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Further aspects of equilibria

⇒ The ionic product of water (K_w)

→ $K_w = [H^+][OH^-]$

at room temperature, $K_w = 1.00 \times 10^{-14}\ mol^2\ dm^{-6}$

→ $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

→ $[H_2O] = 1$

→ $K_c = \dfrac{[H^+] * [OH^-]}{[H_2O]}$

⇒ pH

→ $pH = -\log_{10}[H^+]$

→ calculating pH of water

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

$x \qquad x \qquad x$

if they all have x moles of each then

$H_2O(l) \rightleftharpoons H^{+2}(aq)$

∴ $K_w = [H^+]^2$ → because value of H^+ and OH^- is same so multiplying would become $[H^+]^2$

we know $K_w = 1.00 \times 10^{-14}$

∴ $1.00 \times 10^{-14} = [H^+]^2$

$\sqrt{1.00 \times 10^{-14}} = [H^+]$

$1.00 \times 10^{-7} = [H^+]$

subst 1.00×10^{-7} in $-\log_{10}[H^+]$

$= -\log_{10}[1.00 \times 10^{-7}]$

$= 7.$ ∴ pH of water = 7

→ Calculating pH of a base

$x\,NaOH(aq) \rightarrow x\,Na^+(aq) + x\,OH^-(aq)$

subst x (conc of NaOH and OH^-) in K_w

∴ $K_w = [H^+][OH^-]$

$\dfrac{K_w}{[OH^-]} = [H^+] = \dfrac{1.00 \times 10^{-14}}{x} = [H^+]$ subst value of H^+ in $-\log_{10}[H^+]$

→ Calculating pH of weak acids

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

Total conc of CH_3COOH = 100 moldm^{-3}

dissociated conc of CH_3COOH = 0.5 moldm^{-3}

→ Not a big change in conc of CH_3COOH. So we take eq in calculations.

→ Calculating K_a

$$K_a = \frac{[\text{Product}_1] \times [\text{Product}_2]}{[\text{Reactant}]}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{0.5 \times 0.5}{100} = \frac{0.0025}{}$$

(100 ← unchanged)

K_a = 0.0025 moldm^{-3}

→ Calculating pK_a

$$pK_a = -\log_{10}(K_a)$$

$$pK_a = -\log_{10}(0.0025)$$

→ we use pK_a values to compare the acidities of weak acids.

lower pK_a value is more acidic.

higher pK_a value is less acidic.

⇒ Excercise

Q.

acid	K_a/moldm^{-3}
CH_3COOH	1.8×10^{-5}
$ClCH_2COOH$	1.4×10^{-3}
$Cl_2CHCOOH$	5.5×10^{-2}

→ Calculate the pH of a 0.100 moldm^{-3} solution of $ClCH_2COOH$

$ClCH_2COOH \rightleftharpoons ClCH_2COO^- + H^+$

$K_a = \frac{[ClCH_2COO^-][H^+]}{[ClCH_2COOH]}$, as it has same moles $[H^+] = [ClCH_2COO^-]$

so $K_a = \frac{[H^+]^2}{[ClCH_2COOH]}$ =

$[H^+]^2 = K_a \times [ClCH_2COOH]$

$= 1.4 \times 10^{-3} \times 0.1$

$= 1.4 \times 10^{-4}$

$[H^+] = \sqrt{1.4 \times 10^{-4}}$

$= 0.0118$

$pH = -\log_{10}[H^+]$

$= 1.93$

Q. Methanoic acid $HCOOH$ is a weak acid with $K_a = 1.77 \times 10^{-4}$

i) write an expression for K_a of methanoic acid.

$$HCOOH\ (aq) \rightleftharpoons HCOO^-\ (aq) + H^+\ (aq)$$

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

ii) Calculate the $[H^+]$ in a $0.05\ moldm^{-3}$ of methanoic acid.

H^+ and $HCOO^-$ have same moles

$\therefore [H^+] = [HCOO^-]$

$$K_a = \frac{[H^+]^2}{[HCOOH]}$$

$K_a \times [HCOOH] = [H^+]^2$

$1.77 \times 10^{-4} \times 0.05 = [H^+]^2$

$8.85 \times 10^{-6} = [H^+]^2$

$2.97 \times 10^{-3} = [H^+]$

iii) Calculate the percentage of $HCOOH$ molecules that are ionised

$$\frac{[H^+]}{[HCOOH]} \times 100 \rightarrow \frac{2.97 \times 10^{-3}}{0.05} \times 100 = 5.94\%$$

iv) Calculate pH of this solution

$pH = -\log_{10}[H^+]$

$= -\log_{10}(2.97 \times 10^{-3}) = 2.53$

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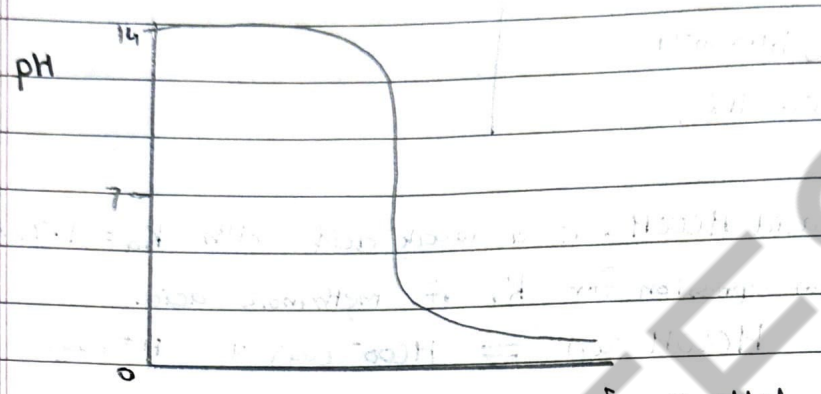
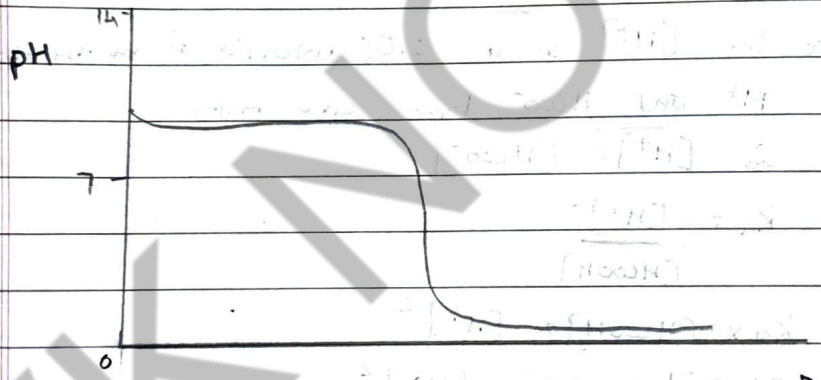
⇒ pH curve for reaction between:

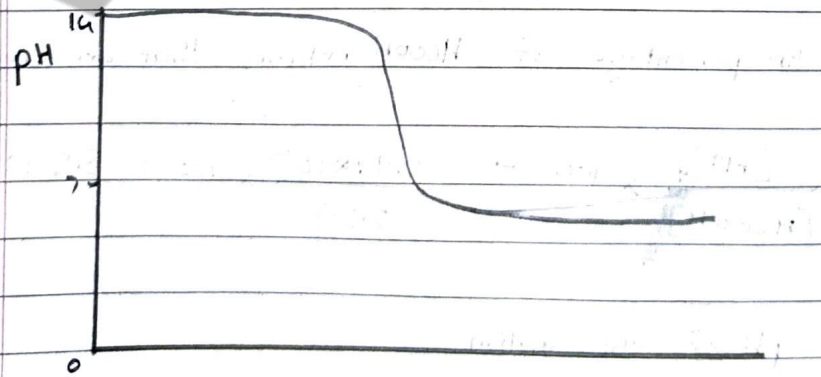
→ Strong acid - Strong base



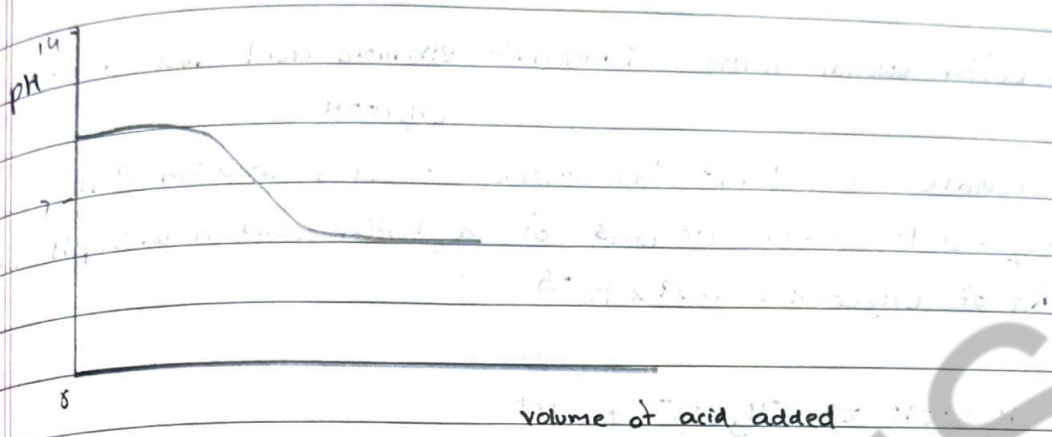
→ Strong acid - weak base



→ weak acid - Strong base



→ weak base - weak acid.



⇒ Indicators

→ an acid-base indicator gives colour change within a specific pH range.

→ The equivalance point of the titration should be the mean value of the pH range of a particular indicator, for the indicator to give a colour change.

⇒ Buffer Solution

→ A solution that resists change in its pH when small amounts of acids or bases are added.

→ A buffer solution consists of a weak acid and its conjugate base or a weak base and its conjugate acid.

⇒ Calculating pH of buffer solution

$$pH = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

$$HA \rightleftharpoons H^+ + A^-$$

acid — conjugate base

$$pH = -\log_{10} K_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

[A⁻] → remaining

[HA] → remaining

=) Excercise

Q. buffer solution with 1 moldm^{-3} ethanoic acid and 1 moldm^{-3} CH_3COOH CH_3COONa calculate to 1cm^3 the volumes of each solution that would be required to make 100 cm^3 of a buffer solution with pH 5.50

K_a of CH_3COOH : 1.79×10^{-5}

→ $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$$pH = pK_a + \log_{10} \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$pH - pK_a = \log_{10} \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$5.50 - [-\log_{10}(K_a)] = \log_{10} \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$5.50 + \log_{10}(1.79 \times 10^{-5}) = \log_{10} \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$5.50 - 4.75$$

$$= 0.753 = \log_{10} \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$10^{0.753} = \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$[CH_3COOH] \times 10^{0.753} = [CH_3COO^-]$$

$$x$$

$$\therefore \quad 5.66x + x = 100$$

$$x = \frac{100}{6.66}$$

CH_3COOH = 15.0 cm^3

CH_3COONa = 85.0 cm^3

Q Calculate the pH of a buffer solution that contains 0.20 moldm^{-3} NaH_2PO_4 and 0.1 moldm^{-3} Na_2HPO_4 ($K_a(H_2PO_4^-) = 6.3 \times 10^{-8}$ moldm^{-3})

$NaH_2PO_4\ (aq) \rightleftharpoons NaHPO_4^- + H^+$

$Na_2HPO_4\ (aq) \rightarrow NaHPO_4^- + Na^+$

$$pH = pK_a + \log_{10}\left(\frac{[NaHPO_4^-]}{[NaH_2PO_4]}\right)$$

$$pH = -\log_{10}(6.3 \times 10^{-8}) + \log_{10}\left(\frac{[0.1]}{[0.2]}\right)$$

$pH = 7.2 + 6.89$

$= \underline{6.90}$

⇒ Solubility of sparingly soluble salts

→ Saturated solution is one in which no more solute can be dissolved

→ The solubility product is the product of the concentrations of each ion in a saturated solution of a sparingly soluble salt at 298K.

ex. $AgCl\ (s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$K_{sp} = [Ag^+][Cl^-] = x^2$

ex. $PbCl_2\ (s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$= [x]\ [2x]^2$

$= x\ 4x^2$

$= \underline{4x^3}$

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⇒ Common Ion effect

→ $Ag(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

↳ $NaCl \rightarrow Na^+(aq) + Cl^-(aq)$

the common ion will cause the equilibrium to shift to the left in eq 1, forming white precipitate.

⇒ Partition Coefficients

→ Some solutes can dissolve in two immiscible solvents.

→ The partition coefficients, is the equilibrium constant of a solute partitioned between two immiscible solvents

oil
water

dissolving ammonia → $K_{pc} = \frac{[NH_3(os)]}{[NH_3(aq)]}$