A2 Physical Chemistry

Introduction to Buffers

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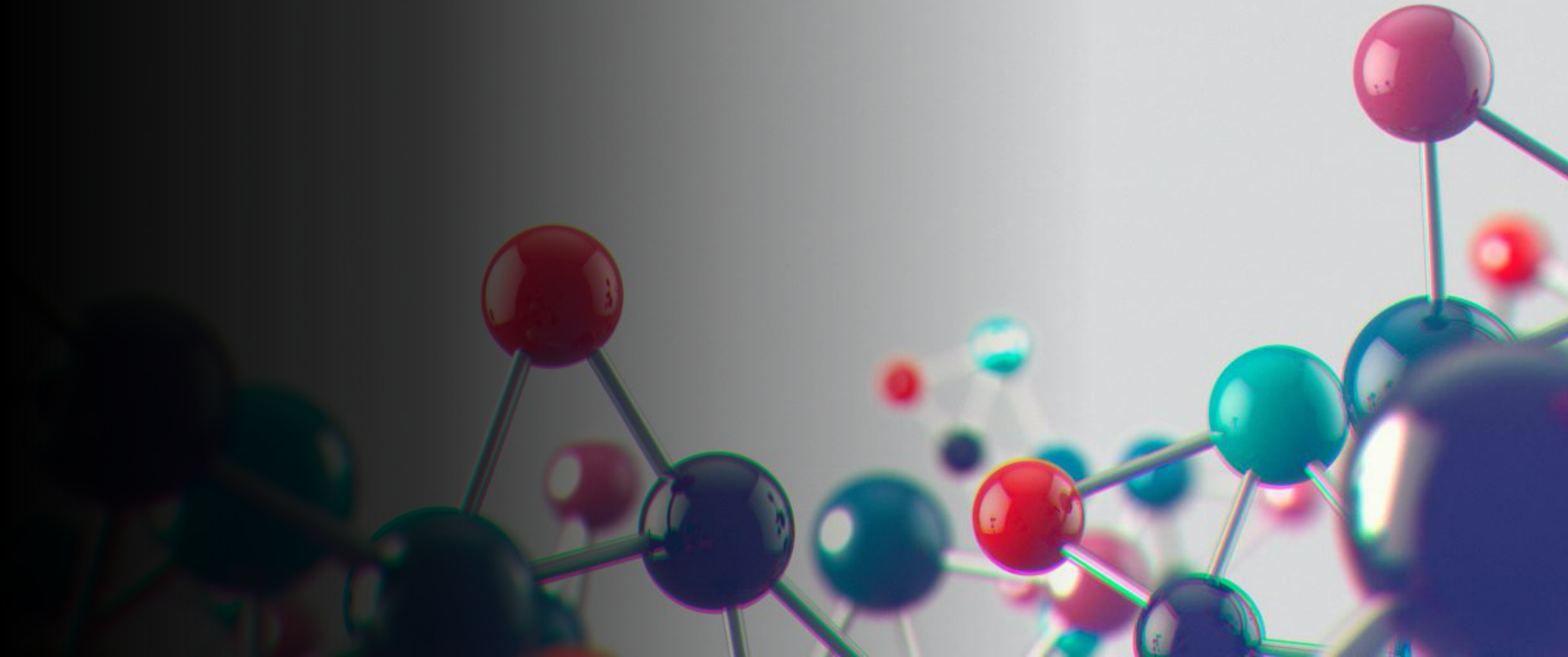

Introduction

From Le Chatelier we know that if we were to add more H^+ ions to this equilibrium, it will shift to towards the left to remove the added H^+ ions.

$$\mathbf{CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}}$$

K_a will be restored to its original value.

Ka for ethanoic acid = 1.74×10^{-5}. If the concentration of ethanoic acid is 0.100 mol dm^{-3}

$$K_a = \frac{[H^+_{(aq)}][CH_3COO^-_{(aq)}]}{[CH_3COOH_{(aq)}]} \qquad 1.74 \times 10^{-5} = \frac{[H^+_{(aq)}]^2}{0.100}$$

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$$[H^+_{(aq)}]^2 = 1.74 \times 10^{-5} \times 0.100$$

$$[H^+_{(aq)}] = 1.32 \times 10^{-3}\ \text{mol dm}^{-3}$$

Mols in 100 cm^3

$\mathbf{CH_3COOH_{(aq)}}$	$\rightleftharpoons$ $\mathbf{H^+_{(aq)}}$ +		$\mathbf{CH_3COO^-_{(aq)}}$
0.0999		1.32×10^{-4}	1.32×10^{-4}

Buffers

A **buffer solution** is a system that minimises pH changes on addition of small amounts of an acid or base.

A buffer solution can be made from a weak acid and a salt of the weak acid eg CH_3COOH/CH_3COONa.

$$\mathbf{CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}}$$

$$\mathbf{CH_3COO^-Na^+_{(aq)} \rightarrow Na^+_{(aq)} + CH_3COO^-_{(aq)}}$$

Acidic Buffers

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Basic Buffers

Basic buffer solutions are made from a mixture of a weak alkali and one of its salts.

Eg NH_3 and $NH_4^+Cl^-$.

$$NH_3 + H_2O \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

From alkali

From salt

How acidic buffer solutions control pH

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

$$K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]}$$

$$[H^+_{(aq)}][A^-_{(aq)}] = K_a \times [HA_{(aq)}]$$

$$[H^+_{(aq)}] = K_a \times \frac{[HA_{(aq)}]}{[A^-_{(aq)}]}$$

How acidic buffer solutions control pH

$$[H^+_{(aq)}] = K_a \times \frac{[HA_{(aq)}]}{[A^-_{(aq)}]}$$

Therefore the pH of an acidic buffer depends on the ratio of [HA] to [A^-] (i.e. the ratio of [acid] to [salt]).

Addition of acid to an acidic buffer

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

Addition of acid to an acidic buffer

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

$[H^+]$ increases.

The CH_3COO^- reacts with the added acid to produce CH_3COOH and neutralises any added H^+.

The Equilibrium moves to **left.**

Addition of alkali to an acidic buffer

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

$[OH^-]$ increases.

The $[H^+]$ ions reacts with the added alkali to produce H_2O and neutralises any added OH^-.

The Equilibrium moves to left.

CH_3COOH dissociates shifting the equilibrium position to the right, restoring the H^+ ions.

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

How alkaline buffer solutions control pH

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_b = \frac{[NH_4^+{}_{(aq)}][OH^-{}_{(aq)}]}{[NH_{3(aq)}]}$$

$$[NH_4^+{}_{(aq)}][OH^-{}_{(aq)}] = K_b \times [NH_{3(aq)}]$$

$$[OH^-{}_{(aq)}] = K_b \times \frac{[NH_{3(aq)}]}{[NH_4^+{}_{(aq)}]}$$

The pH of a basic buffer depends on the ratio of [base] to [salt]

Addition of acid to an alkaline buffer

$$NH_3 + H_2O \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

The added H^+ is removed by reaction with OH^-.

$$H^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow H_2O_{(l)}$$

Some NH_3 reacts to replace the OH^-.

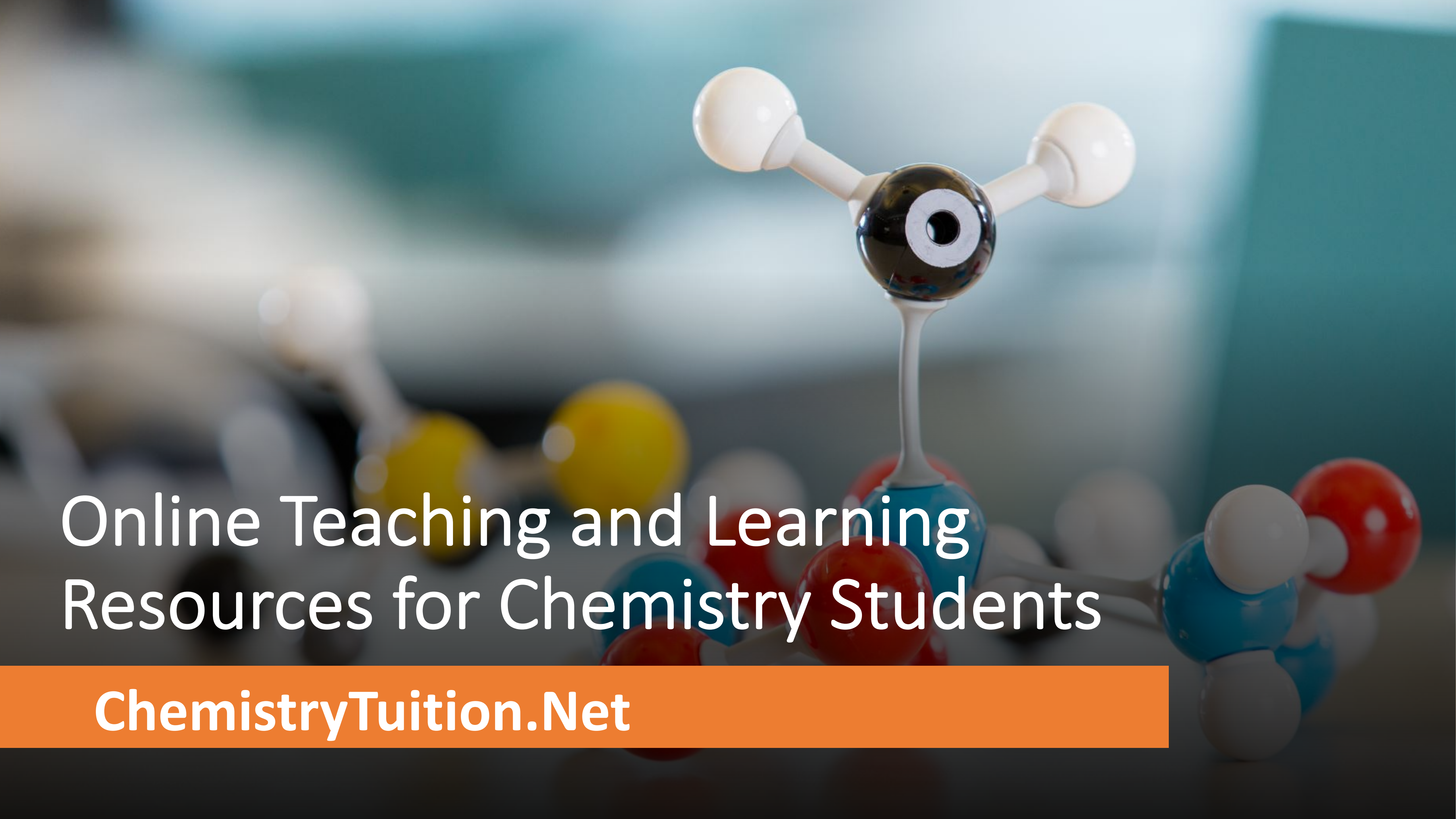
The $[NH_3]$ falls slightly and the $[NH_4^+]$ rises slightly, but as $[NH_3]$ & $[NH_4^+] >> [OH^-]$, the ratio of $[NH_3]/[NH_4^+]$ remains roughly constant.

Addition of alkali to an alkaline buffer

$$NH_3 + H_2O \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

The added OH^- is removed by reaction with NH_4^+ to form NH_3.

The $[NH_3]$ rises slightly and the $[NH_4^+]$ falls slightly, but as $[NH_3]$ & $[NH_4^+]$ >> $[OH^-]$, the ratio of $[NH_3]/[NH_4^+]$ remains roughly constant.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