Going Further: Calculating the *p*H of Bases including Conjugate Bases of Weak Acids (Salts)

Introduction

So far, we have concentrated almost entirely on acids and the way in which they dissociate in water by their reaction with it. Although we have defined bases (in a Lowry-Brønsted context), there has been no quantitative discussion regarding bases. Ignoring bases is rather like ignoring the fact that a coin has a tails side when discussing the statistics of coin tossing.

So, here is a brief explanation of the base chemistry side of things.

Bases and their reaction in water

Let's consider a base B. How will B behave when placed in water?

We can represent this reaction as follows:

$$\underset{\text{BASE}}{B_{(aq)}} + \underset{\text{ACID}}{H_2O_{(aq)}} \rightleftharpoons \underset{\text{CONJ. ACID}}{BH^+_{(aq)}} + \underset{\text{CONJ. BASE}}{OH^-_{(aq)}}$$

The **stronger the base**, the further the equilibrium lies **to the right**. If the reaction went to completion, it would be equivalent to adding the same number of moles of NaOH to water.

- Write an expression for K_b. This is the base equivalent of K_a.

K_b = ____________

Remember the 'trick' with $[H_2O]$ that we did when writing K_a (the **$[H_2O]$ is so large it is effectively a constant**!)

The larger the K_b the farther to the right the equilibrium lies.

Let's look at an example. We'll use the example of **ammonia**.

Ammonia has a K_b value of **1.8×10^{-5}** mol dm^{-3}. We can write an equation for base dissociation.

$$\underset{\text{BASE}}{NH_{3\,(aq)}} + \underset{\text{ACID}}{H_2O_{(aq)}} \rightleftharpoons \underset{\text{C. ACID}}{NH_4^+{}_{(aq)}} + \underset{\text{C.BASE}}{OH^-_{(aq)}}$$

From this equilibrium, we can see that the addition of ammonia (a base) to water increases the $[OH^-]$ so the pH rises.

Using assumptions that we have applied to weak acid calculations, we can arrive at the following expression:

$$K_b = \frac{[OH^-]\,[NH_4^+]}{[NH_3]} \qquad \text{so,} \qquad K_b = \frac{[OH^-_{(aq)}]^2}{[NH_{3(aq)}]}$$

$$[OH^-] = \sqrt{(K_b \times [NH_3])}$$

$$[OH\text{-}] = \sqrt{(1.8 \times 10^{-5}\ \text{mol dm}^{-3} \times 0.100\ \text{mol dm}^{-3})}$$

$$= 0.00134\ \text{mol dm}^{-3}$$

Then we recall $K_w = [H^+]\,[OH^-] = 10^{-14}$

$$[H^+] = \frac{K_w}{0.00134} = \frac{10^{-14}}{0.00134} = 7.5 \times 10^{-12}\ \text{mol dm}^{-3}$$

$$pH = -\log_{10}\ 7.5 \times 10^{-12}\ \text{mol dm}^{-3} = \mathbf{11.1} = pH$$

The connection between K_b and K_a?

Let's consider the general example of HA . You are familiar with this.

$$HA_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

conjugate base (**salt**)

-this can be quantified using K_a

The conjugate base (salt) $A^-_{(aq)}$ also forms an equilibrium with water:

$$A^-_{(aq)} + H_2O_{(aq)} \rightleftharpoons HA_{(aq)} + OH^-_{(aq)}$$

-this can be quantified using K_b

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \qquad K_b = \frac{[HA]\,[OH^-]}{[A^-]}$$

$$K_a \times K_b = \frac{[H^+]\,[A^-]}{[HA]} \times \frac{[HA]\,[OH^-]}{[A^-]}$$

$$K_a \times K_b = \frac{[H^+]\,\cancel{[A^-]}}{\cancel{[HA]}} \times \frac{\cancel{[HA]}\,[OH^-]}{\cancel{[A^-_{(aq)}]}} \qquad \text{(cancelling!)}$$

So . . . .

$$\boxed{K_a \times K_b = K_w = [H^+][OH^-] = 10^{-14}}$$

This means that we can find K_b of the conjugate base if we know K_a of the acid that produced it!

The K_b of the ethanoate ion must be $\frac{K_w}{K_a} = \frac{10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}$ mol dm^{-3}

Calculating the pH of a salt such as sodium ethanoate

$$K_a \times K_b = K_w = 10^{-14}$$

This is a **very useful relationship** as it will allow us to calculate the *p*H of a salt such as sodium ethanoate from knowledge of the K_a of its conjugate acid, i.e. ethanoic acid.

1. Calculate the pH of 0.100 mol dm^{-3} CH_3COONa (sodium ethanoate **salt**)

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2. Calculate the pH of a 0.180 mol dm^{-3} methylamine solution.
   K_b for methylamine is 4.41 x 10^{-4} mol dm^{-3}

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3. Calculate the pH of the 'neutralised' ethanoic acid in the ethanoic acid 'v' sodium hydroxide titration. When you calculated pHs, the pH at 50cm^3 was deliberately avoided. Now calculate its pH?

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4. A final thought-provoking weak acids problem. Calculate the pH of the 0.100M solution of ethanoic acid when only 1 drop (0.05 cm^3 of 0.100) mol dm^{-3} $NaOH_{(aq)}$ has been added. You should get a very odd result. Can you explain it?
   Hint:Think about assumptions that you have made.

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Answers

1. The K_b of the ethanoate ion must be $\frac{K_w}{K_a} = \frac{10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}$ mol dm^{-3}

$[OH^-] = \sqrt{}(K_b \times [CH_3COO^-]) = \sqrt{5.88 \times 10^{-10} \times 0.100} = 7.67 \times 10^{-6}$ mol dm^{-3}

$[H^+] = \frac{10^{-14}}{7.67 \times 10^{-6}} = 1.30 \times 10^{-9}$ mol dm^{-3}

pH = $-\log_{10} 1.30 \times 10^{-9}$ = 8.89

2.

$[OH^-] = \sqrt{}(K_b \times [\text{methylamine}]) = \sqrt{(4.41 \times 10^{-4} \times 0.180)} = 8.91 \times 10^{-3}$ mol dm^{-3}

$[H^+] = \frac{10^{-14}}{8.91 \times 10^{-3}} = 1.12 \times 10^{-12}$ mol dm^{-3}

pH = $-\log_{10} 1.30 \times 10^{-9}$ = 11.95

3.

So, the pH of the 'neutralised' ethanoic acid, where 50 cm^3 of 0.100 mol dm^{-3} NaOH were added to 50cm^3 of 0.100 mol dm^{-3} must have a pH calculated as follows:

Remember that the salt concentration is half of the original acid concentration because the volume has been doubled!
So, as the acid was 0.100 mol dm^{-3}, the salt (ethanoate) will be 0.0500 mol dm^{-3}

$[OH^-] = \sqrt{}(K_b \times [CH_3COO^-]) = \sqrt{}(5.88 \times 10^{-10} \times 0.0500) = 5.42 \times 10^{-6}$ mol dm^{-3}

$[H^+] = \frac{10^{-14}}{5.42 \times 10^{-6}} = 1.85 \times 10^{-9}$ mol dm^{-3}

pH = $-\log_{10} 1.30 \times 10^{-9}$ = 8.73

4. The pH at this point is

pH = pKa + log n_{A^-} / n_{HA}

pH = 4.77 + log $5 \times 10^{-6} / 4.995 \times 10^{-3}$

pH = 4.77 + log 1.001×10^{-3}

pH = 4.77 + (-3.00)

pH = **1.77**

This is odd since this suggests that pH is more acidic after one drop of alkali has been added than when the acid has undergone no neutralisation whatsoever. This just can't be right!
This exposes the error that is made by **ignoring the slight natural dissociation.** When using the *Henderson-Hasselbach* equation, we are assuming that there is no dissociation, other than that which we force by adding strong base. It isn't a problem once some more NaOH has been added. **The error becomes insignificant.**