AP Chemistry Free Response Question 1982 A

A buffer solution contains 0.40 moles of formic acid, HCOOH, and 0.60 moles of sodium formate, HCOONa, in 1.00 L of solution. The equilibrium constant, K_a, of formic acid is 1.8×10^{-4}.

(a) Calculate the pH of this solution

$$\mathrm{p}K_\mathrm{a} = -\log(1.8 \times 10^{-4}) \approx 3.75$$

Since the solution contains both a weak acid and its conjugate base, we can use the Henderson-Hasselbalch equation to calculate the pH. It is not necessary to calculate the actual concentrations of the substances.

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{HCOO^-}]}{[\mathrm{HCOOH}]}\right) = 3.75 + \log\left(\frac{0.60\,\mathrm{mol}}{0.40\,\mathrm{mol}}\right) \approx 3.9$$

(b) **If 100. mL of this buffer solution is diluted to a volume of 1.00 L with pure water, the pH does not change. Discuss why the pH remains constant on dilution.**

According to the Henderson-Hasselbalch equation, the pH does not depend on the exact concentrations of the conjugate acid-base pair, but only on the ratio of their concentrations. Dilution decreases each concentration by the same factor, so the pH is not affected.

(c) **A 5.00 mL sample of 1.00 M HCl is added to 100. mL of the *original* buffer solution. Calculate the [H₃O⁺] of the resulting solution.**

HCl is a strong acid, so it will dissociate completely into H⁺ and Cl⁻ ions. The H⁺ will react with HCOO⁻ in a neutralization reaction which goes to completion.

$$\mathrm{H^+}\ (aq) + \mathrm{HCOO^-}\ (aq) \rightarrow \mathrm{HCOOH}\ (aq)$$
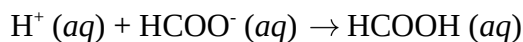
First we calculate the moles of each substance in the solutions to be mixed:

$$n_{H+} = M_{H+}V_{H+} = (1.00\mathrm{M})(0.005\ \mathrm{L}) = 0.005\,\mathrm{mol}$$

(Technically, we should add these moles of H⁺ to the moles of H⁺ that were present in the buffer solution before mixing; however, this can be neglected, since the original amount of was H⁺ will be very small compared to the amount produced by the HCl.)

$$n_{\mathrm{HCOO^-}} = 0.60\,\mathrm{mol}\left(\frac{100\,\mathrm{mL}}{1000\,\mathrm{mL}}\right) = 0.060\,\mathrm{mol}$$

$$n_{\mathrm{HCOOH}} = 0.40\,\mathrm{mol}\left(\frac{100\,\mathrm{mL}}{1000\,\mathrm{mL}}\right) = 0.040\,\mathrm{mol}$$

H^+ is the limiting reagent, so the reaction will proceed until all 0.005 moles of H^+ are reacted.

	H^+ (*aq*)	+	HCOO⁻ (*aq*)	→	HCOOH (*aq*)
I	0.005 mol		0.060		0.040
C	- 0.005 mol		- 0.005 mol		+ 0.005 mol
F	0 mol		0.055 mol		0.045 mol

There are still moles of both the conjugate acid and the conjugate base, so we can again use the Henderson-Hasselbalch equation to calculate the pH.

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{HCOO^-}]}{[\mathrm{HCOOH}]}\right) = 3.75 + \log\left(\frac{0.55\,\mathrm{mol}}{0.45\,\mathrm{mol}}\right) \approx 3.83$$

Finally,

$$[\mathrm{H^+}] = 10^{-\mathrm{pH}} = 10^{-3.83} \approx \boxed{1.5 \times 10^{-4}\,\mathrm{M}}$$

(d) **An 800. mL sample of 2.00 M formic acid is mixed with 200. mL of 4.80 M NaOH. Calculate the [H_3O^+] of the resulting solution.**

Part (d) can be answered in essentially the same way as part (c).

NaOH is a strong base, so it will dissociate completely into Na^+ and OH^- ions. The OH^- will react with HCOOH in a neutralization reaction which goes to completion.

$$\mathrm{HCOOH}\,(aq) + \mathrm{OH^-}\,(aq) \rightarrow \mathrm{H_2O}\,(l) + \mathrm{HCOO^-}\,(aq)$$
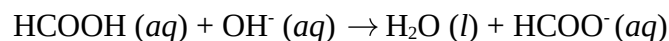
First we calculate the moles of each substance in the solutions to be mixed.

$$n_{\mathrm{OH^-}} = M_{\mathrm{OH^-}}V_{\mathrm{OH^-}} = (4.80M)(0.200\mathrm{L}) = 0.96\,\mathrm{mol}$$

$$n_{\mathrm{HCOOH}} = M_{\mathrm{HCOOH}}V_{\mathrm{HCOOH}} = (2.00M)(0.800\,\mathrm{L}) = 1.6\,\mathrm{mol}$$

$$n_{\mathrm{HCOO^-}} = 0\,\mathrm{mol}$$

OH⁻ is the limiting reagent, so the reaction will proceed until all 0.96 moles of OH⁻ are reacted.

	HCOOH (*aq*) +	OH⁻ (*aq*) →	H₂O (*l*) +	HCOO⁻ (*aq*)
I	1.60 mol	0.96 mol	lots	0
C	-0.96 mol	-0.96 mol	+ 0.96 mol	+ 0.96 mol
F	0.64 mol	0 mol	lots	0.96 mol

There are moles of both the conjugate acid and the conjugate base present, so we can use the Henderson-Hasselbalch equation to calculate the pH.

$$\text{pH} = \text{p}K_{\text{a}} + \log\left(\frac{[\text{HCOO}^-]}{[\text{HCOOH}]}\right) = 3.75 + \log\left(\frac{0.96\,\text{mol}}{0.64\,\text{mol}}\right) \approx 3.92$$

Finally,

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-3.92} \approx \boxed{1.2 \times 10^{-4}\,\text{M}}$$