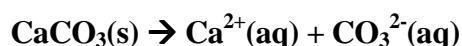


**Marks**  
**4**

- The ocean contains a variety of forms of  $\text{CO}_3^{2-}$  and  $\text{CO}_2$  with a variety of acid-base and solubility equilibria determining their concentrations. There is concern that increasing levels of  $\text{CO}_2$  will lead to increased dissolution of  $\text{CaCO}_3$  and critically affect the survival of life forms that rely on a carbonaceous skeleton.

Calculate the concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  in a saturated solution of  $\text{CaCO}_3$ . (The  $K_{\text{sp}}$  of  $\text{CaCO}_3$  is  $3.3 \times 10^{-9}$ .)

The dissolution of  $\text{CaCO}_3$  follows the reaction,



If the molar solubility of  $\text{CaCO}_3$  is  $S$  then  $[\text{Ca}^{2+}(\text{aq})] = [\text{CO}_3^{2-}(\text{aq})] = S$ .

The solubility product is given by:

$$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})][\text{CO}_3^{2-}(\text{aq})] = (S)(S) = S^2$$

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

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

$$[\text{Ca}^{2+}] = 5.7 \times 10^{-5} \text{ M}$$

$$[\text{CO}_3^{2-}] = 5.7 \times 10^{-5} \text{ M}$$

Calculate the pH of such a solution. (The  $\text{p}K_{\text{a}}$  of  $\text{HCO}_3^-$  is 10.33).

$\text{CO}_3^{2-}$  is a weak base and will react with water to produce  $\text{HCO}_3^-$ :

	$\text{CO}_3^{2-}$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{OH}^-$	$\text{HCO}_3^-$
<b>initial</b>	$5.7 \times 10^{-5}$	large		0	0
<b>change</b>	$-x$	negligible		$+x$	$+x$
<b>final</b>	$5.7 \times 10^{-5} - x$	large		$x$	$x$

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

$$K_{\text{b}} = \frac{[\text{OH}^-(\text{aq})][\text{HCO}_3^-(\text{aq})]}{[\text{CO}_3^{2-}(\text{aq})]} = \frac{x^2}{5.7 \times 10^{-5} - x}$$

As  $\text{p}K_{\text{a}} + \text{p}K_{\text{b}} = 14.00$ ,  $\text{p}K_{\text{b}} = 14.00 - 10.33 = 3.67$ . As  $\text{p}K_{\text{b}} = -\log K_{\text{b}}$ , so

$$K_{\text{b}} = 10^{-3.67}.$$

**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  $x = 4.67 \times 10^{-5} = [\text{OH}^-(\text{aq})]$ . Hence,

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

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

$$\text{pH} = 14.00 - 4.33 = 9.67$$

$$\text{pH} = 9.67$$

**THIS QUESTION CONTINUES ON THE NEXT PAGE**