



CHEMISTRY

2003 NATIONAL QUALIFYING EXAMINATION

Time Allowed
Reading Time: 15 minutes
Examination Time: 120 minutes

INSTRUCTIONS

- This paper is in **two** sections and you must answer each section according to the instructions.
Section A: Answer **ALL** questions — spend no more than 30 minutes on this section.
Section B: Apportion your time equally on the questions in this section.
Answer **any three** of Questions 16, 17, 18 or 19
- All answers must be written in the space provided in the answer book.
- Use **blue** or **black** pen to write your answers, pencil is **NOT** acceptable.
- Rough working must be done only in the indicated areas of the answer book.
- You are not permitted to refer to books, periodic tables or written notes.
- The only permitted aid is a non-programmable electronic calculator.
- Relevant data that may be required for a question will be found on page 2.

DATA

| | | | |
|--|--|--|--------------------------------------|
| Avogadro constant (N) | $6.02 \times 10^{23} \text{ mol}^{-1}$ | Velocity of light (c) | $2.998 \times 10^8 \text{ m s}^{-1}$ |
| 1 faraday | 96,486 coulombs | Density of water at 25°C | 0.9971 g cm^{-3} |
| 1 coulomb | 1 A s | Acceleration due to gravity | 9.81 m s^{-2} |
| Universal gas constant (R) | | 1 newton (N) | 1 kg m s^{-1} |
| 8.314 J K ⁻¹ mol ⁻¹ | | | |
| $8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$ | | | |
| Planck's constant (h) | $6.626 \times 10^{-34} \text{ J s}$ | 1 pascal (Pa) | 1 N m^{-1} |
| Standard temperature and pressure (STP) | | pH = $-\log_{10}[\text{H}^+]$ | |
| 273 K and 101.3 kPa | | pH + pOH = 14 | |
| 0°C and 101.3 kPa | | $K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$ | |
| 0°C and 1 atm | | PV = nRT | |
| 0°C and 760 mm Hg | | E = hv | |
| Molar volume of ideal gas at STP | 22.4 L | c = vλ | |
| | | Q = It | |

ATOMIC NUMBERS & RELATIVE ATOMIC MASSES*

| | | | | | | | | | |
|-------|-------|-------|-------------------|-------|-------|-------|-------|-------|-------|
| 1 H | 1.008 | 23 V | 50.94 | 45 Rh | 102.9 | 67 Ho | 164.9 | 9 Ac | (227) |
| 2 He | 4.003 | 24 Cr | 52.00 | 46 Pd | 106.4 | 68 Er | 167.3 | 90 Th | 232.0 |
| 3 Li | 6.941 | 25 Mn | 54.94 | 47 Ag | 107.9 | 69 Tm | 168.9 | 91 Pa | (231) |
| 4 Be | 9.012 | 26 Fe | 55.85 | 48 Cd | 112.4 | 70 Yb | 173.0 | 92 U | 238.0 |
| 5 B | 10.81 | 27 Co | 58.93 | 49 In | 114.8 | 71 Lu | 175.0 | 93 Np | (237) |
| 6 C | 12.01 | 28 Ni | 58.69 | 50 Sn | 118.7 | 72 Hf | 178.5 | 94 Pu | (244) |
| 7 N | 14.01 | 29 Cu | 63.55 | 51 Sb | 121.8 | 73 Ta | 180.9 | 95 Am | (243) |
| 8 O | 16.00 | 30 Zn | 65.38 | 52 Te | 127.6 | 74 W | 183.9 | 96 Cm | (247) |
| 9 F | 19.00 | 31 Ga | 69.72 | 53 I | 126.9 | 75 Re | 186.2 | 97 Bk | (247) |
| 10 Ne | 20.18 | 32 Ge | 72.59 | 54 Xe | 131.3 | 76 Os | 190.2 | 98 Cf | (251) |
| 11 Na | 22.99 | 33 As | 74.92 | 55 Cs | 132.9 | 77 Ir | 192.2 | 99 Es | (252) |
| 12 Mg | 24.31 | 34 Se | 78.96 | 56 Ba | 137.3 | 78 Pt | 195.1 | 100Fm | (257) |
| 13 Al | 26.98 | 35 Br | 79.90 | 57 La | 138.9 | 79 Au | 197.0 | 101Md | (258) |
| 14 Si | 28.09 | 36 Kr | 83.80 | 58 Ce | 140.1 | 80 Hg | 200.6 | 102No | (259) |
| 15 P | 30.97 | 37 Rb | 85.47 | 59 Pr | 140.9 | 81 Tl | 204.4 | 103Lw | (260) |
| 16 S | 32.07 | 38 Sr | 87.62 | 60 Nd | 144.2 | 82 Pb | 207.2 | 104Db | |
| 17 Cl | 35.45 | 39 Y | 88.91 | 61 Pm | (145) | 83 Bi | 209.0 | 105Jt | |
| 18 Ar | 39.95 | 40 Zr | 91.22 | 62 Sm | 150.4 | 84 Po | (209) | 106Rf | |
| 19 K | 39.10 | 41 Nb | 92.91 | 63 Eu | 152.0 | 85 At | (210) | 107Bh | |
| 20 Ca | 40.08 | 42 Mo | 95.94 | 64 Gd | 157.3 | 86 Rn | (222) | 108Hn | |
| 21 Sc | 44.96 | 43 Tc | (98) [†] | 65 Tb | 158.9 | 87 Fr | (223) | 109Mt | |
| 22 Ti | 47.88 | 44 Ru | 101.1 | 66 Dy | 162.5 | 88 Ra | 226.0 | | |

* The relative values given here are to four significant figures.

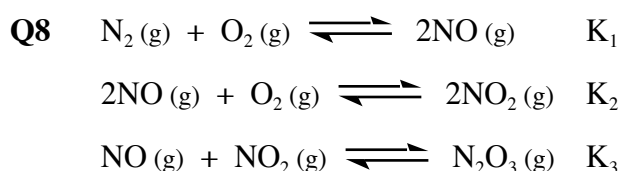
† A value given in parentheses denotes the mass of the longest-lived isotope.

SECTION A

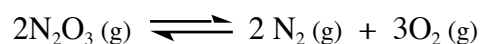
It is intended that candidates devote not more than **30 minutes to this section**. Answer **ALL** fifteen (15) questions in this section. Only one choice is allowed per question and this should be made by clearly crossing the chosen answer box in **the answer book**. If you make a mistake **correct it clearly** so that the examiners can read your answer.

- Q1** What is the total number of isomers for a compound with molecular formula $C_3H_6Cl_2$?
- A 6
 - B 5
 - C 4
 - D 3
 - E 7
- Q2** According to valence bond theory, what hybrid orbitals are used by the central atom in XeF_2 ?
- A sp^3
 - B sp
 - C dsp^3
 - D d^2sp^3
 - E sp^2
- Q3** How many electrons are required to balance the half equation in which dichromate ion, $Cr_2O_7^{2-}$, is converted to chromium (III) ions in acid solution?
- A 6
 - B 4
 - C 8
 - D 5
 - E 1
- Q4** Consider the following reaction at equilibrium:
- $$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \quad \Delta H^\circ = -113 \text{ kJ mol}^{-1}$$
- Which of the following changes would cause a decrease in the NO_2 / NO mole ratio?
- A adding $O_2(g)$
 - B adding a catalyst
 - C increasing the pressure
 - D increasing the temperature
 - E none of the above

- Q5** The solubility product, K_{sp} , of Ag_2CrO_4 (s) is 2.6×10^{-12} at 25°C . What is the solubility of Ag_2CrO_4 in moles per litre?
- A 1.6×10^{-6}
B 2.6×10^{-12}
C 2.1×10^{-8}
D 1.4×10^{-4}
E 8.7×10^{-5}
- Q6** A strong diprotic acid H_2A is dissolved in water at 25°C to yield a solution of pH 1.85. The concentration of acid in this solution (assuming complete dissociation of H_2A to A^{2-}) in mol L^{-1} is between:
- A 0.05 and 0.1
B 0.01 and 0.05
C 0.1 and 0.5
D 0.001 and 0.005
E 0.005 and 0.01
- Q7** A certain element, X, reacts with sulfur to form the compound X_2S_5 . If 0.274 g of the element form 0.568 g of the compound, what is the atomic molar mass of the element?
- A 31.0 g mol^{-1}
B 58.9 g mol^{-1}
C 65.4 g mol^{-1}
D 74.7 g mol^{-1}
E 121.8 g mol^{-1}



Given the above three reactions have equilibrium constants K_1 , K_2 and K_3 , respectively, what would be the expression for the equilibrium constant K for the following reaction, in terms of K_1 , K_2 and K_3 ?



- A $K_1K_2K_3$
B $1 / K_1K_2K_3$
C $K_1^2K_2K_3^2$
D $1 / K_1K_2^2K_3^2$
E $1 / K_1^2K_2K_3^2$

- Q9** Calculate the wavelength of light required to break the bond between two bromine atoms in a bromine molecule. The Br—Br bond energy is 193 kJ mol^{-1} .
- A $6.19 \times 10^{-7} \text{ m}$
 - B $1.03 \times 10^{-30} \text{ m}$
 - C $1.98 \times 10^{-28} \text{ m}$
 - D $1.93 \times 10^{-12} \text{ m}$
 - E $1.25 \times 10^{-8} \text{ m}$
- Q10** A 0.100 M solution of acetic acid is titrated with a 0.05 M solution of NaOH . What is the pH when 60% of the acid has been neutralized? K_a for acetic acid is 1.8×10^{-5} .
- A 2.38
 - B 4.56
 - C 4.74
 - D 4.92
 - E 7.00
- Q11** For the reaction $\text{X} \rightleftharpoons \text{Y}$, an initial concentration of 1.0 M X is allowed to come to equilibrium. If $K = 10$, what is the equilibrium concentration of Y?
- A 0.10 M
 - B 0.50 M
 - C 0.91 M
 - D 1.1 M
 - E 10 M
- Q12** Calculate the concentration of NO_3^- in a solution prepared by mixing 100 mL of 0.15 M $\text{Al}(\text{NO}_3)_3$, 100 mL of 0.25 M $\text{Pb}(\text{NO}_3)_2$ and 50 mL of 0.1 M NaNO_3 .
- A 0.50 M
 - B 0.40 M
 - C 0.25 M
 - D 0.20 M
 - E 0.10 M
- Q13** Calculate the molar mass of an ideal gas that has a density of 1.87 g L^{-1} at $30.0 \text{ }^\circ\text{C}$ and a pressure of 1 atm .
- A 4.60 g mol^{-1}
 - B 24.9 g mol^{-1}
 - C 39.3 g mol^{-1}
 - D 46.5 g mol^{-1}
 - E 93.0 g mol^{-1}

Q14 A current of 10.0 A flows for 2.00 hours through an electrolytic cell containing a molten salt of metal X and results in the deposition of 0.250 moles of metal X at the cathode. The oxidation state of X in the electrolysed salt is:

- A +1
- B +2
- C +3
- D +4
- E +5

Q15 Which of the following are polar molecules?

- 1 NH_3
 - 2 AsF_3
 - 3 CHCl_3
 - 4 BeF_2
 - 5 SnCl_4
- A 1, 2 and 3 only
 - B 1 and 3 only
 - C 2, 3 and 4 only
 - D 2, 4 and 5 only
 - E all of them

SECTION B

Marks will be deducted for incorrect use of significant figures. You are also advised that steps to the solution of problems must be clearly explained. Marks will be deducted for untidy and poorly explained answers.

Answer any three of the four questions in this section.

Q16

(a) Calculate the final pH of the following systems when 5.00 mL of:

(i) 2.00 M HCl

(ii) 0.500 M NaOH

are added to 500. mL of distilled water at 25°C (pH of water at this temperature is 7.00).

(b) An important concept in analytical chemistry is the buffer solution. It consists of a solution of a mixture of a weak acid (HA) and its conjugate base (A^-). It is called a buffer solution because this mixture resists changes in pH when a strong acid or base is added to the system.

Using chemical equations (and showing the states of each species), show what happens when:

(i) HCl gas

(ii) NaOH pellets

are added to the buffer solution.

The pH of the buffer solution is determined by the molar ratio of the weak acid and its conjugate base. If the dissociation constant of the weak acid K_a is known, the pH of the buffer solution can be determined by the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log_{10} ([A^-] / [HA])$$

(c) Derive the Henderson-Hasselbalch equation from the K_a .

(d) 1.00 L of a hypothetical buffer solution contains 0.500 moles each of a weak acid and its conjugate base and the pH of this solution is measured to be 7.00.

What is the $\text{p}K_a$ of this weak acid/conjugate base pair?

(e) Calculate the final pH of the following systems when 5.00 mL of:

(i) 2.00 M HCl

(ii) 0.500 M NaOH

are added to 500. mL of the buffer solution in question (d).

(f) The K_a of acetic acid (CH_3COOH) is 1.75×10^{-5} .

1.00 L of buffer solution containing acetic acid and acetate ions (CH_3COO^-) has a pH of 5.30. The total concentration of acetic acid and acetate ions is 1.00 M.

(i) What is the ratio of acetate ions to acetic acid ($[A^-] / [HA]$)?

(ii) Calculate the concentration of acetic acid and acetate in the buffer solution.

Question 16 continues on the next page.

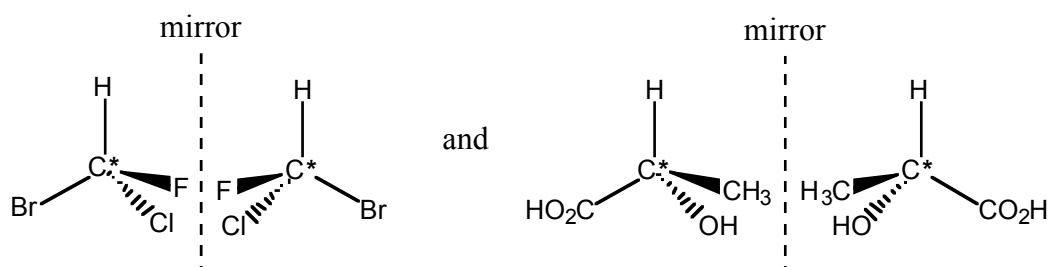
Rather than mixing a weak acid and its conjugate base together, an alternative method involves starting off with just one component of the buffer solution and then adding a strong acid or base.

- (g) How does this work?
- (h) Bob, a budding young chemist, decides to make himself 1.00 L of buffer solution of pH 4.00 using nothing but a 0.500 M solution of sodium acetate and a 2.00 M solution of HCl. For the following question, let the volume of HCl added be V litres.
- (i) What is the volume of sodium acetate added to form the buffer?
- (ii) How many moles of acetic acid are formed?
- (iii) How many moles of acetate ions are left after reaction with HCl?
- (iv) What is the ratio of acetate to acetic acid required to achieve the desired pH?
- (v) Hence calculate the volume of the reagents required to make the buffer.
- (i) The ideal buffering pH is the pH at which the buffer solution will most strongly resist changes to pH upon addition of strong acid or base. At this pH, there are equimolar amounts of the weak acid and conjugate base.

What is the ideal buffering pH of an acetic acid/ acetate buffer solution?

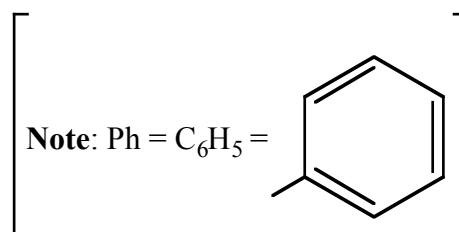
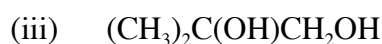
- (j) Not content with his buffer, Bob decides to carry out another experiment. Starting with 250. mL of an acetic acid/ acetate buffer at the ideal buffering pH, he was about to carry out his experiment when he accidentally spilled some 0.340 M NaOH solution into it. He quickly cleaned up and measured the pH of the buffer solution again. This time it registered 1.00 unit higher than the ideal buffering pH.
- (i) What is the ratio of acetate to acetic acid in the new solution?
- The total concentration of acetic acid and acetate in the original buffer was 0.500 M.
- (ii) Calculate the number of moles of acetic acid and acetate in the buffer.
- (iii) Do the same for the final solution, after the addition of NaOH.
- (iv) How much acetate was generated as a result of the accident?
- (v) What is the volume of NaOH that Bob spilled into his buffer?

- Q17** A molecule containing a carbon atom bearing four different groups is said to be **chiral** and exists in two, non-superimposable mirror image forms termed **optical isomers**. For example, CHFCIBr and lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$; the two optical isomers of each are shown below:

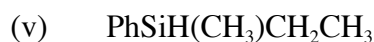


The carbon atom bearing four different groups is referred to as a **chiral centre** or an **asymmetric centre**. The atoms labelled with an asterisk in each of the above examples are asymmetric carbon centres. The wedges are used to emphasise the 3D geometry about the chiral carbon centre. The 'filled-in' wedge indicates that the bond is coming out of the page towards the observer whereas the other 'dotted' wedge indicates that the bond is going back into the page i.e. away from the observer.

- (a) Which of the following molecules are chiral? For each chiral molecule sketch the optical isomers and clearly label the asymmetric carbon centres with an asterisk.



Chirality is not restricted to molecules containing an asymmetric carbon centre. Each of the following species is also chiral:



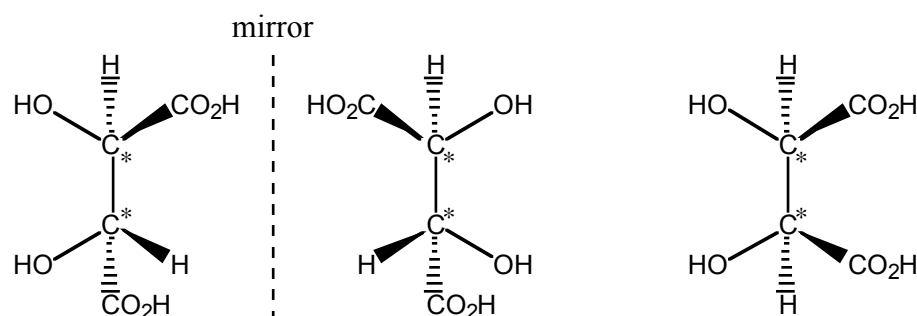
[Note: lone pairs have been omitted. The



fourth group can be a lone pair.]

- (b) For each of the above species (v)-(viii) sketch the optical isomers and clearly label the asymmetric centres with an asterisk.

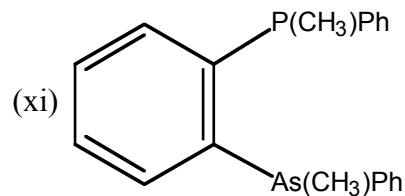
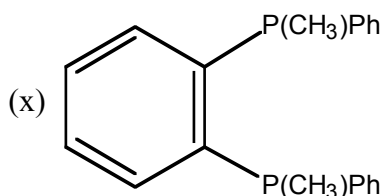
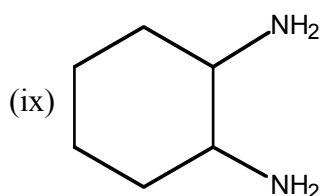
Isomers that only differ in the spatial arrangement of the atoms are termed **stereoisomers**. Optical isomers are examples of stereoisomers. Tartaric acid, $\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{H}$, has two asymmetric carbon centres and exists in three stereoisomeric forms, two of which are optical isomers. The three stereoisomers are shown below:



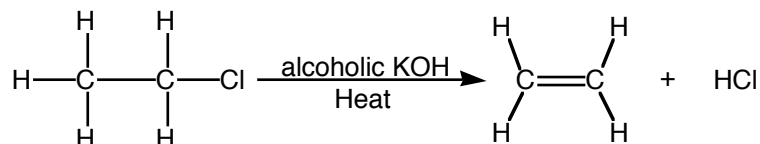
The third structure shown above is NOT chiral as its mirror image is superimposable (i.e. the mirror image is identical to the original).

Question 17 continues on the next page.

- (c) How many stereoisomers are expected for each of the following molecules? Sketch them and clearly label the asymmetric centres with an asterisk. Clearly identify any pairs of optical isomers.

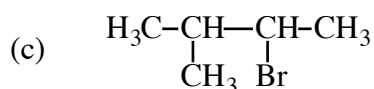
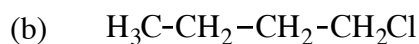
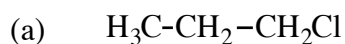


- Q18** Elimination reactions are often used in the preparation of alkenes. One example of an elimination reaction is 'dehydrohalogenation', in which HX (where X is some halogen, e.g. Cl, Br) is eliminated from a haloalkane. For example, heating chloroethane in alcoholic potassium hydroxide gives ethene as the major organic product:

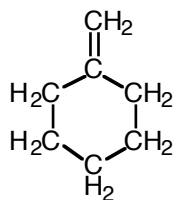


Where more than one elimination product is possible, Zaitsev's rule says that the major product is the alkene with more alkyl substituents on the carbons involved in the double bond.

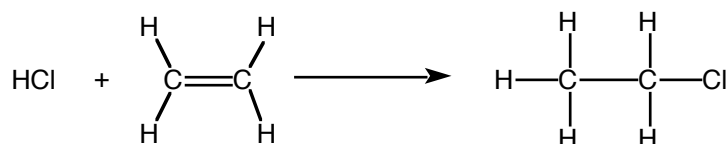
Draw the structure of the major organic product when each of the following are treated with hot alcoholic potassium hydroxide:



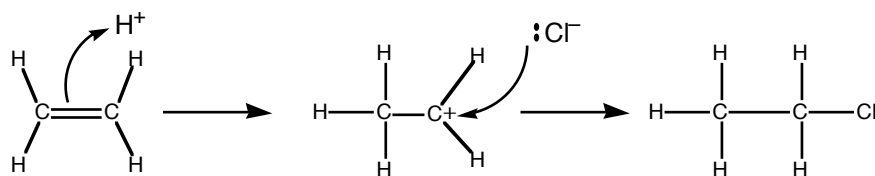
- (d) Draw the structure of the best organic starting material you could use to prepare methylenecyclohexane (structure shown below) using a dehydrohalogenation reaction.



The opposite of elimination is addition, which alkenes undergo readily. Hydrogen halides readily add across alkene double bonds, forming haloalkanes, for example hydrogen chloride adds to ethene to give chloroethane:



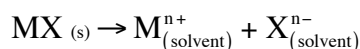
The mechanism of this reaction (the sequence of steps that comprise the overall reaction) is shown below (the arrows represent the movement of a pair of electrons):



1. A pair of electrons from the carbon-carbon double bond is shared with a hydrogen ion, forming a so-called carbo-cation intermediate. In this case the hydrogen may become attached to either carbon atom, but in general the more alkyl groups attached to the positively charged carbon atom, the more stable the carbo-cation intermediate. As you might expect, the major product is formed from the more stable carbo-cation intermediate.
 2. A pair of electrons from a chloride ion is shared with the positively charged carbon atom, forming the final product, chloroethane.
- (e) When gaseous hydrogen chloride is bubbled through a solution of propene, two products may be formed. Draw the structures of both products, and explain which one is the major product and why.
- (f) When 1-chloropentane is treated with hot alcoholic potassium hydroxide, a product **A** is formed, and when gaseous hydrogen chloride is bubbled through a solution of product **A**, product **B** is formed. Name and draw the structures of products **A** and **B**.
- (g) When 1.000 g of any of three isomeric hydrocarbons **P**, **Q** and **R** are burnt in excess oxygen, 3.138 g of carbon dioxide and 1.284 g of water are produced. **P**, **Q** and **R** all react with hydrogen bromide: **P** and **Q** form the same major product, **S**, whereas **R** forms predominately **T**. **S** and **T** both contain 58.32 % bromine by mass. When heated with alcoholic potassium hydroxide, **S** gives **Q** as the major product, and **T** gives **R**. Ignoring stereochemistry, draw the structures for compounds **P-T**.

Q19 An understanding of the factors governing the solubility of solids in different solvents is vital for controlling many real-world systems, from energy production in biological systems to mineral extraction.

For a symmetric ionic solid the reaction of solution is:



A solid will be soluble at equilibrium if the change in Gibbs' Free Energy, $\Delta G_{\text{solution}}^0 < 0$; otherwise the solid will be insoluble or sparingly soluble.

It is useful to consider the solubility as governed by two factors:

$$\Delta G_{\text{solution}}^{\circ} = \Delta H_{\text{solution}}^{\circ} - T\Delta S_{\text{solution}}^{\circ}$$

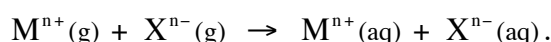
Here $\Delta H_{\text{solution}}^{\circ}$ is the change in enthalpy or heat associated with dissolution, where an endothermic process (energy input) is associated with a positive $\Delta H_{\text{solution}}^{\circ}$. $\Delta S_{\text{solution}}^{\circ}$ is the change in entropy, or disorder. A positive $\Delta S_{\text{solution}}^{\circ}$ can be considered to indicate an overall increase in disorder or randomness, associated with a larger number of possible configurations, caused by such events as increase in particle mobility or quantity, while a negative $\Delta S_{\text{solution}}^{\circ}$ will result if particle movement is restricted.

We can consider the process of dissolving as being made up of two (theoretical) steps.

The first is the breaking apart of the solid lattice into its gas phase constituent ions.

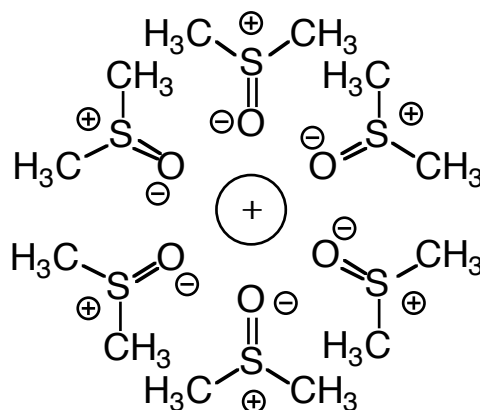
- (a) (i) Write the chemical reaction for this process for sodium chloride solid.
- (ii) Would you expect the enthalpy change of this process ($\Delta H_{\text{lattice}}$) to be positive or negative?
- (iii) Would you expect the entropy change of this process to be positive or negative? Explain.

The second step is the 'solvation' of the gaseous ions. When the solvent is water this process is known as hydration, and can be written:



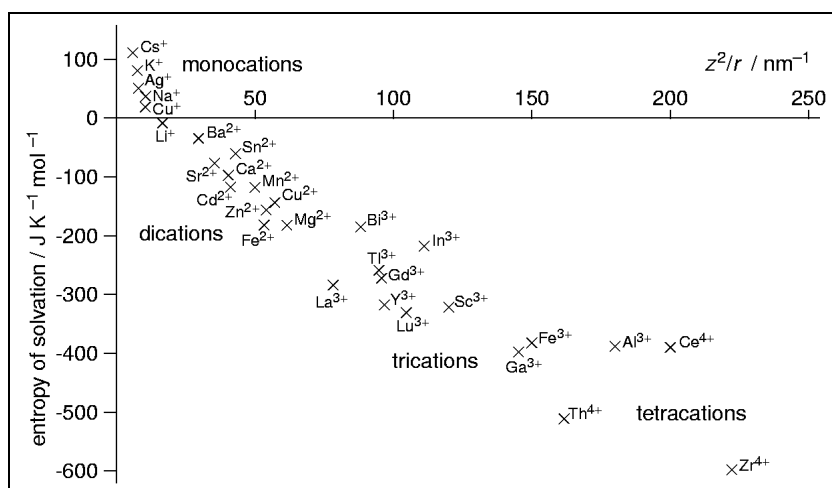
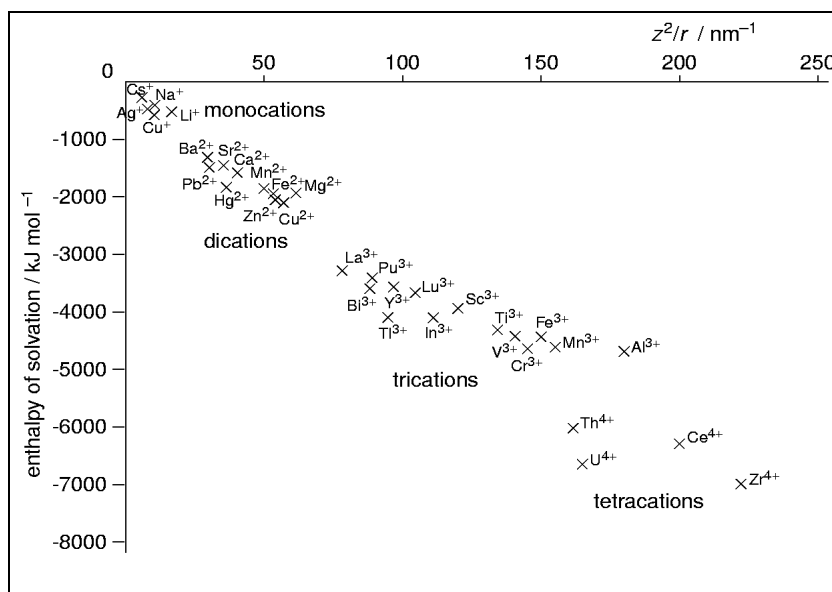
The enthalpy change associated with this process is $\Delta H_{\text{hydration}}$.

In polar solvents the ions attract a 'solvent shell' with charges aligned, eg DMSO (dimethylsulfoxide) will solvate a cation:



The solvation process involves the formation of electrostatic interactions between the ions and solvent particles, an exothermic process. In general particle mixing increases randomness. However, this 'ideal' case is modified where the solute and solvent particles

interact, for instance by solvent shell formation. The ion movement is restricted, as is that of the surrounding solvent molecules, and so there is a negative entropy component. Solvent-solvent particle interactions are broken, which uses energy but increases disorder. It is the relative magnitude of all these effects which determines the overall solvation enthalpy and entropy.



The two graphs shown give hydration enthalpy and entropy for cations as a function of charge density (z^2/r).

- (b)(i) What is the effect on hydration enthalpy of increasing charge density? Is this what you would expect? What about the effect on solvation entropy? Suggest possible justifications for both trends.
- (ii) What is the general relationship between ion size and solvation enthalpy?
- (iii) Why do some cations have a positive hydration entropy?

Question 19 continues on the next page.

- (c) In pure water there is a network of intermolecular hydrogen-bonding, which is disrupted by the introduction of ions. What contribution will this make to
- total enthalpy of hydration?
 - total entropy of hydration?
 - Can we make any predictions about the relative solubility of a cation in a polar aprotic (non-

hydrogen bonding) solvent such as DMSO, $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{S}}-\text{CH}_3$?

- (d) For sodium chloride the following data have been obtained:

| Enthalpy | ΔH° value (kJ mol^{-1}) |
|-------------------------------------|---|
| $\Delta H^\circ_{\text{lattice}}$ | +787.4 |
| $\Delta H^\circ_{\text{hydration}}$ | -783.6 |

Construct an enthalpy cycle (Born-Haber cycle) showing how the ΔH° values combine to give the total $\Delta H^\circ_{\text{solution}}$, and find this value.

- (e) In the table below, the overall entropy and enthalpy of solution in water are given for two ionic solids. In each case
- Calculate $\Delta G^\circ_{\text{solution}}$ at room temperature (298K) and state whether the salt is soluble or insoluble.
 - Predict the effect on solubility of raising the temperature of the system.

| Salt | $\Delta H^\circ_{\text{solution}}$ (J mol^{-1}) | $\Delta S^\circ_{\text{solution}}$ ($\text{J K}^{-1} \text{mol}^{-1}$) |
|-----------------|--|--|
| MgSO_4 | +20 000 | +90 |
| BaSO_4 | +19 000 | -105 |

- (f) Why can we say that, as a general solubility rule, 'like dissolves like' – that is, polar solids dissolve in polar solvents and nonpolar solutes dissolve in nonpolar solvents? (Hint: consider the sign and magnitude of enthalpic and entropic changes involved in various cases).

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