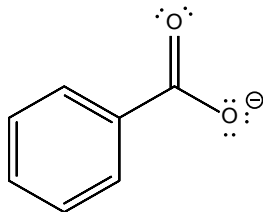


Answers to Practice Test Questions 12

Organic Acids and Bases

1.

(a)



(b) $pK_a = -\log(K_a)$

$$K_a = 10^{-pK_a}$$

$$K_a = 10^{-4.20}$$

$$K_a = 6.3 \times 10^{-5}$$

(c) Benzoic acid is a weak acid.

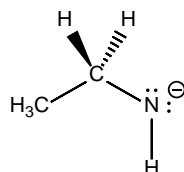
We know this because the pK_a of benzoic acid is larger than 0.

Since it is a weak acid, benzoic acid will not fully dissociate in water.

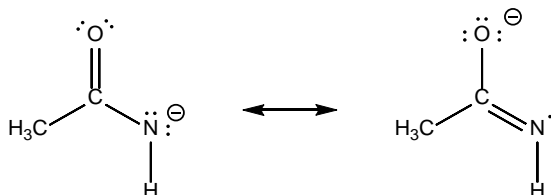
2. The pK_a value describes the acidity of a species. Stronger acids have lower (or more negative) pK_a values than weaker acids. Since the pK_a value for ethanamide is 20 lower than the pK_a value for ethanamine, ethanamide is 10^{20} times more acidic than ethanamine.

Since the strength of an acid depends on the stability of its conjugate base, compare the conjugate bases of both species.

The conjugate base of ethanamine is:



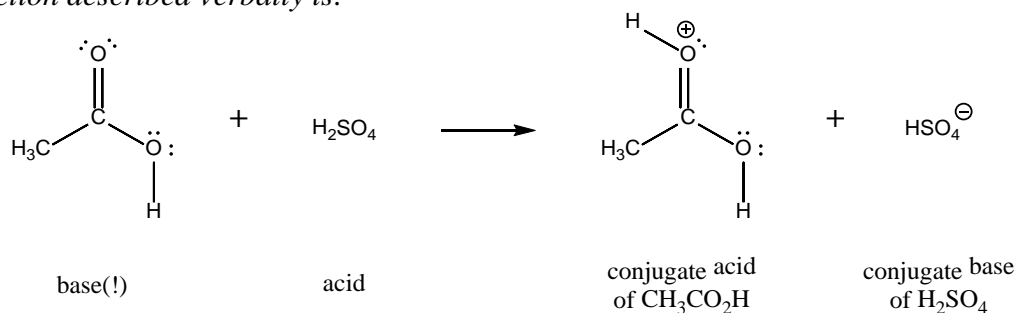
The conjugate base of ethanamide is:



As shown by these two resonance structures, the negative charge in the conjugate base of ethanamide is delocalized over (*shared by*) two atoms – the oxygen and the nitrogen. Delocalization of charge over multiple atoms provides stability compared to concentrating the whole charge on one atom (which is what happens in the conjugate base of ethanamine).

Furthermore, oxygen is more electronegative than nitrogen so there is slightly more negative charge on oxygen than there is on nitrogen. Shifting charge onto more electronegative atoms is also favourable.

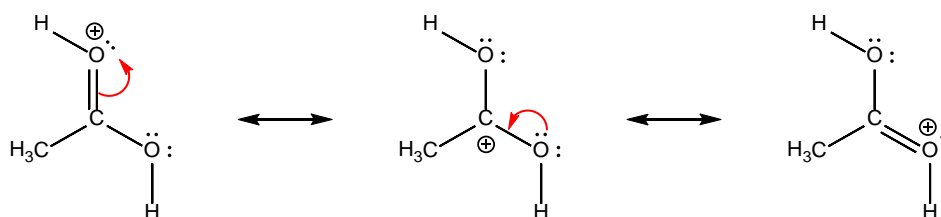
3. The reaction described verbally is:



(a) The acids (i.e. proton donors) in this reaction are H_2SO_4 and the protonated carboxylic acid (example shown is $\text{CH}_3\text{CO}_2\text{H}_2^+$).

Because we are told that this reaction is product-favoured, the acid on the reactant side must be stronger. So, H_2SO_4 is a stronger acid than the protonated carboxylic acid.

(b)



These three resonance structures show that the positive charge of this acid is delocalized over (shared by) three atoms – two oxygen atoms and one carbon atom.

4.

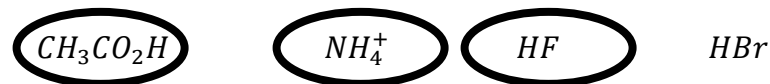
(a)



H_2N^- and H_3C^- are stronger bases than HO^- (the conjugate base of water), so they cannot exist in aqueous solution. Instead, they react with water to give HO^- and either NH_3 or CH_4 (their *very weak* conjugate acids).

H_2S is a stronger acid than H_2O so its conjugate base (HS^-) is a weaker base than HO^- . As such, HS^- can exist in water. The same logic explains why CH_3CO_2^- can exist in water.

(b)



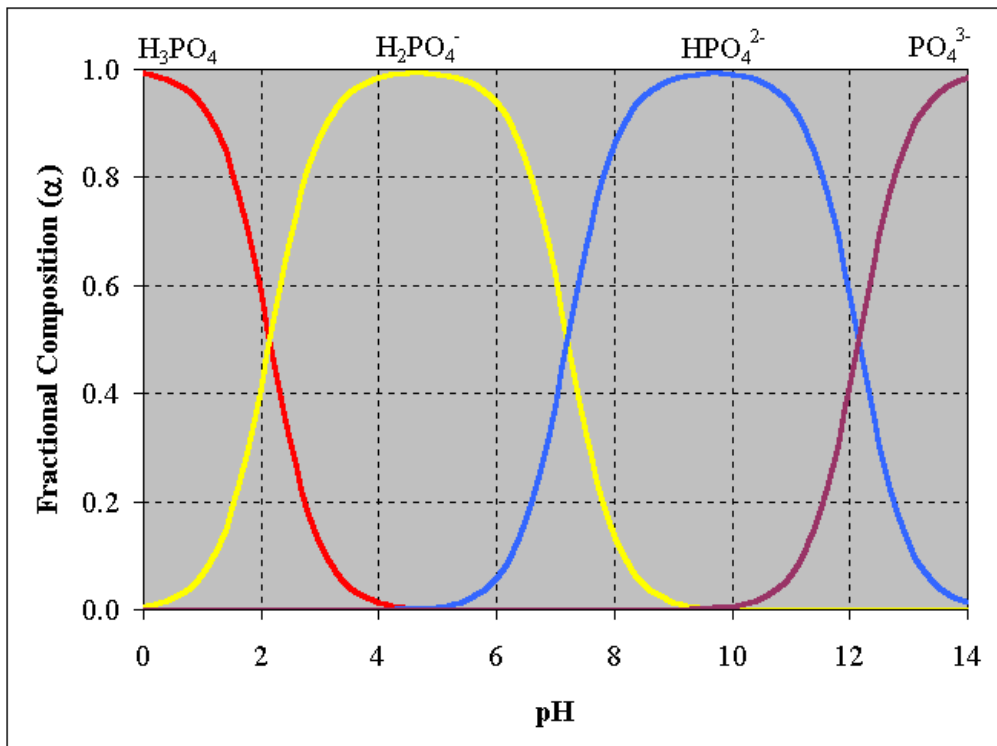
HBr is a stronger acid than H_3O^+ (the conjugate acid of water), so it cannot exist in aqueous solution. Instead, it reacts with water to give a solvated proton ($\text{H}_{(\text{aq})}^+$ or $\text{H}_3\text{O}_{(\text{aq})}^+$) and $\text{Br}_{(\text{aq})}^-$.

HF is a weaker acid than H_3O^+ (due to the high charge density of F^-) so it only partially dissociates (reacts with water) and therefore can exist in water.

5. The strength of an acid is determined based on the stability of its conjugate base. Acids with weaker conjugate bases (i.e. more stable conjugate bases) give up H^+ more easily so they are stronger acids.

The conjugate base of HF is F^- which is a much smaller ion than Cl^- , Br^- or I^- . As such, the negative charge is spread over a smaller surface area so F^- has a higher charge density than the other halide anions. This makes F^- less stable than the other halide anions and therefore makes HF a weaker acid than the other hydrogen halides.

6.

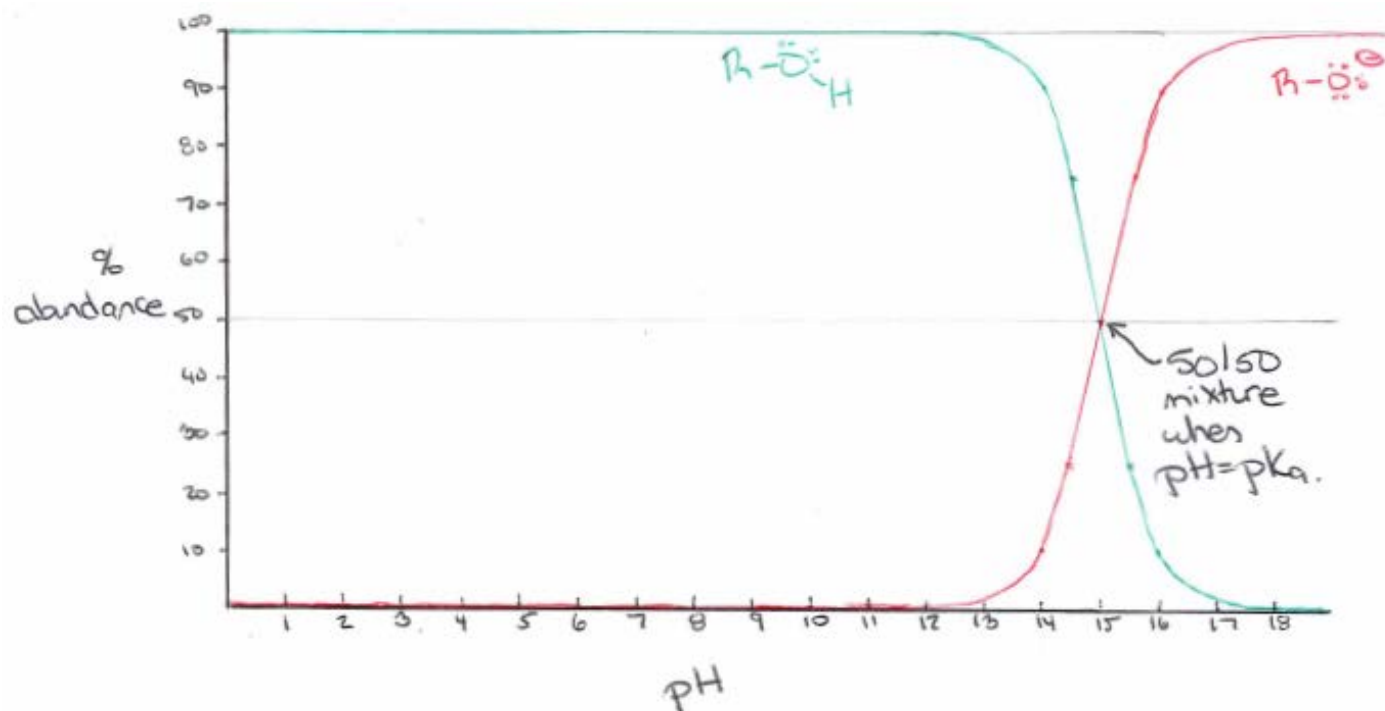


Note that the curves cross at the pK_a values. The pK_a of an acid is equal to the pH at which it exists in a 1 : 1 ratio (or 50/50 mixture) with its conjugate base.

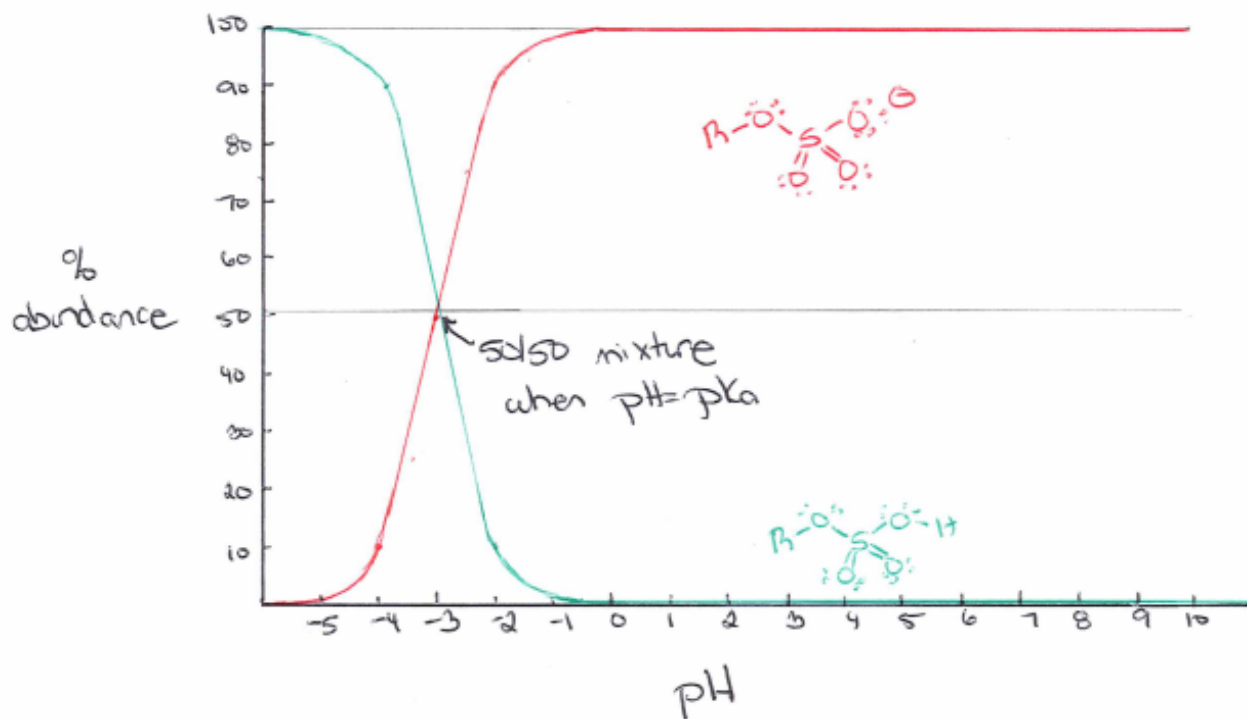
At one pH unit below the pK_a value, there is 10 times as much acid as conjugate base and, at one pH unit above the pK_a value, there is 10 times as much conjugate base as acid.

7. Consider the dominant form of each species (alcohol and sulfate ester) at pH ~7. This is best illustrated by looking at distribution curves. In both cases, one species dominates at pH ~7.

Distribution curve for an alcohol with $pK_a = 15$



Distribution curve for a sulfate ester with $pK_a = -3$



The pK_a of the alcohol is significantly higher than 7, so it exists almost entirely in protonated form at pH ~7. As such, it exists as a neutral species at physiological pH.

The pK_a of the sulfate ester is significantly lower than 7, so it exists almost entirely in deprotonated form at pH ~7. As such, it exists as a charged species at physiological pH.

Charged species tend to be more soluble in water than neutral species because the strongest intermolecular forces are ion-dipole attractions. These tend to be stronger than dipole-dipole attractions (the strongest possible intermolecular forces between neutral species such as an alcohol and water) and increase the solubility of the drug in polar solvents like water.

This trick is primarily used for drugs with large nonpolar regions. Dipole-dipole attractions would tend to be significant enough to dissolve a small alcohol in water.

8.		\rightleftharpoons		+	
	$HA_{(aq)}$		$H^+_{(aq)}$		$A^-_{(aq)}$
I (M)	0.25		10^{-7}		0
C (M)	$-x$		$+x$		$+x$
E (M)	$0.25 - x \approx 0.25$		$10^{-7} + x \approx x$		x

Step 1: Write a balanced chemical equation for the reaction

see above

Step 2: Organize all known information

see above

ICE tables are useful tools to solve equilibrium problems; they can be constructed using any property that is directly proportional to moles for all species – in this case, concentration at constant volume

In pure water at 25°C, the concentration of H^+ is $10^{-7} M$. Since the concentration of ascorbic acid is significantly higher than $10^{-7} M$, it is reasonable to assume that this initial small amount of H^+ will be substantially smaller than the amount of H^+ generated by dissociation of the acid. Check this assumption at the end of the calculation!

The initial concentration of HA is relatively high and it is a weak acid. It is therefore reasonable to assume that the majority of HA will remain in protonated form (in other words, that x will be substantially smaller than 0.25). Check this assumption at the end of the calculation!

Step 3: Write equilibrium constant expression

$$K_a = \frac{(a_{H^+})(a_{A^-})}{a_{HA}}$$

Step 4: Calculate K_a from pK_a

$$pK_a = -\log K_a$$

$$K_a = 10^{-pK_a}$$

$$K_a = 10^{-4.17}$$

$$K_a = 6.8 \times 10^{-5}$$

Step 5: Calculate x

$$K_a = \frac{(a_{H^+})(a_{A^-})}{a_{HA}}$$

$$6.8 \times 10^{-5} = \frac{(x)(x)}{0.25}$$

$$(6.8 \times 10^{-5})(0.25) = x^2$$

$$x = \sqrt{(6.8 \times 10^{-5})(0.25)}$$

$$x = 0.0041$$

Step 6: Check assumptions. If invalid, repeat calculation without the invalid assumption.

$$\text{Assumption \#1: } 10^{-7} + x \approx x \quad 10^{-7} + 0.0041 = 0.0041 \quad \text{assumption is okay}$$

$$\text{Assumption \#2: } 0.25 - x \approx 0.25 \quad 0.25 - 0.0041 = 0.2459 \approx 0.25 \quad \text{assumption is okay}$$

Step 7: Calculate pH from a_{H^+}

$$a_{H^+} = x = 0.0041$$

$$pH = -\log(a_{H^+})$$

$$pH = -\log(0.0041)$$

$$pH = 2.39$$

Step 8: Check your work

Does your answer seem reasonable?

Ascorbic acid is a weak acid, so expect a pH below 7.

If this had been a strong acid, the pH would have been $-\log(0.25) = 0.6$. Since it is a weak acid, it makes sense that the pH is higher than that.

9.	$B_{(aq)}$	+	$H_2O_{(l)}$	\rightleftharpoons	$BH_{(aq)}^+$	+	$OH_{(aq)}^-$
I (M)	0.047				0		10^{-7}
C (M)	-x				+x		+x
E (M)	$0.047 - x$				x		$10^{-7} + x \approx x$

Step 1: Write a balanced chemical equation for the reaction

see above

Step 2: Organize all known information

see above

ICE tables are useful tools to solve equilibrium problems; they can be constructed using any property that is directly proportional to moles for all species – in this case, concentration at constant volume

In pure water at 25°C, the concentration of OH^- is 10^{-7} M. Since the concentration of piperidine is significantly higher than 10^{-7} M, it is reasonable to assume that this initial small amount of OH^- will be substantially smaller than the amount of OH^- generated by protonation of the base. Check this assumption at the end of the calculation!

You might initially want to assume that x will be significantly smaller than 0.047. If you make that assumption, you will find that x is approximately 0.007, so this assumption fails. At that point, you may either use the method of successive approximations or follow the approach below.

Step 3: Write equilibrium constant expression

$$K_b = \frac{(a_{BH^+})(a_{OH^-})}{a_B}$$

Step 4: Calculate K_b from pK_b

$$pK_b = -\log K_b$$

$$K_b = 10^{-pK_b}$$

$$K_b = 10^{-2.89}$$

$$K_b = 1.3 \times 10^{-3}$$

Step 5: Calculate x

$$K_b = \frac{(a_{BH^+})(a_{OH^-})}{a_B}$$

$$1.3 \times 10^{-3} = \frac{(x)(x)}{0.047-x}$$

$$(1.3 \times 10^{-3})(0.047 - x) = x^2$$

$$x^2 + (1.3 \times 10^{-3})x - (6.0 \times 10^{-5}) = 0$$

$$x = 0.0072$$

Step 6: Check assumptions. If invalid, repeat calculation without the invalid assumption.

$$\text{Assumption \#1: } 10^{-7} + x \approx x \quad 10^{-7} + 0.0072 = 0.0072 \quad \text{assumption is okay}$$

Step 7: Calculate pH from a_{OH^-}

One approach is to calculate pOH from a_{OH^-} then calculate pH from pOH .

Alternatively, calculate a_{H^+} from a_{OH^-} then calculate pH from a_{H^+} .

Either approach gives the same pH .

$$a_{OH^-} = x = 0.0072$$

$$pOH = -\log(a_{OH^-})$$

$$pOH = -\log(0.0072)$$

$$pOH = 2.14$$

$$pH = 14 - pOH = 14 - 2.14 = 11.86$$

or

$$K_w = (a_{H^+})(a_{OH^-})$$

$$a_{H^+} = \frac{K_w}{a_{OH^-}} = \frac{1.00 \times 10^{-14}}{0.0072} = 1.4 \times 10^{-12}$$

$$pH = -\log(a_{H^+})$$

$$pH = -\log(1.4 \times 10^{-12})$$

$$pH = 11.86$$

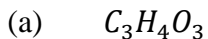
Step 8: Check your work

Does your answer seem reasonable?

Piperidine is a weak base, so expect a pH above 7.

If this had been a strong base, the pH would have been $14 - (-\log(0.047)) = 12.67$. Since it is a weak base, it makes sense that the pH is lower than that.

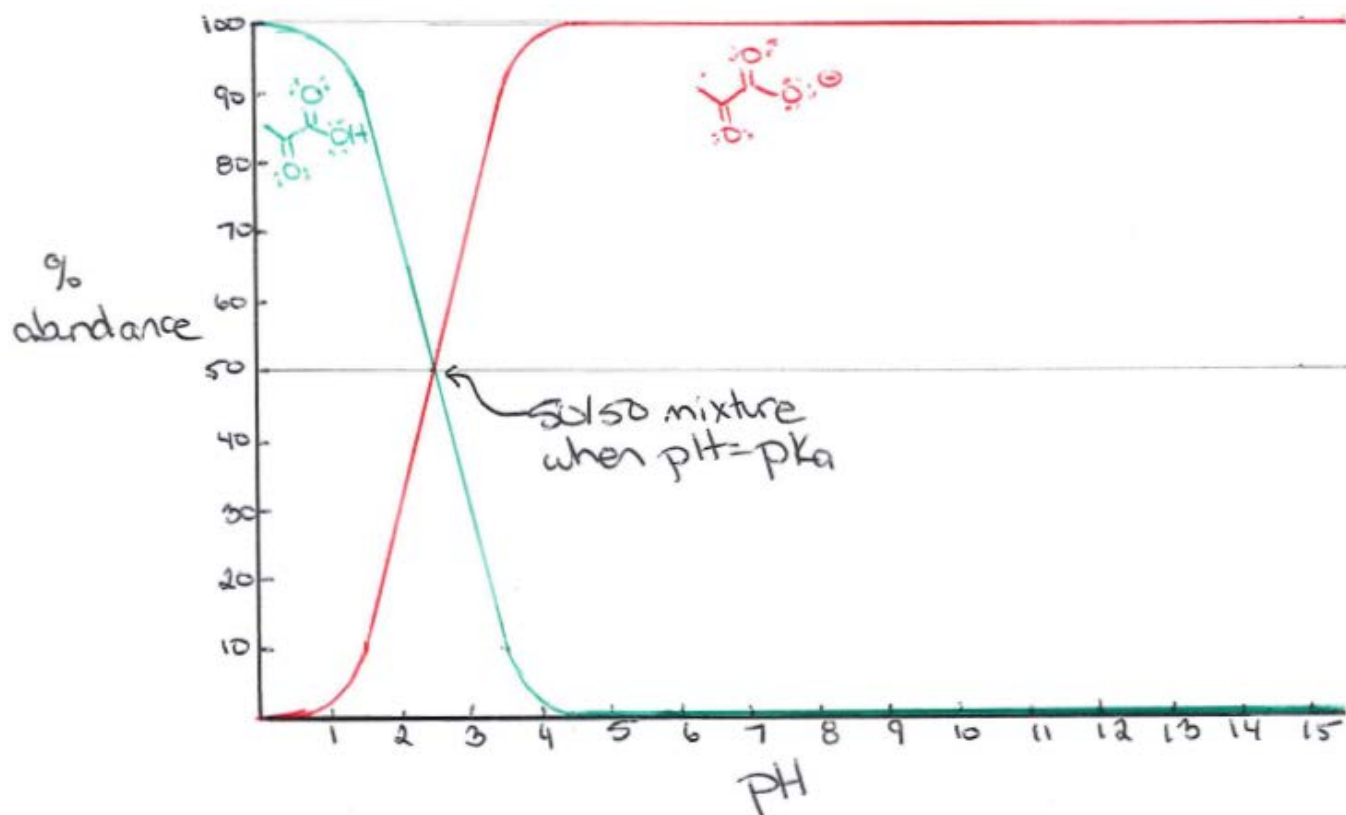
10.



(b) ketone and carboxylic acid

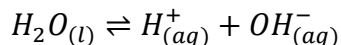
(c) A 10^{-6} M solution of a strong acid would have a pH of approximately 6. A 10^{-6} M solution of a weak acid would therefore have a pH between 6 and 7 (depending on what fraction of the weak acid had been deprotonated).

The distribution curve for pyruvic acid ($pK_a = 2.50$) looks like this:



This distribution curve shows that, at pH 6 (which is 3.5 units higher than the pK_a of pyruvic acid), pyruvic acid exists almost entirely in deprotonated form. In other words, it exists almost entirely as its conjugate base.

(d) Since the pyruvic acid is almost completely dissociated, the equilibrium between water, H^+ and OH^- is what governs pH:



The dissociation of pyruvic acid into H^+ and conjugate base disrupts this equilibrium. As a result, some of the H^+ produced reacts with OH^- already in solution to re-establish equilibrium. In other words, H^+ produced reacts with OH^- until $K_w = 1.00 \times 10^{-14}$ again.

(e) **Step 1: Calculate the amount of H^+ generated when the pyruvic acid dissociates fully**

See parts (c) and (d) for why pyruvic acid dissociates fully when it is at very low concentrations. This is stoichiometry (not an equilibrium ICE table) since the reaction goes to completion.

	$C_3H_4O_3(aq)$	\rightleftharpoons	$H^+_{(aq)}$	+	$C_3H_3O_3^-(aq)$
$M_{initial}$	8.0×10^{-7}		1.0×10^{-7}		0
M_{change}	$- 8.0 \times 10^{-7}$		$+ 8.0 \times 10^{-7}$		$+ 8.0 \times 10^{-7}$
M_{final}	0		9.0×10^{-7}		8.0×10^{-7}

Step 2: Set up ICE table for the $H_2O/H^+/OH^-$ equilibrium after the acid fully dissociates

	$H_2O(l)$	\rightleftharpoons	$H^+_{(aq)}$	+	$OH^-_{(aq)}$
I (M)	n/a		9.0×10^{-7}		1.0×10^{-7}
C (M)	$+ x$		$- x$		$- x$
E (M)	n/a		$9.0 \times 10^{-7} - x$		$1.0 \times 10^{-7} - x$

You could also write $-x$ in the water column and $+x$ in the other two columns. If you do that, you'll get a negative value for x . As long as you factor in that negative sign properly, the calculation will work perfectly well.

It is very important that you use the correct initial concentrations of H^+ and OH^- and that you do NOT approximate them as 0. When the concentration of acid is very small, the initial amounts of H^+ and OH^- become significant.

Step 3: Write equilibrium constant expression

$$K_w = \frac{(a_{H^+})(a_{OH^-})}{a_{H_2O}} = (a_{H^+})(a_{OH^-}) \quad \text{since } a_{H_2O} = 1$$

Step 4: Calculate x

$$K_w = (a_{H^+})(a_{OH^-})$$

$$1.00 \times 10^{-14} = (9.0 \times 10^{-7} - x)(1.0 \times 10^{-7} - x)$$

$$1.00 \times 10^{-14} = (9.0 \times 10^{-14}) - (10.0 \times 10^{-7})x + x^2$$

$$0 = (8.0 \times 10^{-14}) - (1.00 \times 10^{-6})x + x^2$$

or $x^2 - (1.00 \times 10^{-6})x + 8.0 \times 10^{-14} = 0$

Use quadratic equation (or other tools) to solve, giving:

$$x = 8.8 \times 10^{-8}$$

($x = 9.1 \times 10^{-7}$ would give negative concentrations for H^+ and OH^- – which is impossible)

Step 5: Calculate pH from a_{H^+}

$$a_{H^+} = 9.0 \times 10^{-7} - x = 9.0 \times 10^{-7} - 8.8 \times 10^{-8} = 8.1 \times 10^{-7}$$

$$pH = -\log(a_{H^+})$$

$$pH = -\log(8.1 \times 10^{-7})$$

$$pH = 6.09$$

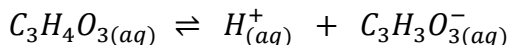
Step 6: Check your work

Does your answer seem reasonable?

Based on the logic explained in part (c), the expected pH was between 6 and 7 – closer to 6 because the acid fully dissociates at this low concentration. 6.09 meets this description perfectly, so it is a reasonable answer.

- (f) This is another “two temperatures; two equilibrium constants” question requiring the use of $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$.

Step 1: Write a balanced chemical equation for the reaction



Step 2: Calculate K_a from pK_a at 25 °C

$$pK_a = -\log K_a$$

$$K_a = 10^{-pK_a}$$

$$K_a = 10^{-2.50}$$

$$K_a = 3.2 \times 10^{-3}$$

Step 3: Match equilibrium constants to the corresponding temperature

$$T_1 = 25 \text{ °C} = 298.15 \text{ K}$$

$$K_1 = 3.2 \times 10^{-3}$$

$$T_2 = 37 \text{ °C} = 310.15 \text{ K}$$

$$K_2 = ???$$

Step 4: Calculate the standard enthalpy change for the reaction (phase change)

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H^\circ = \Delta_f H^\circ(H_{(aq)}^+) + \Delta_f H^\circ(C_3H_3O_{3(aq)}^-) - \Delta_f H^\circ(C_3H_4O_{3(aq)})$$

$$\Delta_r H^\circ = \left(0 \frac{\text{kJ}}{\text{mol}}\right) + \left(-596.22 \frac{\text{kJ}}{\text{mol}}\right) - \left(-607.52 \frac{\text{kJ}}{\text{mol}}\right)$$

$$\Delta_r H^\circ = +11.3 \frac{\text{kJ}}{\text{mol}} = 1.13 \times 10^4 \frac{\text{J}}{\text{mol}}$$

Step 5: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_2}{3.2 \times 10^{-3}}\right) = \left(\frac{1.13 \times 10^4 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}}\right) \left(\frac{1}{298.15 \text{ K}} - \frac{1}{310.15 \text{ K}}\right)$$

$$\ln\left(\frac{K_2}{3.2 \times 10^{-3}}\right) = 0.1764$$

$$\frac{K_2}{3.2 \times 10^{-3}} = e^{0.1764}$$

$$K_2 = (3.2 \times 10^{-3})(e^{0.1764})$$

$$K_2 = 3.8 \times 10^{-3}$$

Step 6: Calculate pK_a from K_a at 37 °C

$$pK_a = -\log K_a$$

$$pK_a = -\log(3.8 \times 10^{-3})$$

$$pK_a = 2.42$$

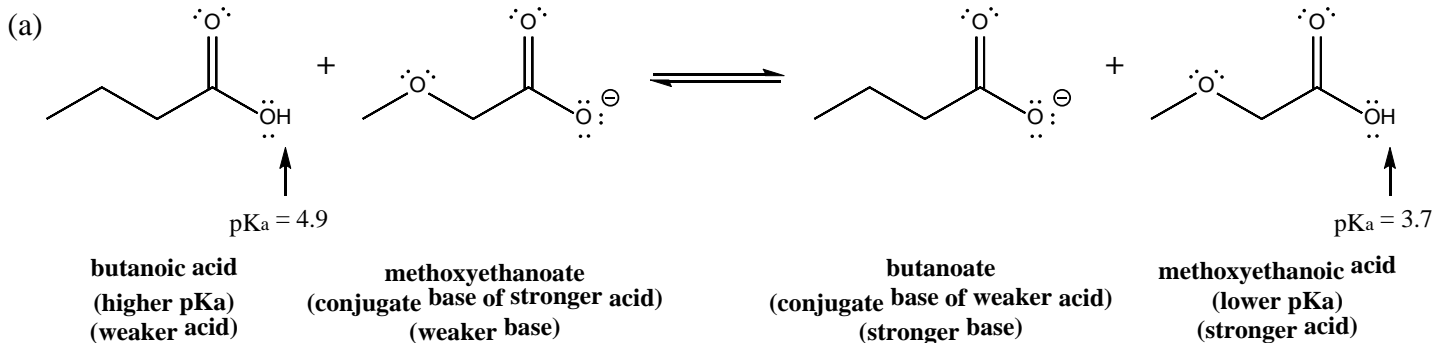
Step 8: Check your work

Does your answer seem reasonable?

The reaction is endothermic so it makes sense that K would be slightly larger at the higher temperature. Since the temperature difference between 25 °C and 37 °C is not larger, it makes sense that the two pK_a values are similar.

- (g) Since the pH is significantly higher than the pK_a of pyruvic acid, we expect most of the acid to have been deprotonated to give the pyruvate ion at at 37 °C and pH 7.

11.



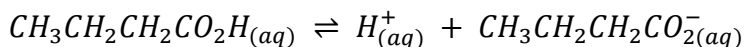
The reaction is reactant-favoured at 25 °C.

The pK_a values tell us the relative strength of the two acids. Methoxyethanoic acid has a lower pK_a value, so it is a stronger acid. By definition, the strength of a conjugate base increases as the strength of its conjugate acid decreases. So, the conjugate base of the weaker acid (butanoic acid) is the stronger base.

If equal amounts of the four species were combined, we would expect the stronger acid and stronger base to react more than the weaker acid and weaker base. As such, the net direction of reaction would be toward the reactants until equilibrium was reached. At equilibrium, there will be higher concentrations of butanoic acid and methoxyethanoate than of butanoate and methoxyethanoic acid.

- (b) *The pK_a for butanoic acid can be used to calculate its K_a value – which is the equilibrium constant for dissociation of the acid into H^+ and its conjugate base. This equilibrium constant can be used to calculate the standard free energy change for that reaction and therefore the standard free energy of formation of the conjugate base.*

Step 1: Write a balanced chemical equation for the reaction



Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25\text{ °C} = 298.15\text{ K}$$

Step 3: Calculate K_a from pK_a

$$pK_a = -\log K_a$$

$$K_a = 10^{-pK_a}$$

$$K_a = 10^{-4.9}$$

$$K_a = 1 \times 10^{-5}$$

Step 4: Calculate the standard free energy change from the equilibrium constant

$$\Delta_r G^\circ = -RT \ln K$$

$$\Delta_r G^\circ = -\left(8.314\ 462 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) (298.15\ \text{K}) \ln(1 \times 10^{-5})$$

$$\Delta_r G^\circ = \left(2.80 \times 10^4 \frac{\text{J}}{\text{mol}}\right) \left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

$$\Delta_r G^\circ = +28.0 \frac{\text{kJ}}{\text{mol}}$$

Step 5: Calculate the standard free energy of formation for $CH_3CH_2CH_2CO_2^-(aq)$

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = [\Delta_f G^\circ(H_{(aq)}^+) + \Delta_f G^\circ(CH_3CH_2CH_2CO_2^-(aq))] - \Delta_f G^\circ(CH_3CH_2CH_2CO_2H_{(aq)})$$

$$\Delta_f G^\circ(CH_3CH_2CH_2CO_2^-(aq)) = \Delta_r G^\circ - \Delta_f G^\circ(H_{(aq)}^+) + \Delta_f G^\circ(CH_3CH_2CH_2CO_2H_{(aq)})$$

$$\Delta_f G^\circ(CH_3CH_2CH_2CO_2^-(aq)) = \left(+28.0 \frac{kJ}{mol}\right) - \left(0 \frac{kJ}{mol}\right) + \left(-399.57 \frac{kJ}{mol}\right)$$

$$\Delta_f G^\circ(CH_3CH_2CH_2CO_2^-(aq)) = -371.6 \frac{kJ}{mol}$$

Step 6: Check your work

Does your answer seem reasonable?

12. When acid is added to NH_3 , NH_4^+ is generated. The pH of the solution is determined by the relative concentrations of these two species and by the K_a value of the conjugate acid (NH_4^+) since $K_a = \frac{(a_{H^+})(a_{conj.base})}{a_{conj.acid}}$.

Taking the logarithm of both sides of this equation, multiplying by -1 and rearranging to isolate pH gives $= pK_a + \log \frac{a_{conj.base}}{a_{conj.acid}}$. This is known as the Henderson-Hasselbalch equation.

This question can be answered using either of the two equations above. In either case, start by using the pK_b of NH_3 to calculate the K_a or pK_a of its conjugate acid, NH_4^+ . Then calculate the desired ratio of NH_3 to NH_4^+ . Finally, use stoichiometry to calculate the amount of HCl necessary to generate that ratio.

Step 1: Calculate K_a or pK_a of NH_4^+

$$K_w = K_a(\text{conjugate acid}) \times K_b(\text{conjugate base}) \quad @ 25^\circ C, K_w = 1 \times 10^{-14}$$

$$K_a(\text{conjugate acid}) = \frac{K_w}{K_b(\text{conjugate base})}$$

$$K_a(NH_4^+) = \frac{K_w}{K_b(NH_3)} \quad K_b(NH_3) = 10^{-pK_b(NH_3)} = 10^{-4.74} = 1.8 \times 10^{-5}$$

$$K_a(NH_4^+) = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$K_a(NH_4^+) = 5.5 \times 10^{-10}$$

and $pK_a(NH_4^+) = -\log[K_a(NH_4^+)] = -\log(5.5 \times 10^{-10}) = 9.26$

At $25^\circ C$, you can use a shortcut that $pK_a(\text{conjugate acid})$ and $pK_b(\text{conjugate base})$ must add up to 14. This does not work at any other temperature. They always add up to pK_w , but pK_w varies with temperature.

Step 2: Calculate desired ratio of NH_4^+ to NH_3 to give pH 9.26

Note that the desired pH is equal to the pK_a of the conjugate acid. We know that $pH = pK_a$ when there is a 1 : 1 ratio of conjugate acid and conjugate base.

So, in this case, we must have equal amounts of NH_3 and NH_4^+ .

If you forgot that (or if you were doing a different question where the pH and pK_a values didn't match) the following approach also works:

$$pH = -\log(a_{H^+})$$

$$a_{H^+} = 10^{-pH} = 10^{-9.26} = 5.5 \times 10^{-10}$$

$$K_a = \frac{(a_{H^+})(a_{conj.base})}{a_{conj.acid}} = \frac{(a_{H^+})(a_{NH_3})}{a_{NH_4^+}}$$

$$\frac{a_{NH_3}}{a_{NH_4^+}} = \frac{K_a}{a_{H^+}}$$

$$\frac{a_{NH_3}}{a_{NH_4^+}} = \frac{5.5 \times 10^{-10}}{5.5 \times 10^{-10}} = 1.0$$

Step 3: Use stoichiometry to calculate the amount of HCl required to convert enough NH_3 into NH_4^+ to give a 1 : 1 ratio

$$\text{Initially, } n_{NH_3} = 0.016 \frac{\text{mol}}{L} \times 0.5000L = 0.0080 \text{ mol}$$

Since all of the NH_4^+ must have been made from NH_3 , that means that the final amounts of NH_4^+ and NH_3 must add up to 0.0080 mol. Combine this with the fact that the two amounts must be equal and you find that you must have 0.0040 mol of each.

	$NH_{3(aq)}$	+	$H^+_{(aq)}$	\rightarrow	$NH_{4(aq)}^+$
n_{initial}	8.0×10^{-3}		4.0×10^{-3}		0
n_{change}	$- 4.0 \times 10^{-3}$		$- 4.0 \times 10^{-3}$		$+ 4.0 \times 10^{-3}$
n_{final}	4.0×10^{-3}		0		4.0×10^{-3}

Step 4: Calculate the volume of 0.025 M HCl required to provide 4.0×10^{-3} mol H^+

$$V_{HCl} = \frac{4.0 \times 10^{-3} \text{ mol}}{0.025 \frac{\text{mol}}{L}} = 0.16 L$$

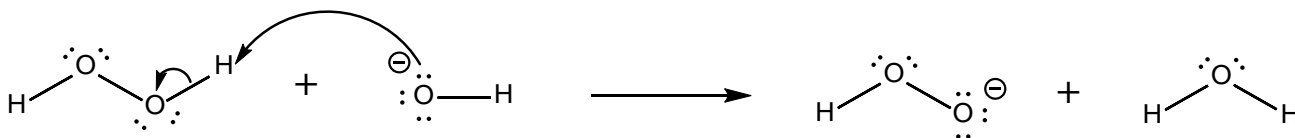
Step 5: Check your work

Does your answer seem reasonable?

The concentrations of HCl and $NH_{3(aq)}$ are similar, so it makes sense that it would take approximately half as much HCl to convert half the NH_3 into NH_4^+ .

13.

(a)



(b)

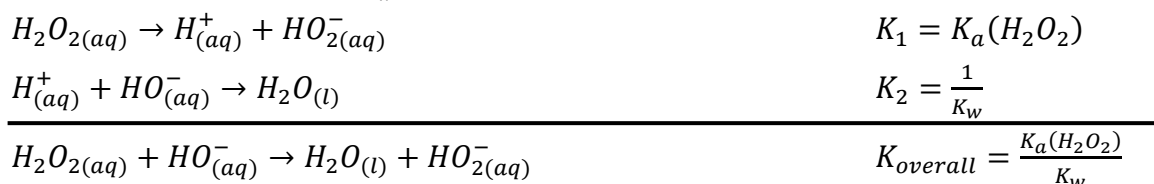
Since the reaction is favoured in the forward direction, H_2O_2 must be a stronger acid than water (and HO^- a stronger base than HO_2^-).

This implies that HO_2^- (the conjugate base of H_2O_2) must be more stable than HO^- (the conjugate base of H_2O). This is likely because of the electronegative oxygen atom bonded to the oxygen bearing the negative charge in HO_2^- . The second oxygen atom will pull electron density away from the O^- , stabilizing it by lessening the charge density on that negative oxygen atom. This is an example of an inductive effect.

- (c) **Step 1: Add the equation for deprotonation of H_2O_2 to the reverse of the equation for dissociation of water into H^+ and OH^-**

Those two equations add up to give the equation in the question. Therefore, the equilibrium constants for those two equations multiply to give the equilibrium constant for the equation in the question.

Recall that, if you reverse the direction in which the reaction is written, the equilibrium constant is inverted. So, if the equilibrium constant for water dissociating is K_w then the equilibrium constant for it reforming is $\frac{1}{K_w}$.



We were given a value for K , and K_w is a constant at 25 °C, so we can solve for $K_a(H_2O_2)$.

$$K_{overall} = K_1 \times K_2 = K_a(H_2O_2) \times \frac{1}{K_w} = \frac{K_a(H_2O_2)}{K_w}$$

$$K_a(H_2O_2) = K_{overall} \cdot K_w = (200)(1 \times 10^{-14}) = 2 \times 10^{-12}$$

Step 2: Use K_a to calculate pK_a

$$pK_a = -\log K_a$$

$$pK_a = -\log(2 \times 10^{-12}) = 11.7$$

Step 3: Check your work

Does your answer seem reasonable?

The pK_a of water is 14. It seems reasonable that the pK_a of H_2O_2 would be similar to the pK_a of water.

- (d) **Step 1: Calculate K_b of conjugate base from K_a of conjugate acid**

$$K_w = K_a(\text{conjugate acid}) \times K_b(\text{conjugate base}) \quad @ 25 \text{ }^\circ\text{C}, K_w = 1 \times 10^{-14}$$

$$K_b(\text{conjugate base}) = \frac{K_w}{K_a(\text{conjugate acid})}$$

$$K_b(HO_2^-) = \frac{K_w}{K_a(H_2O_2)}$$

$$K_b(HO_2^-) = \frac{1 \times 10^{-14}}{2 \times 10^{-12}}$$

$$K_b(HO_2^-) = 5 \times 10^{-3}$$

Step 2: Use K_b to calculate pK_b

$$pK_b = -\log K_b$$

$$pK_b = -\log(5 \times 10^{-3}) = 2.3$$

Step 3: Check your work

Does your answer seem reasonable?

At 25 °C, we expect the pK_a of an acid and the pK_b of its conjugate base to add up to 14.

(This could have been used as an alternative approach to calculating pK_b . Then calculate K_b from pK_b .)

14. *The following answers were accepted. This list may not be exhaustive.*

- The forward reaction is favoured by entropy since more moles of gas are produced than consumed.
- The forward reaction is favoured by enthalpy because a very strong $H - H$ bond is formed. The $H - H$ bond is so strong because H is a very small atom so the internuclear distance is short.
- HO^- is a more stable anion than H^- because O is more electronegative than H and therefore better able to sustain a negative charge.
- HO^- is a more stable anion than H^- because O is larger than H therefore the charge density of O^- is lower than that of H^- .
- H^- is a stronger base than the conjugate base of water (HO^-) so it cannot exist in water. We know this because water is a stronger acid than the conjugate acid of H^- (H_2).