

- Ascorbic acid (Vitamin C) is a monoprotic acid of formula  $C_6H_8O_6$ . Calculate the pH of a 0.10 M solution of ascorbic acid, given the  $K_a$  of ascorbic acid is  $8.0 \times 10^{-5}$  M.

As ascorbic acid is a weak acid,  $[H_3O^+]$  must be calculated:

	$C_6H_8O_6$	$H_2O$	$\rightleftharpoons$	$H_3O^+$	$C_6H_7O_6^-$
initial	0.1	large		0	0
change	-x	negligible		+x	+x
final	$0.10 - x$	large		x	x

The equilibrium constant  $K_a$  is given by:

$$K_a = \frac{[H_3O^+(aq)][C_6H_7O_6^-(aq)]}{[C_6H_8O_6(aq)]} = \frac{x^2}{(0.10 - x)}$$

As  $K_a = 8.0 \times 10^{-5}$  is very small,  $0.10 - x \sim 0.10$  and hence:

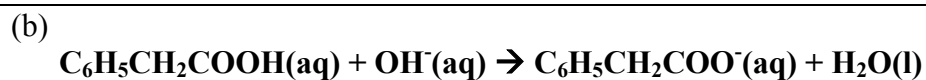
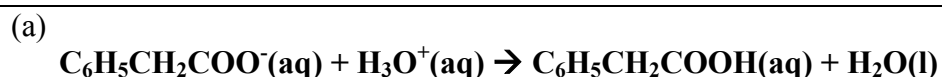
$$x^2 = 0.1 \times (8.0 \times 10^{-5}) \text{ or } x = 2.8 \times 10^{-3} \text{ M} = [H_3O^+(aq)]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[H_3O^+(aq)] = -\log_{10}[0.0028] = 2.5$$

Answer: pH = 2.5

- Write equations to show what happens to a buffer solution containing equimolar amounts of  $C_6H_5CH_2COOH$  and  $C_6H_5CH_2COOK$  when:  
(a)  $H_3O^+$  is added, (b)  $OH^-$  is added.



- Calculate the pH of a solution that is 0.010 M in benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , and 0.010 M in  $\text{C}_6\text{H}_5\text{CO}_2\text{Na}$ . The  $K_a$  of benzoic acid is  $6.4 \times 10^{-5}$  M.

**This solution contains an acid and its conjugate base so the Henderson-Hasselbalch equation can be used:**

$$\text{pH} = \text{p}K_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

As  $[\text{acetic acid}] = [\text{sodium acetate}]$ ,  $\log_{10} \left( \frac{0.010}{0.010} \right) = \log_{10}(1) = 0$  and so

$$\text{pH} = \text{p}K_a = -\log(6.4 \times 10^{-5}) = 4.19$$

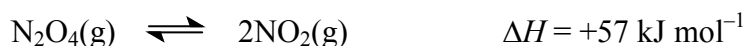
Answer: **4.19**

Would this solution make a good buffer system? Give reasons for your answer?

**Because the concentrations of weak acid and conjugate base are equal, this solution is a good buffer system. (Good buffers require this ratio to be between 0.1 and 10.)**

**As the concentrations are only 0.010 M, the buffer does not have a very great capacity. It will buffer effectively for small amounts of added  $\text{H}^+$  or  $\text{OH}^-$ , but large amounts will quickly cause the weak acid/conjugate base ratio to move outside the 0.1-10 range.**

- The gases  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  are in equilibrium according to the following equation.



In which direction will the reaction move when the following changes are made?

The pressure is increased by decreasing the volume.

**The reaction involves 1 mol  $\rightarrow$  2 mol so the system will react to an increase in pressure by shifting to lower to the left to reduce it: shift to reactants.**

The temperature is increased.

**The reaction is endothermic so the system will react to an increase in temperature by shifting to the right to reduce it: shift to products.**

- Quinine is a natural product that has anti-malarial properties. It was originally extracted for therapeutic use from the bark of the cinchona tree, but is now synthesised by the pharmaceutical industry. Quinine is not very soluble in water and is generally administered as the more soluble hydrochloride salt ( $C_{20}H_{24}N_2O_2 \cdot HCl$ ). The  $pK_a$  of this salt is 4.32. What is the pH of a 0.053 M solution of quinine hydrochloride?

As ascorbic acid is a weak acid,  $[H_3O^+]$  must be calculated:

	acid	$H_2O$	$\rightleftharpoons$	$H_3O^+$	base
initial	0.053	large		0	0
change	-x	negligible		+x	+x
final	$0.053 - x$	large		x	x

The equilibrium constant  $K_a$  is given by:

$$K_a = \frac{[H_3O^+(aq)][base]}{[acid]} = \frac{x^2}{(0.053-x)}$$

As  $pK_a = 4.32$ ,  $K_a = 10^{-4.32}$  and is very small,  $0.053 - x \sim 0.053$  and hence:

$$x^2 = 0.053 \times (10^{-4.32}) \text{ or } x = 1.59 \times 10^{-3} \text{ M} = [H_3O^+(aq)]$$

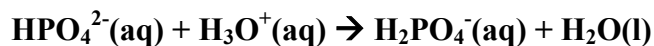
Hence, the pH is given by:

$$pH = -\log_{10}[H_3O^+(aq)] = -\log_{10}[0.00159] = 2.80$$

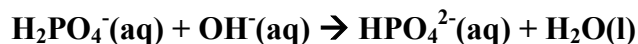
Answer: pH = 2.80

- Use chemical equations to illustrate how  $HPO_4^{2-}/H_2PO_4^-$  can act as a buffer.

The  $HPO_4^{2-}(aq)$  acts as a base and can take up added  $H^+(aq)$ :



The  $H_2PO_4^-(aq)$  acts as an acid and can take up added  $OH^-(aq)$ :



The system thus has the capacity to maintain the pH.

- Butyric acid,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ , is found in rancid butter and parmesan cheese. The  $\text{p}K_a$  of butyric acid is 4.83.  
(a) What is the pH of a 0.10 M water solution of butyric acid?

As  $\text{p}K_a = -\log K_a = 4.83$ ,  $K_a = 10^{-4.83}$ . Denoting butyric acid as HA, the initial concentration of  $[\text{HA}(\text{aq})] = 0.10 \text{ M}$ . The reaction table is then:

	$[\text{HA}(\text{aq})]$	$\rightleftharpoons$	$[\text{H}^+(\text{aq})]$	$[\text{A}^-(\text{aq})]$
<b>t = 0</b>	<b>0.10.</b>		<b>0</b>	<b>0</b>
<b>change</b>	<b>-x</b>		<b>+x</b>	<b>+x</b>
<b>equilibrium</b>	<b>0.10 - x</b>		<b>x</b>	<b>x</b>

$$\text{Hence, } K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]} = \frac{(x)(x)}{0.10-x} = \frac{x^2}{0.10-x}$$

As  $K_a$  is small, the amount of dissociation, x, is also small so  $0.10 - x \sim 0.10$ .

Using this approximation,  $K_a = \frac{x^2}{0.10} = 10^{-4.83}$  hence  $x = 1.22 \times 10^{-3} \text{ M}$ .

As  $x = [\text{H}^+(\text{aq})]$ ,  $\text{pH} = -\log[\text{H}^+(\text{aq})] = -\log(1.22 \times 10^{-3}) = 2.92$

Answer: **2.92**

- (b) Calculate the pH of the solution formed when 0.050 mol of  $\text{NaOH}(\text{s})$  is added to 1.0 L of 0.10 M butyric acid.

As  $\text{NaOH}$  is a strong base, it will dissociate completely and each mole of  $\text{OH}^-$  will react with butyric acid to form one mole of  $\text{A}^-(\text{aq})$ .

1.0 L of 0.10 M HA contains 0.10 mol. After addition of 0.050 mol of  $\text{OH}^-$ , the number of moles of HA =  $(0.10 - 0.050) = 0.05 \text{ mol}$  and the number of moles of  $\text{A}^- = 0.050 \text{ mol}$ .

As 1.0 L of solution is present,  $[\text{HA}(\text{aq})] = 0.05 \text{ M}$  and  $[\text{A}^-(\text{aq})] = 0.05 \text{ M}$ . Substituting into the expression for  $K_a$  gives:

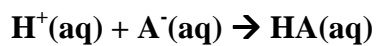
$$K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]} = \frac{[\text{H}^+(\text{aq})] \times (0.05)}{(0.05)} = 10^{-4.83} \text{ so } [\text{H}^+(\text{aq})] = 1.5 \text{ M}$$

Hence,  $\text{pH} = -\log[\text{H}^+(\text{aq})] = 4.83$

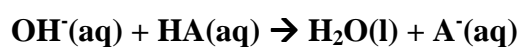
Answer: **4.83**

(c) Using equations, comment on how the final solution in (b) will respond to additions of small amounts of acid or base in comparison to 1 L of water.

**Solution (b) consists of a mixture of a weak acid and its conjugate base: it is a buffer system and will resist changes in pH. If acid is added, the system can respond by removing it using  $A^-$ :**



**If base is added, the system can respond by removing it using HA:**



**Marks**  
**6**

- Lactic acid,  $\text{CH}_3\text{CHOHCOOH}$ , is produced in the body during normal exercise. It is a monoprotic acid with a  $\text{p}K_a$  of 3.86.
- (a) What is the pH of a 0.10 M water solution of lactic acid?

The reaction table is:

	lactic acid(aq)	$\text{H}_2\text{O}(\text{l})$	$\rightleftharpoons$	lactate(aq)	$\text{H}_3\text{O}^+(\text{aq})$
start	0.10	large		0	0
change	-x	-x		+x	+x
equilibrium	0.10-x	large		x	x

As  $\text{p}K_a = -\log_{10}(K_a) = 3.86$ ,  $K_a = 10^{-3.86}$  and:

$$K_a = \frac{[\text{lactate}(\text{aq})][\text{H}_3\text{O}^+(\text{aq})]}{[\text{lactic acid}(\text{aq})]} = \frac{(x)(x)}{(0.10 - x)} = \frac{x^2}{(0.10 - x)} = 10^{-3.86}$$

As  $K_a$  is very small, x is tiny and  $0.10 - x \sim x$ . Hence,

$$K_a \sim \frac{x^2}{(0.10)} = 10^{-3.86} \text{ or } x^2 = (0.10) \times (10^{-3.86}) \text{ so } x = [\text{H}_3\text{O}^+(\text{aq})] = 3.72 \times 10^{-3} \text{ M}$$

As  $\text{pH} = -\log_{10}([\text{H}_3\text{O}^+(\text{aq})])$ :

$$\text{pH} = -\log_{10}(3.72 \times 10^{-3}) = 2.43$$

Answer: **2.43**

- (b) Calculate the pH of the solution formed when 0.02 mol of  $\text{Ca}(\text{OH})_2(\text{s})$  is added to 1.0 L of 0.10 M lactic acid.

1.0 L of 0.10M lactic acid contains 0.10 mol of acid.

$\text{Ca}(\text{OH})_2$  is a strong base. It will dissociate completely to give  $2\text{OH}^-(\text{aq})$  for every 1 mole of  $\text{Ca}(\text{OH})_2$ .  $(2 \times 0.02) = 0.04$  mol of  $\text{OH}^-(\text{aq})$  will be produced. This will neutralize 0.04 mol of the acid leaving  $(0.10 - 0.04) = 0.06$  mol of acid. Assuming that the volume does not change from the addition of the solid,  $[\text{lactic acid}] = 0.060$  M. The neutralization produces lactate anion with  $[\text{lactate}] = 0.040$  M.

The solution now contains acid and its conjugate base. It is a buffer and the pH can be calculated using the Henderson-Hasselbalch equation can be used:

$$\text{pH} = \text{p}K_a + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 3.86 + \log_{10}\left(\frac{0.040}{0.060}\right) = 3.86$$

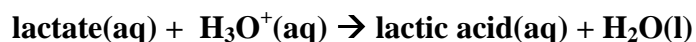
Answer: **3.86**

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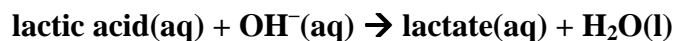
(c) Using equations, comment on how the final solution in (b) will respond to additions of small amounts (e.g. less than 0.01 mol) of acid or base in comparison to additions of the same amounts of acid or base to 1 L of water.

**The solution in (b) will act as a buffer. As it contains both an acid (lactic acid) and a base (lactate), it can react with both added base and acid to maintain a near constant pH.**

**Added  $\text{H}_3\text{O}^+$  will be consumed by the reaction of the lactate anion:**



**Added  $\text{OH}^-$  will be consumed by the reaction of the lactic acid:**



**As long as the amounts of lactic acid and lactate are large in comparison to the added acid or base, the pH is approximately constant and is described by the Henderson-Hasselbalch equation.**

**If acid or base is added to water, the  $[\text{H}_3\text{O}^+(\text{aq})]$  or  $[\text{OH}^-(\text{aq})]$  will change according to the amount added and the pH will change rapidly.**

**Marks**  
**2**

- Codeine, a cough suppressant extracted from crude opium, is a weak base with a  $pK_b = 5.79$ . What is the pH of a 0.020 M solution of codeine?

As codeine, is a weak base and so  $[OH^-]$  must be calculated. for example using a reaction table:

	codeine	H <sub>2</sub> O	$\rightleftharpoons$	codeineH <sup>+</sup>	OH <sup>-</sup>
<b>initial</b>	<b>0.020</b>	<b>large</b>		<b>0</b>	<b>0</b>
<b>change</b>	<b>-x</b>	<b>negligible</b>		<b>+x</b>	<b>+x</b>
<b>final</b>	<b>0.020 - x</b>	<b>large</b>		<b>x</b>	<b>x</b>

The equilibrium constant  $K_b$  is given by:

$$K_b = \frac{[\text{codeineH}^+][\text{OH}^-]}{[\text{codeine}]} = \frac{x^2}{(0.020 - x)}$$

As  $pK_b = -\log_{10}K_b = 5.79$ ,  $K_b = 10^{-5.79}$ . Hence,

$$\frac{x^2}{(0.020 - x)} = 10^{-5.79}$$

As  $K_b$  is very small,  $0.020 - x \sim 0.020$  and hence:

$$x^2 = 0.020 \times 10^{-5.79} \quad \text{or} \quad x = 1.8 \times 10^{-4} \text{ M} = [\text{OH}^-(\text{aq})]$$

Hence, the pOH is given by:

$$\text{pOH} = -\log_{10}[\text{OH}^-] = -\log_{10}[1.8 \times 10^{-4}] = 3.74$$

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

$$\text{pH} = 14.0 - 3.74 = 10.26$$

Answer: **10.26**

**3**

- A buffer solution is formed with 0.250 M CH<sub>3</sub>COOH and 0.350 M CH<sub>3</sub>COONa. What is the pH of this buffer solution? ( $K_a$  of acetic acid =  $1.8 \times 10^{-5}$  M.)

The pH of a buffer solution is given by the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\left(\frac{\text{base}}{\text{acid}}\right)$$

As  $\text{p}K_a = -\log_{10}K_a = -\log_{10}(1.8 \times 10^{-5}) = 4.74$ . With  $[\text{base}] = [\text{CH}_3\text{COONa}] = 0.350 \text{ M}$  and  $[\text{acid}] = [\text{CH}_3\text{COOH}] = 0.250 \text{ M}$ ,

ANSWER CONTINUES ON THE NEXT PAGE

$$\text{pH} = 4.74 + \log\left(\frac{0.350}{0.250}\right) = 4.89$$

As the buffer contains a higher concentration of base than acid, the  $\text{pH} > \text{p}K_{\text{a}}$ .

Answer: **4.89**

Calculate the pH of the solution formed when  $6.3 \times 10^{-2}$  mol of NaOH is added to 1.0 L of the buffer solution.

In a 1.0 L solution of the buffer, there is 0.250 mol of  $\text{CH}_3\text{COOH}$  and 0.350 mol of  $\text{CH}_3\text{COO}^-$ .

The  $\text{OH}^-$  will react with the  $\text{CH}_3\text{COOH}$  to produce  $\text{CH}_3\text{COO}^-$ . The concentration of the former will therefore decrease whilst the concentration of the latter will increase. After the  $\text{OH}^-$  is added:

$$\text{number of moles of } \text{CH}_3\text{COOH} = (0.250 - 6.3 \times 10^{-2}) \text{ M} = 0.187 \text{ mol}$$

$$\text{number of moles of } \text{CH}_3\text{COO}^- = (0.350 + 6.3 \times 10^{-2}) \text{ M} = 0.413 \text{ mol}$$

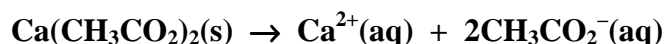
As the volume of solution does not change, these are also the new acid and base concentrations. Hence, the buffer now has:

$$\text{pH} = 4.74 + \log\left(\frac{0.413}{0.187}\right) = 5.09$$

As base has been added, there is an increase in the pH. As it is being added to a buffer system, this change is small. Addition of this quantity of base to water would increase the pH by 1.20 units.

Answer: **5.09**

- Write the balanced chemical equation for the dissolution of solid  $\text{Ca}(\text{CH}_3\text{CO}_2)_2$  in water.



What is the pH of a solution that has 158.2 g of  $\text{Ca}(\text{CH}_3\text{CO}_2)_2$  dissolved in 1.000 L of water? The  $\text{p}K_{\text{a}}$  of acetic acid,  $\text{CH}_3\text{COOH}$ , is 4.76.

The molar mass of  $\text{Ca}(\text{CH}_3\text{CO}_2)_2$  is:

$$\begin{aligned}\text{molar mass} &= (40.08 (\text{Ca}) + 4 \times 12.01 (\text{C}) + 6 \times 1.008 (\text{H}) + 4 \times 16.00 (\text{O})) \text{ g mol}^{-1} \\ &= 158.168 \text{ g mol}^{-1}\end{aligned}$$

Thus, 158.2 g corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{158.2 \text{ g}}{158.168 \text{ g mol}^{-1}} = 1.000 \text{ mol}$$

When  $\text{Ca}(\text{CH}_3\text{CO}_2)_2$  is dissolved, it produces  $\text{Ca}^{2+}(\text{aq}) + 2\text{CH}_3\text{CO}_2^{-}$ . Hence, if 1.000 mol of  $\text{Ca}(\text{CH}_3\text{CO}_2)_2$  is dissolved in 1.0 L,  $[\text{CH}_3\text{CO}_2^{-}]_{\text{initial}} = 2.000 \text{ M}$ .

As  $\text{CH}_3\text{CO}_2^{-}$  is a weak base,  $[\text{CH}_3\text{CO}_2^{-}]$  must be calculated by considering the equilibrium:

	$\text{CH}_3\text{CO}_2^{-}$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{CH}_3\text{CO}_2\text{H}$	$\text{OH}^{-}$
initial	2.000	large		0	0
change	-x	negligible		+x	+x
final	$2.000 - x$	large		x	x

The equilibrium constant  $K_{\text{b}}$  is given by:

$$K_{\text{b}} = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^{-}]}{[\text{CH}_3\text{CO}_2^{-}]} = \frac{x^2}{(2.000 - x)}$$

For an acid and its conjugate base:

$$\text{p}K_{\text{a}} + \text{p}K_{\text{b}} = 14.00 \text{ so } \text{p}K_{\text{b}} = 14.00 - 4.76 = 9.24$$

As  $\text{p}K_{\text{b}} = 9.24$ ,  $K_{\text{b}} = 10^{-9.24}$ .  $K_{\text{b}}$  is very small so  $2.000 - x \sim 2.000$  and hence:

$$x^2 = 2.000 \times 10^{-9.24} \text{ or } y = 0.0000393 \text{ M} = [\text{OH}^{-}]$$

Hence, the pOH is given by:

$$\text{pOH} = -\log_{10}[\text{OH}^{-}] = \log_{10}[0.0000393] = 4.47$$

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

$$\text{pH} = 14.000 - 4.47 = 9.53$$

$$\text{pH} = 9.53$$

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Calculate the pH of this solution after the addition of 0.250 mol of HCl gas?

The solution contain 2.000 mol of  $\text{CH}_3\text{CO}_2^-$ . This will react with 0.250 mol of  $\text{HCl(g)}$  to produce 0.250 mol of  $\text{CH}_3\text{CO}_2\text{H}$ , leaving  $(2.000 - 0.250) \text{ mol} = 1.750 \text{ mol}$  of  $\text{CH}_3\text{CO}_2^-$  in unreacted.

As the solution has a volume of 1.000 L,  $[\text{CH}_3\text{CO}_2\text{H}] = 0.250 \text{ M}$  and  $[\text{CH}_3\text{CO}_2^-] = 1.750 \text{ M}$ .

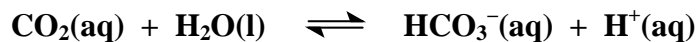
The solution contains a weak acid and its conjugate base. The pH of this buffer solution can be calculated using the Henderson-Hasselbalch equation;

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{base}]}{[\text{acid}]} = 4.76 + \log \frac{1.750}{0.250} = 5.61$$

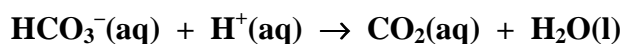
$$\text{pH} = 5.61$$

- Both  $\text{HCO}_3^-(\text{aq})$  and  $\text{CO}_2(\text{aq})$  are present in human blood. How does their presence ensure that the pH of blood is maintained at  $\sim 7.2$ , even if  $\text{H}^+(\text{aq})$  or  $\text{OH}^-(\text{aq})$  are produced by processes in the body?

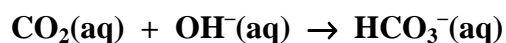
**$\text{CO}_2(\text{aq})$  and  $\text{HCO}_3^-(\text{aq})$  constitute a buffer system:**



**Excess  $\text{H}^+$  is removed by:**



**Excess  $\text{OH}^-$  is removed by:**

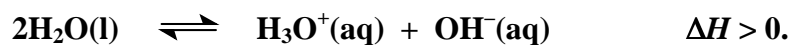


How does hyperventilation (very rapid breathing) interfere with this balance? What is the effect?

**Hyperventilation removes  $\text{CO}_2$  from the blood. This shifts the above buffer equilibrium to the left (Le Chatelier's principle),  $[\text{H}^+(\text{aq})]$  decreases and the blood pH increases.**

- The pH value of pure water at 25 °C is 7.00. How, if at all, does that value change when the temperature is changed to 37 °C (a person's body temperature)? Explain.

**The auto-ionisation of water is an endothermic reaction**



**Increasing the temperature will push this reaction to the right (Le Chatelier's principle), so the  $[\text{H}_3\text{O}^+(\text{aq})]$  will increase and the pH will therefore *decrease*.**

Is pure water at 37 °C acidic, basic or neutral? Circle your choice.

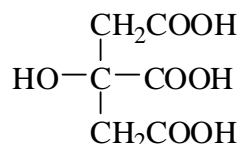
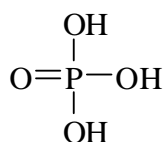
acidic

basic

neutral

**(Pure water is neutral as  $[\text{H}_3\text{O}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$ . This is the criterion for a neutral solution NOT pH = 7.)**

- Consider the two triprotic acids, phosphoric acid and citric acid.



Acid	Formula	$K_{a1}$	$K_{a2}$	$K_{a3}$
phosphoric	$\text{H}_3\text{PO}_4$	$7.1 \times 10^{-3}$	$6.3 \times 10^{-8}$	$4.5 \times 10^{-13}$
citric	$\text{C}_6\text{H}_8\text{O}_7$	$7.1 \times 10^{-4}$	$1.7 \times 10^{-5}$	$6.4 \times 10^{-6}$

Explain why  $K_{a1} > K_{a2} > K_{a3}$  for both acids.

**It is more difficult to remove a proton from a negatively charged species, so  $K_{a1} > K_{a2} > K_{a3}$  for all acids. *i.e.*  $K_{a1}$ ,  $K_{a2}$  and  $K_{a3}$  correspond to removal of  $\text{H}^+$  from  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  respectively. This process gets harder and harder because a positively charged proton is having to be removed from a negatively charged molecule.**

For phosphoric acid, the  $K_a$  values differ by about 5 orders of magnitude while for citric acid there is a much smaller difference. Explain.

**The number of resonance structures for the various conjugate bases are:**

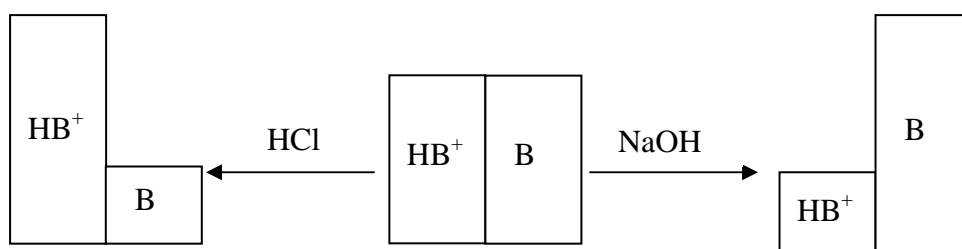
**2 for  $\text{H}_2\text{PO}_4^-$ ; 3 for  $\text{HPO}_4^{2-}$ ; and 4 for  $\text{PO}_4^{3-}$   
2 for  $\text{C}_6\text{H}_7\text{O}_7^-$ ; 4 for  $\text{C}_6\text{H}_6\text{O}_7^{2-}$ ; and 8 for  $\text{C}_6\text{H}_5\text{O}_7^{3-}$**

**The conjugate bases for citric acid are more stable (because they have greater resonance stabilisation) so the corresponding acids are all stronger.**

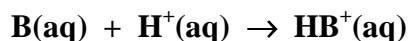
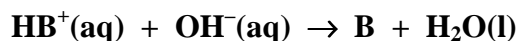
**Alternatively, the increasing negative charges in the conjugate bases are being formed in different parts of the molecule in the case of citric acid, whereas they are all very close to each other in phosphoric acid. Again, the formation of the conjugate base series of citric acid is therefore easier and the acids are therefore stronger.**

**Marks**  
**7**

- A buffer system with a weak base B and its conjugate acid  $\text{HB}^+$  is shown in the diagram below with equal concentrations. Complete the diagram by showing the relative concentrations after the addition of some HCl or NaOH.



Write down the balanced net ionic equations for both these reactions.



Calculate the pH of a buffer if it contains 0.200 mol of  $\text{NaNO}_2$  and 0.300 mol of  $\text{HNO}_2$  in 1.00 L of water. The  $\text{p}K_a$  of  $\text{HNO}_2$  is 3.15.

The concentrations of acid ( $\text{HNO}_2$ ) and base ( $\text{NO}_2^-$ ) are:

$$\begin{aligned} \text{concentration of acid} &= \text{number of moles} / \text{volume} \\ &= (0.300 \text{ mol} / 1.00 \text{ L}) = 0.300 \text{ mol L}^{-1} \end{aligned}$$

$$\text{concentration of base} = (0.200 \text{ mol} / 1.00 \text{ L}) = 0.200 \text{ mol L}^{-1}$$

The pH of this buffer can then be calculated using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 3.15 + \log \frac{0.200}{0.300} = 2.97$$

$$\text{pH} = 2.97$$

What is the pH if (a) 0.05 mol of  $\text{HCl}(\text{g})$  and (b) 0.25 mol of  $\text{HCl}(\text{g})$  is added?

**HCl will react with the  $\text{NO}_2^-$  to form  $\text{HNO}_2$ .**

**(a) 0.05 mol of  $\text{HCl}(\text{g})$  will react with 0.05 mol of the  $\text{NO}_2^-$  present to form an additional 0.05 mol of  $\text{HNO}_2$ . The amount of  $\text{NO}_2^-$  will decrease by 0.05 mol:**

$$\text{concentration of acid} = (0.35 \text{ mol} / 1.00 \text{ L}) = 0.35 \text{ mol L}^{-1}$$

$$\text{concentration of base} = (0.15 \text{ mol} / 1.00 \text{ L}) = 0.15 \text{ mol L}^{-1}$$

ANSWER CONTINUES ON THE NEXT PAGE

**Hence:**

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{base}]}{[\text{acid}]} = 3.15 + \log \frac{0.15}{0.35} = 2.78$$

**(b) 0.25 mol of HCl(g) will react *all* of the NO<sub>2</sub><sup>-</sup>. As there is only 0.200 mol of NO<sub>2</sub><sup>-</sup> present, 0.05 mol of HCl will remain unreacted. As HCl is a strong acid, this will completely ionize to give [H<sup>+</sup>(aq)] = 0.05 mol L<sup>-1</sup>. Hence:**

$$\text{pH} = -\log_{10}[\text{H}^{+}(\text{aq})] = -\log_{10}(0.05) = 1.30$$

(a) pH = **2.78**

(b) pH = **1.30**

**Marks  
5**

- The concentration of a dissolved gas is related to its partial pressure by  $c = kp$ . What is the concentration of  $\text{CO}_2$  dissolved in blood if the partial pressure of  $\text{CO}_2$  in the lungs is 0.053 atm? The  $k$  for  $\text{CO}_2$  is  $0.034 \text{ mol L}^{-1} \text{ atm}^{-1}$ .

Using  $c = kp$ ,

$$c = (0.034 \text{ mol L}^{-1} \text{ atm}^{-1})(0.053 \text{ atm}) = 0.0018 \text{ mol L}^{-1}$$

Answer: **0.0018 mol L<sup>-1</sup>**

Calculate the pH of blood if all of this  $\text{CO}_2$  reacted to give  $\text{H}_2\text{CO}_3$ .  
The  $K_a$  of  $\text{H}_2\text{CO}_3$  is  $4.5 \times 10^{-7}$ .

If  $[\text{H}_2\text{CO}_3(\text{aq})] = 0.0018 \text{ mol L}^{-1}$ , the pH can be calculated using the reaction table:

	$\text{H}_2\text{CO}_3$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	$\text{HCO}_3^-$
<b>initial</b>	<b>0.0018</b>	<b>large</b>		<b>0</b>	<b>0</b>
<b>change</b>	<b>-x</b>	<b>negligible</b>		<b>+x</b>	<b>+x</b>
<b>final</b>	<b>0.0018 - x</b>	<b>large</b>		<b>x</b>	<b>x</b>

The equilibrium constant  $K_a$  is given by:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{0.0018 - x}$$

As  $K_a = 4.5 \times 10^{-7}$  and is very small,  $0.0018 - x \sim 0.0018$  and hence:

$$x^2 = 0.0018 \times (4.5 \times 10^{-7}) \quad \text{or} \quad x = 2.8 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$$

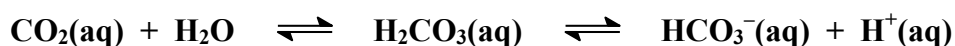
Hence:

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+(\text{aq})] = -\log_{10}(2.8 \times 10^{-5}) = 4.54$$

Answer: **4.54**

Hyperventilation results in a decrease in the partial pressure of  $\text{CO}_2$  in the lungs. What effect will this have on the pH of the blood? Use a chemical equation to illustrate your answer.

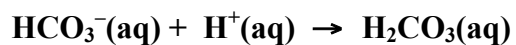
If the  $\text{CO}_2$  partial pressure decreases, the equilibrium below will shift to the left. This will decrease  $[\text{H}^+(\text{aq})]$  and the pH will increase.



ANSWER CONTINUES ON THE NEXT PAGE

The pH of blood is maintained around 7.4 by the  $\text{H}_2\text{CO}_3 / \text{HCO}_3^-$  buffer system. Explain how a buffer works, illustrating your answer with chemical equations.

**A buffer resists changes in pH. It contains substantial quantities of a weak acid and its conjugate base. In the  $\text{H}_2\text{CO}_3/\text{HCO}_3^-$  buffer, added acid is removed by the reaction:**



**Added base is removed by the reaction:**

