Marks 8

- Solution A consists of a 1.00 M aqueous solution of HOCl at 25 °C. The pK_a of HOCl is 7.54. Calculate the pH of Solution A.

As HOCl is a weak acid, [H^+(aq)] must be calculated by considering the equilibrium:

	HOCl(aq)	$\rightleftharpoons$	OCl^-(aq)	H^+(aq)
initial	1.00		0	0
change	$-x$		$+x$	$+x$
final	$1.00 - x$		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[OCl^-(aq)][H^+(aq)]}{[HOCl]} = \frac{x^2}{(1.00-x)}$$

As pK_a = 7.54, $K_a = 10^{-7.54}$. K_a is very small so $1.00 - x \sim 1.00$ and hence:

$x^2 = 1.00 \times 10^{-7.54}$ **or** $x = 0.000170$ **M = [H^+(aq)]**

Hence, the pH is given by:

$\text{pH} = -\log_{10}[H^+(aq)] = -\log_{10}[0.000170] = 3.77$

pH = **3.77**

At 25 °C, 1.00 L of Solution B consists of 74.4 g of NaOCl dissolved in water. Calculate the pH of Solution B.

The molar mass of NaOCl is:

molar mass = (22.99 (Na) + 16.00 (O) + 35.45 (Cl)) g mol^{-1} = 74.44 g mol^{-1}

The number of moles present in 74.4 g is therefore:

number of moles = mass / molar mass = (74.4 g) / (74.44 g mol^{-1}) = 0.999 mol

If this is present in 1.00 L, then [OCl^-] = 0.999 M.

As it is a weak base, [OH^-] must be calculated by considering the equilibrium:

	OCl^-	H_2O	$\rightleftharpoons$	HOCl	OH^-
initial	0.999	large		0	0
change	$-y$	negligible		$+y$	$+y$
final	$0.999 - y$	large		y	y

ANSWER CONTINUES ON THE NEXT PAGE

The equilibrium constant K_b is given by:

$$K_b = \frac{[HOCl][OH^-]}{[OCl^-]} = \frac{y^2}{(0.999 - y)}$$

For an acid and its conjugate base:

$pK_a + pK_b = 14.00$

$pK_b = 14.00 – 7.54 = 6.46$

As $pK_b = 6.46$, $K_b = 10^{--6.46}$. K_b is very small so $0.999 – y \sim 0.999$ and hence:

$y^2 = 0.999 \times 10^{–6.46}$ or $y = 0.000589$ M = $[OH^-]$

Hence, the pOH is given by:

$pOH = -\log_{10}[OH^-] = \log_{10}[0.000589] = 3.23$

Finally, pH + pOH = 14.00 so

$pH = 14.00 – 3.23 = 10.77$

pH = **10.77**

Solution B (0.40 L) is poured into Solution A (0.60 L). What amount of NaOH (in mol) must be added to give a solution, after equilibration, with a pH of 8.20?

The number of moles of HOCl in 0.60 L is:

number of moles = concentration × volume
= $(1.00 \text{ mol L}^{-1}) \times (0.60 \text{ L}) = 0.60$ mol

The number of moles of OCl^- in 0.60 L is:

number of moles = concentration × volume
= $(0.999 \text{ mol L}^{-1}) \times (0.40 \text{ L}) = 0.40$ mol

The added NaOH will react with the HOCl to form more OCl^-:

$HOCl(aq) + OH^-(aq) \rightarrow OCl^-(aq) + H_2O(l)$

If x mol of NaOH is added then this reaction will lead to:

number of moles of HOCl = $(0.60 – x)$ mol
number of moles of OCl^- = $(0.40 + x)$ mol

ANSWER CONTINUES ON THE NEXT PAGE

The solution has a volume of 1.00 L so:

[HOCl] = (0.60 – x) M and [OCl$^-$] = (0.40 + x) M

Using the Henderson-Hasselbalch equation with pH = 8.20:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{OCl^-(aq)}]}{[\mathrm{HOCl(aq)}]} = 7.54 + \log\frac{(0.40+x)}{(0.60-x)} = 8.20$$

$$\log\frac{(0.40+x)}{(0.60-x)} = 0.66 \quad \text{or} \quad \frac{(0.40+x)}{(0.60-x)} = 10^{0.66} = 4.57$$

Solving this gives x = 0.42 mol.

Answer: **0.42 mol**