

($[Ag^+] = 2S$ and $[CrO_4^{-2}] = S$)

Ionic Strength: $I = \frac{1}{2}\{[K^+] + [NO_3^-] + [Ag^+] + [CrO_4^{-2}](-2)^2\}$

$I = \frac{1}{2}\{[0.0253] + [0.0253] + [2S] + [S](-2)^2\}$

$I = 0.0253 + 3S$; *Assume* $I = 0.0253 + \cancel{3S} = 0.0253$

$f_{Ag^+} = 0.859$ and $f_{CrO_4^{-2}} = 0.544$ so $K_s = \dfrac{1.2\times10^{-12}}{(0.859)^2(0.544)} = 2.99\times10^{-12}$

$[Ag^+]^2\ [CrO_4^{-2}] = (2S)^2\ (S) = 4\ S^3$; $S = \sqrt[3]{\dfrac{2.99\times10^{-12}}{4}} = 9.08\times10^{-5}$

Check: $I = 0.0253 + 3(9.08\times10^{-5}) = 0.0256 \approx 0.0253$ *Ionic strength guess is OK*

$[Ag^+] = 1.82\times10^{-4}$

g) $[Ag^+]$ from Ag_2CrO_4 in 0.0253 M K_2CrO_4

Equilibria: $[Ag^+]^2\ [CrO4^{-2}] = \dfrac{1.2\times10^{-12}}{(f_{Ag^+})^2 f_{CrO4^{-2}}}$

Charge balance: $[K^+] + [Ag^+] = 2[CrO_4^{-2}]$ (assume $[H^+] = [OH^-]$)

Mass balance: $[K^+] = 2(0.0253)$

($[Ag^+] = 2S$ and $[CrO_4^{-2}] = S + 0.0253$)

Ionic Strength: $I = \frac{1}{2}\{[K^+] + [Ag^+] + [CrO_4^{-2}](-2)^2\}$

$I = \frac{1}{2}\{[2(0.0253)] + [2S] + [0.0253 + S](-2)^2\} = 0.0759 + 3S$

Assume $I = 0.0759 + \cancel{3S} = 0.0759$

$f_{Ag^+} = 0.797$ and $f_{CrO_4^{-2}} = 0.403$ so $K_s = \dfrac{1.2\times10^{-12}}{(0.797)^2(0.403)} = 4.69\times10^{-12}$

$K_s = [Ag^+]^2\ [CrO_4^{-2}] = (2S)^2\ (\cancel{S}+0.0253)$; $S = \sqrt{\dfrac{4.69\times10^{-12}}{4\ (0.0253)}} = 6.81\times10^{-6}$

Check: $I = 0.0759 + 3(6.81\times10^{-6}) = 0.0759$ *Ionic strength guess is good*

$[Ag^+] = 1.36\times10^{-5}$