Swimming pool chemistry

Learning objectives

1. Describe how the water in swimming pools is disinfected.
2. Calculate concentration of various ions present in the water.
3. Interpret data obtained from a mass spectrometer.
4. Determine the structure of organic molecules.

Introduction

Chlorine ($\text{Cl}_2$) is now rarely added directly to pools in the UK because of the hazards associated with its storage and use. Other chlorinating agents are used instead.

In a typical swimming pool, sodium chlorate(I) is added to disinfect the water. The chlorate(I) ion is the conjugate base of the weak acid $\text{HOCl}$. The equilibrium constant $K_a$ for $\text{HOCl} = 2.9 \times 10^{-8}$ mol dm$^{-3}$ at 298 K. Both the chlorate(I) ion and the acid $\text{HOCl}$ are involved in the disinfecting.

Some data were obtained from a swimming pool in Taunton, on a particular day in September. The combined concentration of $\text{HOCl(aq)}$ was measured as 0.50 parts per million (ppm). The $pH$ was 7.3.

Questions

Part one

1. Convert the combined concentration of $\text{HOCl(aq)}$ and $\text{OCl}^-(aq)$ from parts per million into mol dm$^{-3}$.

2. Calculate the concentration of $\text{HOCl(aq)}$.

Sodium hydrogen carbonate and $\text{CO}_2$ gas are also added to buffer the swimming pool water. The $K_a$ value for carbonic acid (the weak acid formed when $\text{CO}_2$ dissolves in water) is $4.2 \times 10^{-7}$ mol dm$^{-3}$. The ‘total alkalinity’ (combined concentration of all the bases present) was measured as $1.08 \times 10^{-3}$ mol dm$^{-3}$.

3. Assuming the only bases detected in the total alkalinity test are $\text{OCl}^-$ and $\text{HCO}^-$, calculate the concentration of carbonic acid in the swimming pool.

4. Explain the effect on the concentration of $\text{HOCl}$ of adding extra $\text{CO}_2$ gas.
Calcium chloride is also added to swimming pool water. Another calcium compound, calcium sulfate, is a slightly soluble component of the grout used in between the tiles inside the swimming pool. The solubility product ($K_{sp}$) of a salt is the equilibrium constant for an ionic substance in saturated solution, such that $K_{sp}$ for a salt $M_aX_b = [M]^a[X]^b$ with the units that depend on $a$ and $b$.

5. Give a general expression for the units of a solubility product of salt $M_aX_b$ in terms of $a$ and $b$.

6. $K_{sp}$ for calcium sulfate has a value of $2.4 \times 10^{-5}$ mol$^2$ dm$^{-6}$ at 298 K. If the concentration of chloride ions from the CaCl$_2$ added is 0.1 mol dm$^{-3}$, what is the concentration of the sulfate ions in the swimming pool?

7. Explain how adding calcium chloride helps to prevent grout dissolving.

8. The enthalpy change of solution for NaCl(s) is $+3.9$ kJ mol$^{-1}$ and for CaSO$_4$(s) it is $-17.8$ kJ mol$^{-1}$. Why is CaSO$_4$ only sparingly soluble and NaCl very soluble?
Part 2

Sometimes organic compounds are added to swimming pool water instead of, or in addition to HOCl and OCl\(^{-}\). One example is trichloroisocyanuric acid. This undergoes hydrolysis to form an equilibrium with HOCl and isocyanuric acid.

\[ \text{(a) trichloroisocyanuric acid} \]
\[ \text{(b) isocyanuric acid} \]

Figure 1: the structure of (a) trichloroisocyanuric acid and (b) isocyanuric acid

9. Some data from the mass spectra of trichloroisocyanuric acid are shown below. The isotopes chlorine-35 and chlorine-37 occur in the ratio 3 : 1. (a) Identify the species detected at the peaks listed in the table. Note that molecules often fragment inside mass spectrometers and there can be rearrangement of the atoms in the fragments.

<table>
<thead>
<tr>
<th>Mass/charge ratio</th>
<th>Relative height of peak as a percentage of the most abundant peak</th>
<th>Species giving rise to the peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>17.9</td>
<td>NCO(^{+})</td>
</tr>
<tr>
<td>70</td>
<td>100.0</td>
<td>and</td>
</tr>
<tr>
<td>72</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>81.4</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>26.4</td>
<td></td>
</tr>
<tr>
<td>154</td>
<td>18.4</td>
<td></td>
</tr>
<tr>
<td>156</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td>158</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>231</td>
<td>24.6</td>
<td></td>
</tr>
<tr>
<td>233</td>
<td>23.4</td>
<td></td>
</tr>
<tr>
<td>235</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>237</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>
(b) Account for the relative heights of the peaks at mass/charge (m/c):
   i. 154, 156 and 158
   ii. 231, 233, 235 and 237.

(c) Use the relative heights of the peaks at m/c 231, 233, 235 and 237 to
calculate the relative molecular mass of trichloroisocyanuric acid to two
decimal places.
(d) It seems likely that the peak at m/c 70 is due to two species. A high resolution
mass spectrometer would resolve the single peak at m/c into two separate
peaks. Calculate what their relative heights would be.

10. How many peaks would you expect to see in the proton NMR spectra of
isocyanuric acid?

11. Discuss whether you think that isocyanuric acid will have delocalised \( \pi \) system
like benzene.

12. Write a balanced equation for the reaction of trichloroisocyanuric acid and
water.

13. Discuss the oxidation state of the chlorine in trichloroisocyanuric acid.
Electronegativity values are given below.

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.1</td>
<td>1.0</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.9</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>1.5</td>
<td>1.8</td>
<td>2.1</td>
<td>2.5</td>
<td>3.0</td>
<td></td>
</tr>
</tbody>
</table>

Pauling electronegativity values for some elements

Most ketones and aldehydes exist in solution as two tautomeric forms that are in
dynamic equilibrium. The two tautomers (the ‘keto’ and ‘enol’ forms) interchange
rapidly in the presence of H\(^+\) ions. An example of these forms for propanone is
shown below:

![Figure 2: the structures of (a) the keto and (b) the enol – tautomers of propanone](image)

14. Suggest a mechanism for the conversion of the keto to the enol tautomer of
propanone.

15. Suggest a structure for cyanuric acid, the tautomeric form of isocyanuric acid.