## Objectives

- 1. Use K<sub>w</sub> to determine relative amounts of hydroxide and hydronium ions in solution and assess whether the solution is acidic, basic, or neutral
- 2. Calculate equilibrium concentrations and pH using any appropriate approximations
- 3. Determine the pH or pOH of a solution and identify the relationship between these quantities
- 4. Carry out all kinds of pH calculations and calculations using pH to find other quantities

## **Key Questions**

1. Write the expressions for  $K_c$  and  $K_a$  of water. Recall that  $[H_2O] \approx 55$  M. Using this information, the expression for the  $K_a$  of water, and the fact that water's  $K_a$  is  $1.8 \times 10^{-16}$ , calculate the value of  $[\mathrm{H_3O^+}] \times [\mathrm{OH^-}].$ 

Start with writing the equation:

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H_2O + H_2O \longrightarrow H_3O^+ + OH
Then the K_c expression: K_c = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}
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To go from  $K_c$  to  $K_a$ , we remove a factor of  $[H_2O]$ :

$$K_{a} = \frac{[H_{3}O^{+}][OH^{-}]}{[H_{2}O]}$$

$$\begin{split} K_a &= \frac{[H_3O^+][OH^-]}{[H_2O]} \\ Finally, rearrange to solve for the desired [H_3O^+][OH^-]: \end{split}$$

$$K_a \times [H_2O] = [H_3O^+][OH^-] = 1.8 \times 10^{-16} \times 55 = 1.0 \times 10^{-14}$$

- 2. What is the name for the value calculated in the previous problem?  $K_{w}$
- 3. Use the value of K<sub>w</sub> to calculate the hydronium and hydroxide ion concentrations in pure water. Also calculate the pH and pOH of pure water.

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In pure water, [H_3O^+] = [OH^-], so K_w = [H_3O^+]^2 and [H_3O^+] = [OH^-] = (K_w)^{\frac{1}{2}}
(K_w)^{\frac{1}{2}} = (1.0 \times 10^{-14})^{\frac{1}{2}} = 1.0 \times 10^{-7}
pH = -log[H_3O^+] = 7
pOH = -log[OH^-] = 7
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4. For the following concentrations, state whether the associated solution will be acidic, basic, or neutral, and calculate the corresponding hydroxide or hydronium concentration.

For a neutral solution,  $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ , so if  $[H_3O^+] > 1.0 \times 10^{-7}$ , the solution is acidic and if  $[H_3O^+] < 1.0 \times 10^{-7}$ , the solution is basic. Similarly, if  $[OH^-] > 1.0 \times 10^{-7}$ , the solution is basic and if  $[OH^-] < 1.0 \times 10^{-7}$ , the solution is acidic.

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Since K_w = 1.0 \times 10^{-14} = [H_3O^+] \times [OH^-], [H_3O^+] = K_w / [OH^-] and [OH^-] = K_w / [H_3O^+].
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- (a)  $[H_3O^+] = 7.2 \times 10^{-4} \text{ M}$ acidic,  $[OH^-] = 1.4 \times 10^{-11}$
- (b)  $[H_3O^+] = 5.8 \times 10^{-10} \text{ M}$ basic,  $[OH^{-}] = 1.7 \times 10^{-5}$
- (c)  $[OH^{-}] = 1.8 \times 10^{-6} \text{ M}$ basic,  $[H_3O^+] = 5.6 \times 10^{-9}$
- (d)  $[OH^{-}] = 1.0 \times 10^{-7} \text{ M}$ neutral,  $[H_3O^+] = 1.0 \times 10^{-7}$

5. Given an initial concentration of 0.5 M  $H_2S$  and its  $K_a$  of  $1.1 \times 10^{-7}$ , determine the equilibrium concentration of HS<sup>-</sup>, the pH of the solution, and [OH<sup>-</sup>].

| (R) | $H_2S + H_2O \Longrightarrow H_3O^+ + HS^-$ |   |    |    |  |  |
|-----|---|---|----|----|--|--|
| I   | 0.5   | _ | 0  | 0  |  |  |
| C   | -x  | _ | +x | +x |  |  |
| E   | 0.5-x                                       | _ | X  | X  |  |  |

$$\begin{array}{l} {\rm K_a} = \frac{{\rm [H_3O^+][HS^-]}}{{\rm [H_2S]}} \implies 1.1 \times 10^{-7} = \frac{x^2}{0.5 - x} \\ {\rm Rearrange:} \ 1.1 \times 10^{-7} (0.5 - x) = x^2 \implies 5.5 \times 10^{-8} - 1.1 \times 10^{-7} x = x^2 \\ \implies x^2 - 5.5 \times 10^{-8} + 1.1 \times 10^{-7} x = 0 \end{array}$$

Now, use quadratic equation to find x = -0.000235, 0.000234. The negative root gives a nonsensical negative concentration, so take the positive root. From the RICE table, we see that x is the equilibrium concentration of HS<sup>-</sup> so that part of the answer is finished. pH is given by pH =  $-\log[H_3O^+]$  and x is also  $[H_3O^+]$ , so  $pH = -\log(0.000234) = 3.63$ . As we saw previously, we can get  $[OH^-]$  from  $K_w/$  $[H_3O^+]$ , so  $[OH^-] = 1.0 \times 10^{-14} / 2.34 \times 10^{-4} = 4.27 \times 10^{-11} M$ .

6. How many moles of NH<sub>3</sub> must be dissolved in 1.00 liters of aqueous solution to produce a solution with a pH of 11.47? The  $K_a$  of  $NH_4^+$  is  $5.8 \times 10^{-10}$ .

This will ultimately be a RICE table problem, but first we have to use the pH to calculate the equilibrium concentration of OH<sup>-</sup>. We want OH<sup>-</sup> in this case because NH<sub>3</sub> is a base and will react with water in the reaction  $NH_3 + H_2O \Longrightarrow NH_4^+ + OH^-$ . To go from pH to pOH, use the relation that pH + pOH = 14, so 14 - pH = pOH = 14 - 11.47 = 2.53. Like pH,  $pOH = -log[OH^-]$ , so  $[OH^-] = 10^{-pOH} = 10^{-2.53} = 2.95 \times 10^{-3}$ . This time, our unknown is actually the initial concentration of NH<sub>3</sub>, but we know we start with none of our products but end up with  $[OH^-] = 2.95 \times 10^{-3}$ , so we know the change and can fill in our RICE table accordingly and actually end up with an easier problem than normal.

| (R)          | $NH_3 + H_2O \Longrightarrow NH_4^+ + OH^-$ |   |                       |                       |  |
|--------------|---|---|-----------------------|-----------------------|--|
| I            | X   | _ | 0                     | 0                     |  |
| $\mathbf{C}$ | $-2.95 \times 10^{-3}$                      | _ | $+2.95\times10^{-3}$  | $+2.95\times10^{-3}$  |  |
| $\mathbf{E}$ | $x - 2.95 \times 10^{-3}$                   | _ | $2.95 \times 10^{-3}$ | $2.95 \times 10^{-3}$ |  |

 $\mathrm{NH_{3}}$  is a base, so we need a  $\mathrm{K_{b}}$  expression, despite being given a  $\mathrm{K_{a}}$  value, so convert to  $\mathrm{K_{b}}$ using  $K_b = K_w / K_a = 1.0e-14 / 5.8 \times 10^{-10} = 1.7 \times 10^{-5}$ 

$$K_{a} = \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{3}]} \implies 1.7 \times 10^{-5} = \frac{(2.95 \times 10^{-3})^{2}}{x - 2.95 \times 10^{-3}}$$

Now set up the  $K_b$  expression:  $K_a = \frac{[NH_4^+][OH^-]}{[NH_3]} \implies 1.7 \times 10^{-5} = \frac{(2.95 \times 10^{-3})^2}{x - 2.95 \times 10^{-3}}$  Rearrange and solve for x to get x = 0.515. This is the initial concentration of NH<sub>3</sub> required to make a solution of pH = 11.47, but because the problem specifies the total volume is 1 L, it is also the number of moles desired.

7. Calculate the percent ionization of the weak acid, HA, given a 0.25 M HA solution and a K<sub>a</sub> of  $5.3 \times 10^{-7}$ .

The percent ionization is given by the ratio of dissociated acid to the initial amount of acid. For every molecule of acid that dissociates, one molecule of H<sub>3</sub>O<sup>+</sup> and one molecule of conjugate base is produced, assuming a 1:1 stoichiometry, so percent ionization is given by the equation  $\%I = \frac{[H_3O^+]}{(HA)_0} \times 100\%$  We have the initial concentration of acid, (HA)<sub>0</sub>, so we just need a RICE table to calculate the equilibrium hydronium concentration.

| (R)          | $HA + H_2O \Longrightarrow H_3O^+ + A^-$ |   |    |    |  |  |
|--------------|--|---|----|----|--|--|
| I            | 0.25                                     | _ | 0  | 0  |  |  |
| $\mathbf{C}$ | $-\mathbf{x}$                            | _ | +x | +x |  |  |
| $\mathbf{E}$ | 0.25 - x                                 | _ | x  | x  |  |  |

 $K_a=5.3\times 10^{-7}=\frac{x^2}{0.25-x},~x=-0.000364,0.000364,$  again discarding the negative root to get  $x=3.64\times 10^{-4}=[H_3O^+].$  Dividing this by the initial acid concentration and multiplying by 100% gives the percent ionization:  $\%I=[H_3O^+]~/~(HA)_0\times 100\%=0.14\%.$