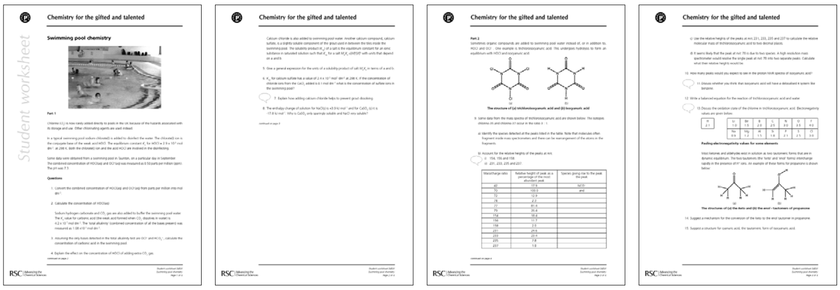
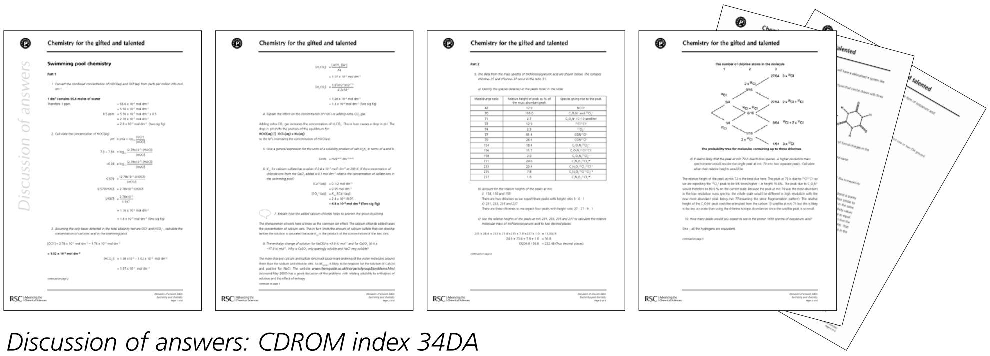
Swimming pool chemistry



Student worksheet: CDROM index 34SW



Discussion of answers: CDROM index 34DA

Topics

Part 1 Equilibria (K_c, K_{sp}, K_a, buffers, Le Chatelier's principle) and entropy (solvent effects).

Part 2 Mass spectra (quite involved spectra to interpret), oxidation numbers, curly arrow mechanisms, nuclear magnetic resonance (NMR) spectroscopy, delocalisation, tautomerism and relative molecular mass calculations.

Level

Post-16 students who are close to the end of their chemistry course.

Prior knowledge

K_c, pH, Le Chatelier's principle, buffers, spectra, NMR and curly arrows.

Rationale

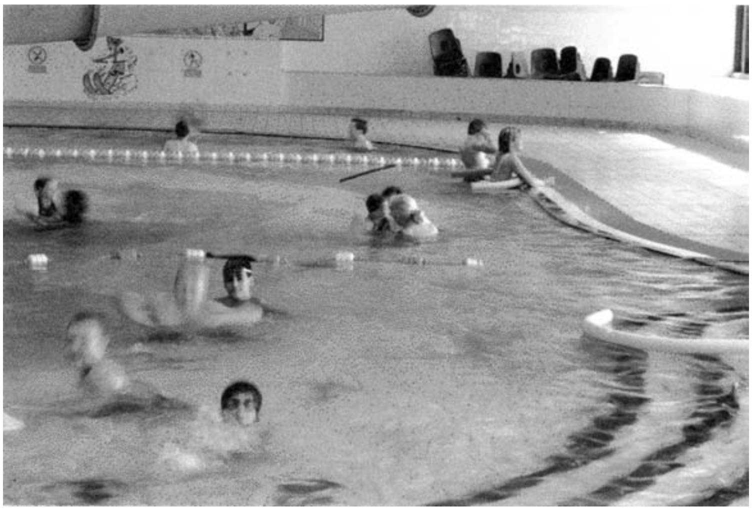
This activity is synoptic in nature, with questions on many different aspects of chemistry. It is context driven *ie* looks at a collection of interesting chemistry that can be derived from swimming pools. Some extension work is introduced – *eg* keto-enol tautomerism.

Use

The activity comes in two parts and these can be given separately to the students. Part 1 can be used at the end of teaching equilibrium or at the end of a course. Part 2 should be attempted at the end of a course.

This symbol means those questions are best tackled as a discussion if a group of students is doing this activity. A written response is not normally required.

Swimming pool chemistry



Part 1

Chlorine (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 HOCl. The equilibrium constant K_a for HOCl = 2.9 x 10^{-8} mol dm^{-3} at 298 K. Both the chlorate(I) ion and the acid 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 HOCl(aq) and OCl^-(aq) was measured as 0.50 parts per million (ppm). The pH was 7.3.

Questions

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

2. Calculate the concentration of HOCl(aq).

   Sodium hydrogen carbonate and CO_2 gas are also added to buffer the swimming pool water. The K_a value for carbonic acid (the weak acid formed when CO_2 dissolves in water) is 4.2 x 10^{-7} mol dm^{-3}. The 'total alkalinity' (combined concentration of all the bases present) was measured as 1.08 x10^{-3} mol dm^{-3}.

3. Assuming the only bases detected in the total alkalinity test are OCl^- and HCO_3^- , calculate the concentration of carbonic acid in the swimming pool.

4. Explain the effect on the concentration of HOCl of adding extra CO_2 gas.

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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 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 x 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 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?

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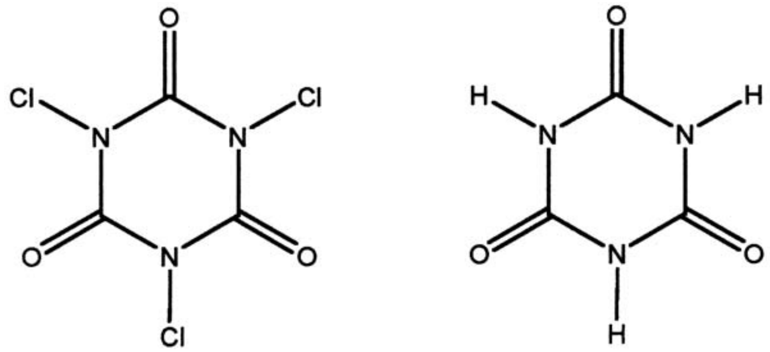
Part 2

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.



(a) (b)

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.

   b) Account for the relative heights of the peaks at m/c
      i) 154, 156 and 158.
      ii) 231, 233, 235 and 237.

Mass/charge ratio	Relative height of peak as a percentage of the most abundant peak	Species giving rise to the peak
42	17.9	NCO^+
70	100.0	and
72	12.9	
74	2.3	
77	81.4	
79	26.4	
154	18.4	
156	11.7	
158	2.0	
231	24.6	
233	23.4	
235	7.8	
237	1.0	

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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 70 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 a delocalised π system like benzene.

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

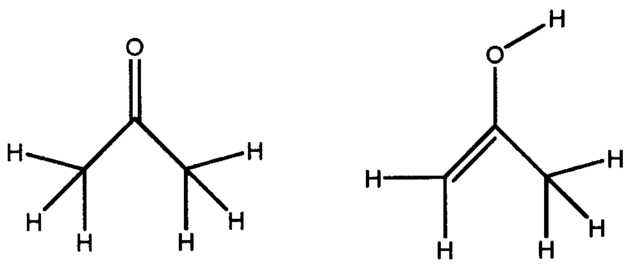
13. Discuss the oxidation state of the chlorine in trichloroisocyanuric acid. Electronegativity values are given below.

H
2.1

Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0

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:



(a) (b)

The structures of (*a*) the *keto* and (*b*) the *enol* - tautomers of propanone

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.

Swimming pool chemistry

Part 1

1. *Convert the combined concentration of HOCl(aq) and OCl⁻(aq) from parts per million into mol dm⁻³.*

1 dm³ contains 55.6 moles of water

Therefore 1 ppm $= 55.6 \times 10^{-6}$ mol dm^{-3}

$= 5.56 \times 10^{-5}$ mol dm^{-3}

0.5 ppm $= 5.56 \times 10^{-5}$ mol dm^{-3} x 0.5

$= 2.78 \times 10^{-5}$ mol dm^{-3}

= 2.8 x 10⁻⁵ mol dm⁻³ (two sig fig)

2. *Calculate the concentration of HOCl(aq).*

$$pH = pKa + \log_{10}\frac{[OCl^-]}{[HOCl]}$$

$$7.3 - 7.54 = \log_{10}\frac{(2.78 \times 10^{-5} - [HOCl])}{[HOCl]}$$

$$-0.24 = \log_{10}\frac{(2.78 \times 10^{-5} - [HOCl])}{[HOCl]}$$

$$0.575 = \frac{(2.78 \times 10^{-5} - [HOCl])}{[HOCl]}$$

$$0.575[HOCl] = 2.78 \times 10^{-5} - [HOCl]$$

$$[HOCl] = \frac{2.78 \times 10^{-5}}{1.575}$$

$= 1.76 \times 10^{-5}$ mol dm^{-3}

= 1.8 x 10⁻⁵ mol dm⁻³ (two sig fig)

3. *Assuming the only bases detected in the total alkalinity test are OCl^- and HCO_3^-, calculate the concentration of carbonic acid in the swimming pool.*

$[OCl^-] = 2.78 \times 10^{-5}$ mol dm^{-3} $- 1.76 \times 10^{-5}$ mol dm^{-3}

$= 1.02 \times 10^{-5}$ mol dm^{-3}

$[HCO_3^-] = 1.08 \times 10^{-3} - 1.02 \times 10^{-5}$ mol dm^{-3}

$= 1.07 \times 10^{-3}$ mol dm^{-3}

continued on page 2

$$[H_2CO_3] = \frac{[HCO_3^-][H^+]}{Ka}$$

$= 1.07 \times 10^{-3}$ mol dm^{-3}

$$[H_2CO_3] = \frac{1.07 \times 10^{-3} \times 10^{-7.3}}{4.2 \times 10^{-7}}$$

$= 1.28 \times 10^{-4}$ mol dm^{-3}

= 1.3×10^{-4} mol dm^{-3} (two sig fig)

4. *Explain the effect on the concentration of HOCl of adding extra CO_2 gas.*

Adding extra CO_2 gas increases the concentration of H_2CO_3. This in turn causes a drop in pH. The drop in pH shifts the position of the equilibrium for:
$HOCl(aq) \rightleftharpoons OCl^-(aq) + H^+(aq)$
to the left, increasing the concentration of HOCl(aq).

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

Units = mol$^{(a+b)}$ dm$^{-3(a+b)}$

6. *K_{sp} for calcium sulfate has a value of 2.4×10^{-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 sulfate ions in the swimming pool?*

$[Ca^{2+}(aq)]$ = 0.1/2 mol dm^{-3}
= 0.05 mol dm^{-3}
$[SO_4^{2-}(aq)]$ = K_{sp} /$[Ca^{2+}(aq)]$
= 2.4×10^{-5} /0.05
= 4.8×10^{-4} mol dm^{-3} (two sig fig)

7. *Explain how the added calcium chloride helps to prevent the grout dissolving.*

The phenomenon at work here is known as the common ion effect. The calcium chloride added raises the concentration of calcium ions. This in turn limits the amount of calcium sulfate that can dissolve before the solution is saturated, because K_{sp} is the product of the concentration of the two ions.

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?*

The more charged calcium and sulfate ions must cause more ordering of the water molecules around them than the sodium and chloride ions. So ΔS_{system} is likely to be negative for the solution of $CaSO_4$ and positive for NaCl. The website ***www.chemguide.co.uk/inorganic/group2/problems.html*** (accessed May 2007) has a good discussion of the problems with relating solubility to enthalpies of solution and the effect of entropy.

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Part 2

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:

Mass/charge ratio	Relative height of peak as a percentage of the most abundant peak	Species giving rise to the peak
42	17.9	NCO^+
70	100.0	$C_2O_2N^+$ and $^{35}Cl_2^+$
71	2.7	$C_2O_2N^+$ (C–13 satellite)
72	12.9	$^{35}Cl^{37}Cl^+$
74	2.3	$^{37}Cl_2^+$
77	81.4	$CON^{35}Cl^+$
79	26.4	$CON^{37}Cl^+$
154	18.4	$C_2O_2N_2{}^{35}Cl_2^+$
156	11.7	$C_2O_2N_2{}^{35}Cl^{37}Cl^+$
158	2.0	$C_2O_2N_2{}^{37}Cl_2^+$
231	24.6	$C_3N_3O_3{}^{35}Cl_3^{+\bullet}$
233	23.4	$C_3N_3O_3{}^{35}Cl_2{}^{37}Cl^{+\bullet}$
235	7.8	$C_3N_3O_3{}^{35}Cl^{37}Cl_2^{+\bullet}$
237	1.0	$C_3N_3O_3{}^{37}Cl_3^{+\bullet}$

   b) Account for the relative heights of the peaks at m/c.

      i) 154, 156 and 158

There are two chlorines so we expect three peaks with height ratio 9 : 6 : 1.

      ii) 231, 233, 235 and 237

There are three chlorines so we expect four peaks with height ratio 27 : 27 : 9 : 1.

   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.

231 x 24.6 + 233 x 23.4 + 235 x 7.8 + 237 x 1.0 = 13204.8

24.6 + 23.4 + 7.8 + 1.0 = 56.8

13204.8 / 56.8 = 232.48 (two decimal places).

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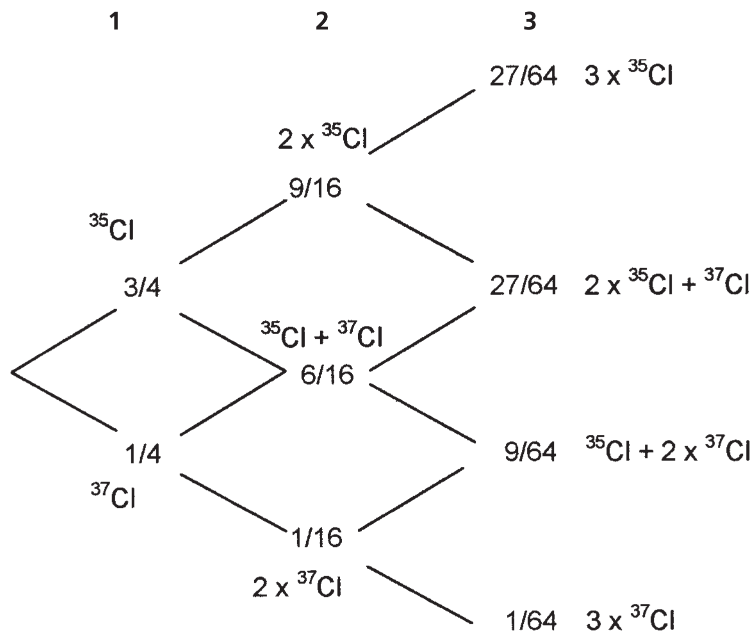
The number of chlorine atoms in the molecule



The probability tree for molecules containing up to three chlorines

d) It seems likely that the peak at m/c 70 is due to two species. A higher resolution mass spectrometer would resolve the single peak at m/c 70 into two separate peaks. Calculate what their relative heights would be.

The relative height of the peak at m/c 72 is the best clue here. The peak at 72 is due to $^{35}Cl^{37}Cl^{+}$, so we are expecting the $^{35}Cl_2^{+}$ peak to be 9/6 times higher – *ie* height 19.4%. The peak due to $C_2O_2N^{+}$ would therefore be 80.6 % on the current scale. Because the peak at m/c 70 was the most abundant in the low resolution mass spectra, the whole scale would be different in high resolution with the new most abundant peak being m/c 77 (assuming the same fragmentation pattern). The relative height of the $C_2O_2N^{+}$ peak could be estimated from the carbon-13 satellite at m/c 71 but this is likely to be less accurate than using the chlorine isotope abundances since the satellite peak is so small.

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

One – all the hydrogens are equivalent.

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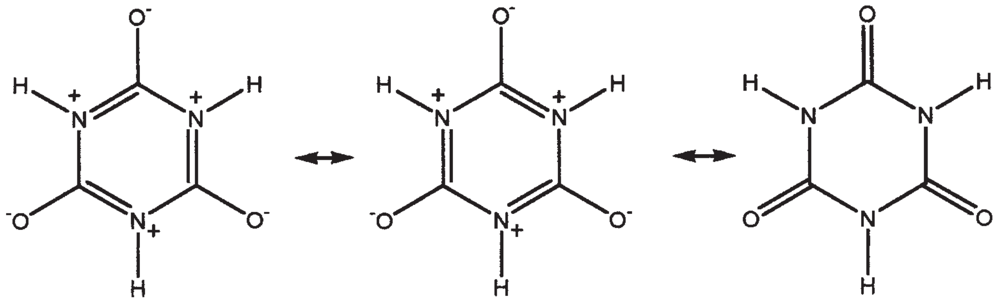
11. Discuss whether you think that isocyanuric acid will have a delocalised π system like benzene.

It will have a delocalised system because there are resonance structures that can be drawn with three π bonds in the ring.



The delocalised ring is not as stable as benzene because of the large number of formal charges in the resonance structures.

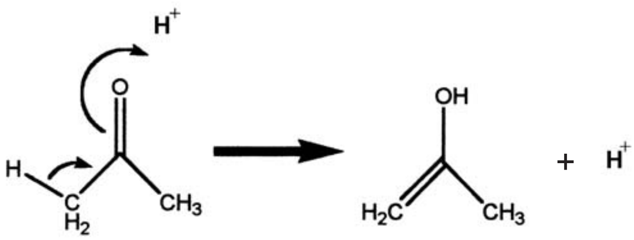
12. Write a balanced equation for the reaction of trichloroisocyanuric acid and water.

$C_3O_3N_3Cl_3 + 3H_2O \rightarrow 3HOCl + C_3O_3N_3H_3$

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

If we put absolute faith in the Pauling electronegativity value we conclude that the bond is purely covalent and the oxidation number of the chlorine is zero. The reaction with water is then similar to a disproportionation reaction. However, electronegativity values are not absolute values in the same way that thermodynamic data are; they are a rough guide. There are other electronegativity values, different from the ones that Pauling suggested, and these do not put nitrogen and chlorine as equal. If we lose complete faith in the electronegativity values then it seems reasonable to suggest that the hydrolysis is not a redox reaction (since water is neither an oxidising agent nor reducing agent). That suggests that the oxidation number of chlorine is +1 in the trichloroisocyanuric acid, as it is in the product HOCl.

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



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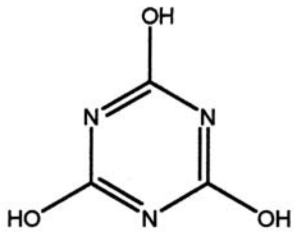
15. Suggest a structure for cyanuric acid, the tautomeric form of isocyanuric acid.



Interestingly it does not seem to form stable intermediates (with just one or two OH groups).