

- Aqua ligands in coordination complexes are generally acidic. Briefly explain this phenomenon using  $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$  as an example.

**$\text{Co}^{3+}$  has a high charge and is relatively small: it has a high charge density. When attached to water, it polarises the O–H bond in the aqua ligand.**

**This weakens the O–H bond causing the complex to be acidic in aqueous solution.**

Solution A consists of a 0.10 M aqueous solution of  $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)](\text{NO}_3)_3$  at 25 °C. Calculate the pH of Solution A. The  $\text{p}K_a$  of  $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+} = 5.69$ .

As  $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$  is a weak acid,  $[\text{H}_3\text{O}^+]$  must be calculated using a reaction table (acid =  $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$  and base =  $[\text{Co}(\text{NH}_3)_5(\text{OH})]^{2+}$ )

	acid	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	base
initial	0.10	large		0	0
change	-x	negligible		+x	+x
final	$0.10 - x$	large		x	x

The equilibrium constant  $K_a$  is given by:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{base}]}{[\text{acid}]} = \frac{x^2}{0.10 - x}$$

As  $\text{p}K_a = -\log_{10}K_a$ ,  $K_a = 10^{-5.69}$  and is very small,  $0.10 - x \sim 0.10$  and hence:

$$x^2 = 0.10 \times 10^{-5.69} \quad \text{or} \quad x = 4.5 \times 10^{-4} \text{ M} = [\text{H}_3\text{O}^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}(4.5 \times 10^{-4}) = 3.35$$

$$\text{pH} = 3.35$$

At 25 °C, 1.00 L of Solution B consists of 28.5 g of  $[\text{Co}(\text{NH}_3)_5(\text{OH})](\text{NO}_3)_2$  dissolved in water. Calculate the pH of Solution B.

The molar mass of  $[\text{Co}(\text{NH}_3)_5(\text{OH})](\text{NO}_3)_2$  is:

$$\begin{aligned} \text{molar mass} &= (58.93 \text{ (Co)} + 7 \times 14.01 \text{ (N)} + 7 \times 16.00 \text{ (O)} + 16 \times 1.008 \text{ (H)}) \text{ g mol}^{-1} \\ &= 285.128 \text{ g mol}^{-1} \end{aligned}$$

The number of moles present in 28.5 g is therefore:

$$\text{number of moles} = \text{mass} / \text{molar mass} = (28.5 \text{ g}) / (285.128 \text{ g mol}^{-1}) = 0.100 \text{ mol}$$

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If this is present in 1.00 L, then  $[\text{base}] = 0.100 \text{ M}$ .

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

	base	H <sub>2</sub> O	$\rightleftharpoons$	acid	OH <sup>-</sup>
initial	0.100	large		0	0
change	-y	negligible		+y	+y
final	0.100 - y	large		y	y

The equilibrium constant  $K_b$  is given by:

$$K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(0.100 - y)}$$

For an acid and its conjugate base:

$$\text{p}K_a + \text{p}K_b = 14.00$$

$$\text{p}K_b = 14.00 - 5.69 = 8.31$$

As  $\text{p}K_b = 8.31$ ,  $K_b = 10^{-8.31}$ .  $K_b$  is very small so  $0.100 - y \sim 0.100$  and hence:

$$y^2 = 0.100 \times 10^{-8.31} \text{ or } y = 2.21 \times 10^{-5} \text{ M} = [\text{OH}^-]$$

Hence, the pOH is given by:

$$\text{pOH} = -\log_{10}[\text{OH}^-] = \log_{10}[2.21 \times 10^{-5}] = 4.65$$

Finally,  $\text{pH} + \text{pOH} = 14.00$  so

$$\text{pH} = 14.00 - 4.65 = 9.35$$

$$\text{pH} = 9.35$$

Using both Solutions A and B, calculate the volumes (in mL) required to prepare a 1.0 L solution with a  $\text{pH} = 7.00$ .

The ratio of acid to conjugate base needed can be calculated using the Henderson-Hasselbalch equation,  $\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$ :

$$7.00 = 5.69 + \log \frac{[\text{base}]}{[\text{acid}]} \text{ so } \frac{[\text{base}]}{[\text{acid}]} = 10^{1.31} = 20.4$$

As the base and acid have the same concentration, this is also the ratio of the volumes needed. As  $V_{\text{acid}} + V_{\text{base}} = 1.0 \text{ L}$  and  $V_{\text{base}} / V_{\text{acid}} = 20.4$ :

$$V_{\text{acid}} = 0.047 \text{ L and } V_{\text{base}} = 0.953 \text{ L}$$