Marks 4

- The ocean contains a variety of forms of CO_3^{2-} and CO_2 with a variety of acid-base and solubility equilibria determining their concentrations. There is concern that increasing levels of CO_2 will lead to increased dissolution of $CaCO_3$ and critically affect the survival of life forms that rely on a carbonaceous skeleton.

  Calculate the concentrations of Ca^{2+} and CO_3^{2-} in a saturated solution of $CaCO_3$. (The K_{sp} of $CaCO_3$ is 3.3×10^{-9}.)

The dissolution of $CaCO_3$ follows the reaction,

$$CaCO_3(s) \rightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$$

If the molar solubility of $CaCO_3$ is S then $[Ca^{2+}(aq)] = [CO_3^{2-}(aq)] = S$.

The solubility product is given by:

$$K_{sp} = [Ca^{2+}(aq)][CO_3^{2-}(aq)] = (S).(S) = S^2$$

As $K_{sp} = 3.3 \times 10^{-9}$,

$$S^2 = 3.3 \times 10^{-9} \text{ or } S = 5.7 \times 10^{-5} \text{ M}$$

$[Ca^{2+}]$ = **5.7×10^{-5} M**	$[CO_3^{2-}]$ = **5.7×10^{-5} M**

Calculate the pH of such a solution. (The pK_a of HCO_3^- is 10.33).

CO_3^{2-} is a weak base and will react with water to produce HCO_3^-:

	CO_3^{2-}	H_2O	$\rightleftharpoons$	OH^-	HCO_3^-
initial	**5.7×10^{-5}**	**large**		**0**	**0**
change	**$-x$**	**negligible**		**$+x$**	**$+x$**
final	**$5.7 \times 10^{-5} - x$**	**large**		**x**	**x**

The equilibrium constant K_b is given by:

$$K_b = \frac{[OH^-(aq)][HCO_3^-(aq)]}{[CO_3^{2-}(aq)]} = \frac{x^2}{5.7\times10^{-5} - x}$$

As pK_a + pK_b = 14.00, pK_b = 14.00 – 10.33 = 3.67. As pK_b = -logK_b, so

$$K_b = 10^{-3.67}.$$

ANSWER CONTINUES ON THE NEXT PAGE

As the concentration of the base is so small, the 'small *x*' approximation cannot be used and it is necessary to solve the quadratic equation. From above,

$$x^2 + 10^{-3.67}x - (5.7 \times 10^{-5} \times 10^{-3.67}) = 0$$

Solving this using the quadratic formula gives $x = 4.67 \times 10^{-5} = [OH^-(aq)]$. Hence,

$$pOH = -\log_{10}[OH^-(aq)] = 4.33$$

Finally, since pH + pOH = 14.00,

$$pH = 14.00 - 4.33 = 9.67$$

pH = **9.67**

THIS QUESTION CONTINUES ON THE NEXT PAGE