## Answers to Exercise 12.4

## More Weak Acid Calculations

1. 

(a) Step 1: Calculate nominal concentration of solution (initial concentration of acid)
$1.25 \mathrm{~g} \times \frac{1 \mathrm{~mol}}{43.028 \mathrm{~g}}=0.0291 \mathrm{~mol}$
$\frac{0.0291 \mathrm{~mol}}{1.000 \mathrm{~L}}=0.0291 \mathrm{M}$
Step 2: Calculate $K_{a}$ from $p K_{a}$
$K_{a}=10^{-p K_{a}}=10^{-4.72}=1.9 \times 10^{-5}$
Step 3: Write a balanced chemical equation and organize all known information

|  | $H A_{(a q)}$ | $\rightleftharpoons$ | $H_{(a q)}^{+}$ | + |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{I}(\mathrm{M})$ | 0.0291 |  | $10^{-7}$ |  |
| $\mathrm{C}(\mathrm{M})$ | $-x$ |  | $+x$ |  |
| E (M) | $0.0291-x \approx 0.0291$ | $10^{-7}+x \approx x$ |  | $+x$ |
|  |  |  |  |  |

Step 4: Write equilibrium constant expression and calculate $x$
$K_{a}=\frac{\left(a_{H^{+}}\right)\left(a_{A^{-}}\right)}{a_{H A}}$
$1.9 \times 10^{-5}=\frac{(x)(x)}{0.0291}$
$\left(1.9 \times 10^{-5}\right)(0.0291)=x^{2}$
$x=\sqrt{\left(1.9 \times 10^{-5}\right)(0.0291)}$
$x=7.4 \times 10^{-4}$
Step 5: Check assumptions. If invalid, repeat calculation without the invalid assumption.
Assumption \#1: $0.0291-x \approx 0.0291 \quad 0.0291-0.00074=0.0283$ close but not quite
Assumption \#2: $10^{-7}+x \approx x \quad 10^{-7}+0.00074=0.00074 \quad$ assumption okay
Step 6: Try again without the first assumption (keep second one)
$K_{a}=\frac{\left(a_{H^{+}}\right)\left(a_{A^{-}}\right)}{a_{H A}}$
$1.9 \times 10^{-5}=\frac{(x)(x)}{(0.0291-x)}$
$\left(1.9 \times 10^{-5}\right)(0.0291-x)=x^{2}$
$5.5 \times 10^{-7}-\left(1.9 \times 10^{-5}\right) x=x^{2}$
$x^{2}+\left(1.9 \times 10^{-5}\right) x-\left(5.5 \times 10^{-7}\right)=0$
Use quadratic equation (or other tools) to solve, giving:
$x=7.3 \times 10^{-4}$
( $x=-7.5 \times 10^{-4}$ would give negative concentrations for $H^{+}$and $A^{-}$which is impossible)

## Step 7: Calculate pH from $\boldsymbol{a}_{\boldsymbol{H}^{+}}$

$a_{H^{+}}=x=7.3 \times 10^{-4}$
$p H=-\log \left(a_{H^{+}}\right)=-\log \left(7.3 \times 10^{-4}\right)=3.13$
Step 8: Check your work
It's an acid, so expect a pH below 7. If this had been a strong acid, the pH would have been $-\log (0.0291)=1.537$. Since it's a weak acid, it makes sense that the pH is higher. Note that if we had stuck with both initial assumptions, we'd have calculated $\mathrm{pH}=$ $-\log \left(7.4 \times 10^{-4}\right)=3.13$. So, maybe we could have left it as "close enough" after all...
(b) Step 1: Calculate nominal concentration of solution (initial concentration of acid)
$1.25 \mathrm{~g} \times \frac{1 \mathrm{~mol}}{68.4594 \mathrm{~g}}=0.0183 \mathrm{~mol}$
$\frac{0.0183 \mathrm{~mol}}{1.000 \mathrm{~L}}=0.0183 \mathrm{M}$
Step 2: Calculate $K_{a}$ from $p K_{a}$
$K_{a}=10^{-p K_{a}}=10^{-1.96}=1.1 \times 10^{-2}$
Step 3: Write a balanced chemical equation and organize all known information

|  | $H A_{(a q)}$ | $\rightleftharpoons$ | $H_{(a q)}^{+}$ | + |
| :--- | :---: | :---: | :---: | :---: |
| I (M) | 0.0183 |  | $10^{-7}$ |  |
| C (M) | $-x$ |  | $+x$ |  |
| E (M) | $0.0183-x$ |  | $10^{-7}+x \approx x$ |  |

Step 4: Write equilibrium constant expression and calculate $x$
$K_{a}=\frac{\left(a_{H^{+}}\right)\left(a_{A^{-}}\right)}{a_{H A}}$
$1.1 \times 10^{-2}=\frac{(x)(x)}{(0.0183-x)}$
$\left(1.1 \times 10^{-2}\right)(0.0183-x)=x^{2}$
$2.0 \times 10^{-4}-\left(1.1 \times 10^{-2}\right) x=x^{2}$
$x^{2}+\left(1.1 \times 10^{-2}\right) x-2.0 \times 10^{-4}=0$
Use quadratic equation (or other tools) to solve, giving:
$x=9.7 \times 10^{-3}$
( $x=-2.1 \times 10^{-2}$ would give negative concentrations for $H^{+}$and $A^{-}$which is impossible)
Step 5: Check assumption. If invalid, repeat calculation without it.
Assumption: $10^{-7}+x \approx x \quad 10^{-7}+0.0097=0.0097 \quad$ assumption okay
Step 6: Calculate $\mathbf{p H}$ from $\boldsymbol{a}_{\boldsymbol{H}^{+}}$
$a_{H^{+}}=x=9.7 \times 10^{-3}$
$p H=-\log \left(a_{H^{+}}\right)=-\log \left(9.7 \times 10^{-3}\right)=2.01$
Step 8: Check your work
It's an acid, so expect a pH below 7. If this had been a strong acid, the pH would have been $-\log (0.0183)=1.739$. Since it's a weak acid, it makes sense that the pH is higher.
(c) Step 1: Calculate nominal concentration of solution (initial concentration of acid)
$1.25 \mathrm{~g} \times \frac{1 \mathrm{~mol}}{63.0128 \mathrm{~g}}=0.0198 \mathrm{~mol}$
$\frac{0.0198 \mathrm{~mol}}{1.000 \mathrm{~L}}=0.0198 \mathrm{M}$
Step 2: Calculate $K_{a}$ from $p K_{a}$
$K_{a}=10^{-p K_{a}}=10^{-3.39}=4.1 \times 10^{-4}$
Step 3: Write a balanced chemical equation and organize all known information

| $H A_{(a q)}$ | $\rightleftharpoons$ | $H_{(a q)}^{+}$ | + |
| :--- | :---: | :---: | :---: |
| 0.0198 | $10^{-7}$ |  | $A_{(a q)}^{-}$ |
| $-x$ |  | $+x$ |  |
| $98-x \approx 0.0198$ | $10^{-7}+x \approx x$ |  | $+x$ |
| 98 |  |  |  |

Step 4: Write equilibrium constant expression and calculate $x$
$K_{a}=\frac{\left(a_{H^{+}}\right)\left(a_{A^{-}}\right)}{a_{H A}}$
$4.1 \times 10^{-4}=\frac{(x)(x)}{0.0198}$
$\left(4.1 \times 10^{-4}\right)(0.0198)=x^{2}$
$x=\sqrt{\left(4.1 \times 10^{-4}\right)(0.0198)}$
$x=2.8 \times 10^{-3}$
Step 5: Check assumptions. If invalid, repeat calculation without the invalid assumption.
Assumption \#1: $0.0198-x \approx 0.0198 \quad 0.0198-0.0028=0.0170$ not close enough
Assumption \#2: $10^{-7}+x \approx x \quad 10^{-7}+0.0028=0.0028 \quad$ assumption okay
Step 6: Try again without the first assumption (keep second one)
$K_{a}=\frac{\left(a_{H^{+}}\right)\left(a_{A^{-}}\right)}{a_{H A}}$
$4.1 \times 10^{-4}=\frac{(x)(x)}{(0.0198-x)}$
$\left(4.1 \times 10^{-4}\right)(0.0198-x)=x^{2}$
$5.5 \times 10^{-7}-\left(8.1 \times 10^{-6}\right) x=x^{2}$
$x^{2}+\left(4.1 \times 10^{-4}\right) x-\left(8.1 \times 10^{-6}\right)=0$
Use quadratic equation (or other tools) to solve, giving:
$x=2.6 \times 10^{-3}$
( $x=-3.1 \times 10^{-3}$ would give negative concentrations for $H^{+}$and $A^{-}$which is impossible)
Step 7: Calculate $\mathbf{p H}$ from $\boldsymbol{a}_{\boldsymbol{H}^{+}}$
$a_{H^{+}}=x=2.6 \times 10^{-3}$
$p H=-\log \left(a_{H^{+}}\right)=-\log \left(2.6 \times 10^{-3}\right)=2.58$
Step 8: Check your work
It's an acid, so expect a pH below 7. If this had been a strong acid, the pH would have been $-\log (0.0198)=1.703$. Since it's a weak acid, it makes sense that the pH is higher.
2. General approach: Use the equilibrium constant expression, but this time, the activity of $\mathrm{H}^{+}$can be calculated directly from the pH provided.
Step 1: Calculate $K_{a}$ from $p K_{a}$
$K_{a}=10^{-p K_{a}}=10^{-3.39}=4.1 \times 10^{-4}$
Step 2: Calculate $\boldsymbol{a}_{\boldsymbol{H}^{+}}$from $\boldsymbol{p H}$
$a_{H^{+}}=10^{-p H}=10^{-2.00}=1.0 \times 10^{-2}$
Step 3: Write a balanced chemical equation and organize all known information
$\mathrm{I}(\mathrm{M}) \quad$ ? ?
$\mathrm{C}(\mathrm{M}) \quad-x$
$\mathrm{E}(\mathrm{M}) \quad ? ? ?-x \approx ? ?$
$\rightleftharpoons$
$H$
10
$H_{(a q)}^{+}$
$10^{-7}$
$+\quad A_{(a q)}^{-}$
10
$+x \quad+x$
$10^{-7}+x \approx x$
$x$

Since we don't know $a_{H A}$, start by assuming that both assumptions will be valid.
$a_{H^{+}}=1.0 \times 10^{-2}$ therefore $x=1.0 \times 10^{-2}$
Step 4: Write equilibrium constant expression and calculate $\boldsymbol{a}_{\boldsymbol{H A}}$
$K_{a}=\frac{\left(a_{H^{+}}\right)\left(a_{A^{-}}\right)}{a_{H A}}$
$4.1 \times 10^{-4}=\frac{\left(1.0 \times 10^{-2}\right)\left(1.0 \times 10^{-2}\right)}{a_{H A}}$
$a_{H A}=\frac{\left(1.0 \times 10^{-2}\right)\left(1.0 \times 10^{-2}\right)}{4.1 \times 10^{-4}}=0.25$
Step 5: Check assumptions. If invalid, repeat calculation without the invalid assumption.
Assumption \#1: $0.25-x \approx 0.25 \quad 0.25-0.01=0.24 \quad$ close enough*
Assumption \#2: $10^{-7}+x \approx x \quad 10^{-7}+0.01=0.01 \quad$ assumption okay
*If you were to repeat the calculation without making the assumption, you'd get the same answer once rounded to the correct number of sig. fig. The solution to 1 (a) demonstrated how this is possible.

Step 6: Calculate concentration of acid from activity
$M_{H A}=a_{H A} \times 1 M=0.25 M$
Step 7: Check your work
Does your answer seem reasonable?
The solution has a higher concentration than in question 1(c) and therefore has a lower pH.
3. General approach: Use the equilibrium constant expression, but this time, the activity of $\mathrm{H}^{+}$can be calculated directly from the pH provided. Once you know the concentration of acid required, use stoichiometry to calculate the mass of acid required to make the solution.
Step 1: Calculate $\boldsymbol{K}_{\boldsymbol{a}}$ from $\boldsymbol{p} \boldsymbol{K}_{\boldsymbol{a}}$
$K_{a}=10^{-p K_{a}}=10^{-4.72}=1.9 \times 10^{-5}$
Step 2: Calculate $\boldsymbol{a}_{\boldsymbol{H}^{+}}$from $\boldsymbol{p H}$
$a_{H^{+}}=10^{-p H}=10^{-2.72}=1.9 \times 10^{-3}$
Step 3: Write a balanced chemical equation and organize all known information

|  | $H A_{(a q)}$ | $\rightleftharpoons$ | $H_{(a q)}^{+}$ | + |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{I}(\mathrm{M})$ | $? ? ?$ |  | $A_{(a q)}^{-}$ |  |
| $\mathrm{C}(\mathrm{M})$ | $-x$ |  | $+x$ |  |
| $\mathrm{E}(\mathrm{M})$ | $? ? ?-x \approx ? ? ?$ |  | $10^{-7}+x \approx x$ |  |

Since we don't know $a_{H A}$, start by assuming that both assumptions will be valid.
$a_{H^{+}}=1.9 \times 10^{-3}$ therefore $x=1.9 \times 10^{-3}$
Step 4: Write equilibrium constant expression and calculate $\boldsymbol{a}_{\boldsymbol{H A}}$
$K_{a}=\frac{\left(a_{H^{+}}\right)\left(a_{A^{-}}\right)}{a_{H A}}$
$1.9 \times 10^{-5}=\frac{\left(1.9 \times 10^{-3}\right)\left(1.9 \times 10^{-3}\right)}{a_{H A}}$
$a_{H A}=\frac{\left(1.9 \times 10^{-3}\right)\left(1.9 \times 10^{-3}\right)}{1.9 \times 10^{-5}}=0.19$
Step 5: Check assumptions. If invalid, repeat calculation without the invalid assumption.
Assumption \#1: $0.19-x \approx 0.19 \quad 0.19-0.0019=0.19 \quad$ assumption okay
Assumption \#2: $10^{-7}+x \approx x \quad 10^{-7}+0.0019=0.0019 \quad$ assumption okay
Step 6: Calculate concentration of acid from activity
$M_{H A}=a_{H A} \times 1 M=0.19 \mathrm{M}$
Step 7: Calculate moles of acid required to make solution
$n_{H A}=250 . \mathrm{mL} \times 0.19 \frac{\mathrm{~mol}}{\mathrm{~L}} \times \frac{1 \mathrm{~L}}{1000 \mathrm{~mL}}=0.048 \mathrm{~mol}$
Step 8: Calculate mass of acid required to make solution
$m_{H A}=0.048 \mathrm{~mol} \times \frac{43.028 \mathrm{~g}}{1 \mathrm{~mol}}=2.0 \mathrm{~g}$
Step 9: Check your work
Does your answer seem reasonable?
The solution has a higher concentration than in question 1(a) and therefore has a lower pH.

