SUPPORTING INFORMATION

A microfluidic platform for university-level analytical chemistry laboratories

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Determining pH versus Q_B/Q_T for titration of a strong acid and strong base

<u>Case 1</u>: $Q_{KOH}/Q_T < Q_{KOH,e}/Q_T$

Here we consider the acid solution (titrand) as being incompletely titrated by the base (titrant).

Therefore, the remaining [H⁺] is calculated as:

 $[H^+] = [HC1] \times Q_{HC1} / Q_T - [KOH] \times Q_{KOH} / Q_T$

<u>Case 2</u>: $Q_{KOH}/Q_T > Q_{KOH,e}/Q_T$

Here we consider the base solution (titrand) as being incompletely titrated by the acid (titrant).

Therefore, the remaining [OH⁻] is calculated as:

$$[OH^{-}] = [KOH] \times Q_{KOH} / Q_{T} - [HCl] \times Q_{HCl} / Q_{T}$$

For case two, the concentration of H^+ is given by $[H^+] = K_w/[OH^-]$.

Titration of a weak acid with a strong base

Goal: find $Q_{B,pKa}/Q_T$ (i.e., Q_B/Q_T that results in pH = pK_a)

As described in Equation (11) from the main text, pH is given by the Henderson-Hasselbalch equation.

$$pH = pK_a + log\left(\frac{[B]_i \times \frac{Q_B}{Q_T}}{[A]_i \times \frac{Q_A}{Q_T} - [B]_i \times \frac{Q_B}{Q_T}}\right)$$

 $pH = pK_a$ when the following condition is true:

$$[\mathbf{B}]_{i} \times \frac{\mathbf{Q}_{B}}{\mathbf{Q}_{T}} = [\mathbf{A}]_{i} \times \frac{\mathbf{Q}_{A}}{\mathbf{Q}_{T}} - [\mathbf{B}]_{i} \times \frac{\mathbf{Q}_{B}}{\mathbf{Q}_{T}}$$
$$2[\mathbf{B}]_{i} \times \frac{\mathbf{Q}_{B}}{\mathbf{Q}_{T}} = [\mathbf{A}]_{i} \times \frac{\mathbf{Q}_{A}}{\mathbf{Q}_{T}}$$

Since

$$Q_B + Q_A = Q_T$$
, then $Q_A = Q_T - Q_B$

Therefore,

$$2[B]_{i} \times Q_{B} = [A]_{i} \times (Q_{T} - Q_{B})$$
$$2[B]_{i} \times Q_{B} = Q_{T}[A]_{i} - [A]_{i} \times Q_{B}$$
$$Q_{B}(2[B]_{i} + [A]_{i}) = Q_{T}[A]_{i}$$

Therefore, the above derivation of the flow rate of the base which is required to achieve a condition where the $pH = pK_a$, can be summarized in a general format as follows:

$$Q_{B,pKa}/Q_{T} = \frac{[A]_{i}}{2[B]_{i} + [A]_{i}}$$
(S1)

For the system demonstrated in this work, $[KOH]_i = [CH_3COOH]_i = 1M$, $Q_T = 2 \text{ mL h}^{-1}$.

Therefore, Eq. 11 reduces to

$$pH = pK_a + log\left(\frac{\frac{Q_{KOH}}{Q_T}}{\frac{Q_{CH_3COOH}}{Q_T} - \frac{Q_{KOH}}{Q_T}}\right)$$

And $pH = pK_a$ when the following holds true:

$$\frac{Q_{\text{KOH}}}{Q_{\text{T}}} = \frac{Q_{\text{CH}_{3}\text{COOH}}}{Q_{\text{T}}} - \frac{Q_{\text{KOH}}}{Q_{\text{T}}}$$

 $2Q_{\rm KOH} = Q_{\rm CH3COOH}$

Since $Q_{KOH} + Q_{CH3COOH} = 2$, it follows that $Q_{CH3COOH} = 2 - Q_{KOH}$

Therefore, $2Q_{KOH} = 2 - Q_{KOH}$, and $Q_{KOH} = 2/3$ mL h⁻¹, $Q_{CH3COOH} = 4/3$ mL h⁻¹