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AUSTRALIAN SCIENCE INNOVATIONS

ASI School ID:

AUSTRALIAN SCIENCE OLYMPIADS

AUSTRALIAN SCIENCE OLYMPIADS

NATIONAL QUALIFYING EXAM 2011

CHEMISTRY – SECTIONS A & B

TO BE COMPLETED BY THE STUDENT USE CAPITAL LETTERS

Student Name: ……

Home Address: ……

…… **Post Code:** ……

Telephone: (……) …… **Mobile:** ……

E-Mail: …… **Date of Birth:** ……/……/……

□ **Male** □ **Female** **Year 10** □ **Year 11** □ **Other:** …….

Name of School: ……**State:** ……..

Students competing in the 2011 National Qualifying Examinations must be in Year 11 or an earlier year in 2011.

The Australian Olympiad teams in Biology, Chemistry and Physics will be selected from students participating in the Science Summer School. To be eligible for selection for the Summer School students will need to be an Australian citizen or permanent resident at the time offers are made.

To be eligible for selection in one of the Australian Science Olympiad teams, students must be eligible to hold an Australian passport by the time of team selection (March 2012)

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CHEMISTRY

2011 National Qualifying Examination

Time Allowed:

Reading Time: 10 minutes

Examination Time: 120 minutes

INSTRUCTIONS

- *Attempt ALL questions in ALL sections of this paper.*
- Permitted materials: Non-programmable non-graphical calculator, pens, pencils, erasers and a ruler.
- Answer SECTION A on the Multiple Choice Answer Sheet provided. Use a pencil.
- Answer SECTION B in the spaces provided in this paper. Write in pen and use a pencil only for graphs.
- Ensure that your diagrams are clear and labelled.
- All numerical answers must have correct units.
- Marks will not be deducted for incorrect answers.
- Rough working must be done only on pages 22 to 23 of this booklet.
- Relevant data that may be required for a question will be found on page 3.
- Do not staple the multiple choice answer sheet to this booklet.

MARKS

SECTION A	15 multiple choice questions	30 marks
SECTION B	3 short answer questions	90 marks
	Total marks for the paper	120 marks

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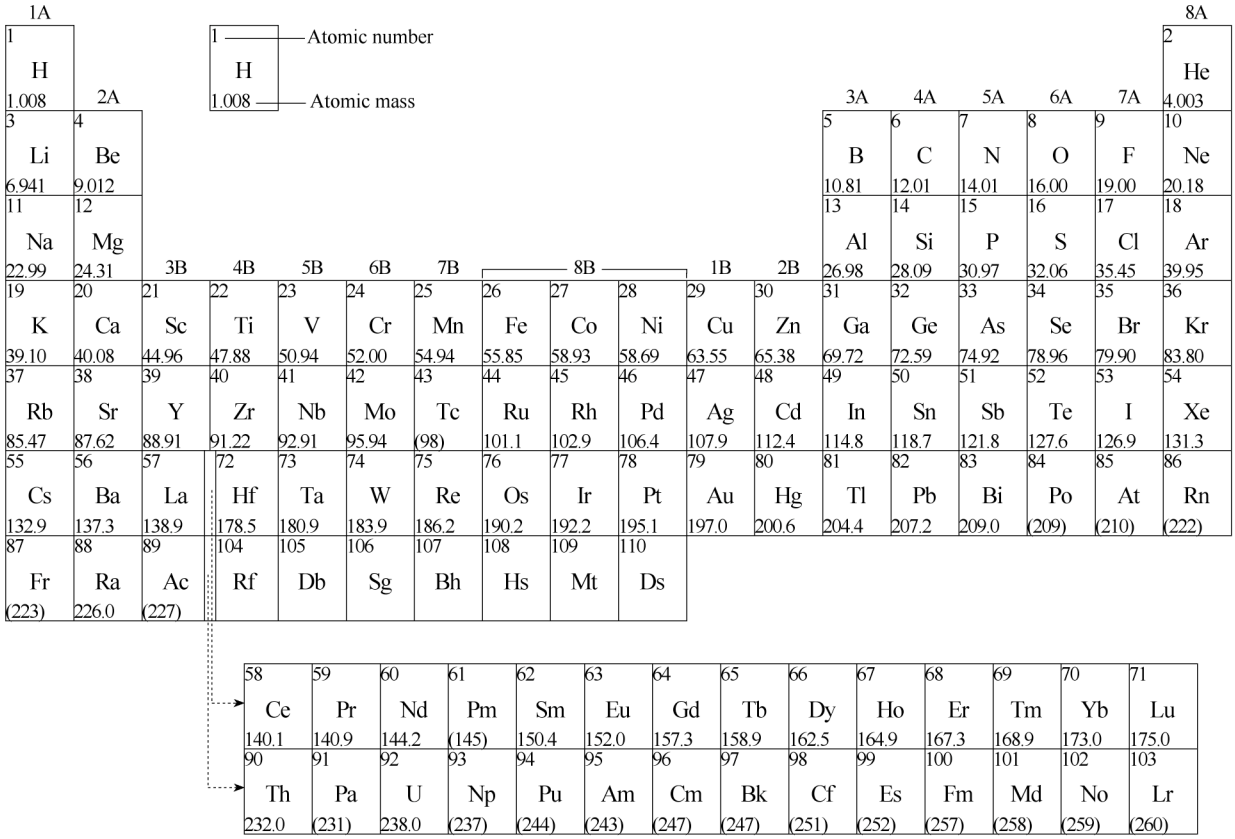
DATA

Avogadro constant (N)	6.02×10^{23} mol^{-1}	Velocity of light (c)	2.998×10^{8} m s^{-1}
1 faraday	96,486 coulombs	Density of water at 25°C	0.9971 g cm^{-3}
1 coulomb	1 A s^{-1}	Acceleration due to gravity	9.81 m s^{-2}
Universal gas constant (R) 8.314 J K^{-1} mol^{-1} 8.206 x 10^{-2} L atm K^{-1} mol^{-1}		1 newton (N)	1 kg m s^{-2}
Planck's constant (h)	6.626×10^{-34} J s	1 pascal (Pa)	1 N m^{-2}
Standard temperature and pressure (STP) 273 K and 100 kPa 0°C and 100 kPa 0°C and 1 bar 0°C and 750 mm Hg		$pH = -\log_{10}[H^+]$ $pH + pOH = 14.00$ at 25°C $K_a = [H^+][A^-] / [HA]$ PV = nRT E = hν c = νλ Surface area of sphere A = $4\pi r^2$	
Molar volume of ideal gas at STP	22.7 L		
1 bar = 100 kPa			

Periodic table of the Elements



Atomic mass values given here are to four significant figures. A value given in parentheses denotes the mass of the longest-lived isotope.

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SECTION A: MULTIPLE CHOICE
USE THE ANSWER SHEET PROVIDED

1. Which one of the following bonds is the most polar?

   a. H—F

   b. H—O

   c. H—N

   d. H—Cl

   e. H—C

2. Which one of the following electron configurations is not possible?

   a. $1s^2 2s^2 2p^6$

   b. $1s^2 2s^2 2p^5 3s^1$

   c. $1s^2 2s^2 2p^6 3s^2$

   d. $1s^2 2s^1 3p^1$

   e. $1s^2 2s^3 2p^5 3s^2$

3. 2,4,6-Trinitrotoluene (TNT, $C_7H_5N_3O_6$) can be used in synthetic chemistry; however, its use is limited because of its highly explosive nature. Upon detonation TNT decomposes as a mixture of the following reactions:

$$2\ C_7H_5N_3O_6 \rightarrow 3\ N_2 + 5\ H_2O + 7\ CO + 7\ C$$
$$2\ C_7H_5N_3O_6 \rightarrow 3\ N_2 + 5\ H_2 + 12\ CO + 2\ C$$

   When 20 mol of TNT was exploded with complete conversion into products, 30 mol of hydrogen gas was produced. How many moles of carbon monoxide were also produced?

   a. 28 mol

   b. 49 mol

   c. 72 mol

   d. 100 mol

   e. 119 mol

4. Which one of the following compounds would produce a basic 0.1 mol L^{-1} solution?

   a. NaCℓ

   b. $NaOOCCH_3$

   c $NH_4C\ell$

   d. $(NH_4)_2SO_4$

   e. CH_3COOH

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5. Which of the following best describes a neutral solution at any temperature?

   a. $[HO^-] > [H_3O^+]$

   b. $[HO^-] < [H_3O^+]$

   c. $[HO^-] = [H_3O^+]$

   d. p$H = 7$

   e. The solution contains no acidic nor basic species.

6. How many *d*-electrons does a Cr^{3+} ion have?

   a. 0

   b. 1

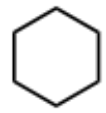
   c. 2

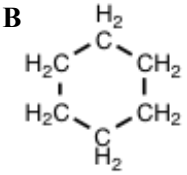
   d. 3

   e. 4

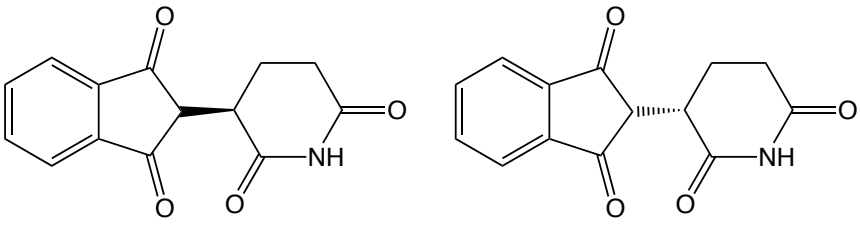
7. When drawing organic molecules black wedged lines, , denote bonds pointing out of the page and dashed wedged lines, , denote bonds going into the page.

   Carbon atoms and implicit hydrogen atoms are not drawn, so that **A** is identical to **B** which has all atoms drawn in.

   A 

   B 

   What is the difference between the following two molecules?



   1 **2**

   a. They have a different molecular formula.

   b. They have different bond connectivity.

   c. They are the same compound just drawn differently.

   d. They have a different arrangement in three-dimensional space.

   e. They have a different molecular weight.

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8. An accurate measurement of the mass of an unknown compound gave a result of 260.0429. What is the formula of the compound?

Atomic masses: C = 12.0000, H = 1.0078, N = 14.0030, O = 15.9949

a. $C_{13}H_8O_6$

b. $C_{12}H_8N_2O_5$

c. $C_8H_8N_2O_8$

d. $C_9H_{14}N_3O_6$

e. all of the above

9. Why does the addition of a suitable catalyst to a system speed up the rate of reaction?

a. It lowers the activation energy of the reaction.

b. It lowers the amount of heat gained by the system.

c. It lowers the amount of heat released by the system.

d. It lowers the potential energy of the products.

e. It lowers the potential energy of the reactants.

10. Which one of the following acts as a base when hydrofluoric acid is dissolved in an aqueous solution of sodium chloride?

a. $C\ell^-$

b. HF

c. H_2O

d. $NaC\ell$

e. Na^+

11. Consider the following weak acids with their associated K_a values.

Acid	K_a
$HC\ell O$	3.5×10^{-8}
$HC\ell O_2$	1.2×10^{-2}
HCN	6.2×10^{-10}
$H_2PO_4^-$	6.2×10^{-8}

Which one of the following gives the correct order of **increasing** strength of the conjugate base of each acid?

a. $C\ell O_2^-$, $C\ell O^-$, HPO_4^{2-}, CN^-

b. $C\ell O_2^-$, HPO_4^{2-}, $C\ell O^-$, CN^-

c. CN^-, HPO_4^{2-}, $C\ell O^-$, $C\ell O_2^-$

d. CN^-, $C\ell O^-$, HPO_4^{2-}, $C\ell O_2^-$

e. HPO_4^{2-}, CN^-, $C\ell O^-$, $C\ell O_2^-$

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12. Which of the following statements best describes characteristics of an endothermic reaction?
    a. The sign of ΔH is positive, and the products have less potential energy than the reactants.
    b. The sign of ΔH is positive, and the products have more potential energy than the reactants.
    c. The sign of ΔH is negative, and the products have less potential energy than the reactants.
    d. The sign of ΔH is negative, and the products have more potential energy than the reactants.
    e. ΔH equals 0, and the products' and the reactants' potential energy could be more or less.

13. Which one of the following best describes the molecular geometry (shape) of H_2Te?
    a. bent
    b. linear
    c. square planar
    d. square pyramidal
    e. tetrahedral

14. Which one of the following statements correctly describes a system that has reached equilibrium?
    a. The number of moles of product is greater than the number of moles of starting material.
    b. The number of moles of product is equal to the number of moles of starting material.
    c. The rate of the forward reaction is greater than the rate of the reverse reaction.
    d. The rate of the forward reaction is less than the rate of the reverse reaction.
    e. The rate of the forward reaction is equal to the rate of the reverse reaction.

15. What brings about **emission** of visible and ultraviolet radiation from atoms?
    a. electrons changing from lower to higher energy levels
    b. the atoms condensing from a gas to a liquid or solid
    c. electrons moving about the atoms within an orbital
    d. electrons changing from higher to lower energy levels
    e. neutral atoms losing electrons to form anions

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SECTION B: 3 SHORT ANSWER QUESTIONS
ANSWER IN THE SPACES PROVIDED

16. Dendritic crystals of silver are formed when copper metal is added to a solution of silver nitrate ($AgNO_3$). The copper metal forms Cu^{2+} ions and displaces silver from solution.

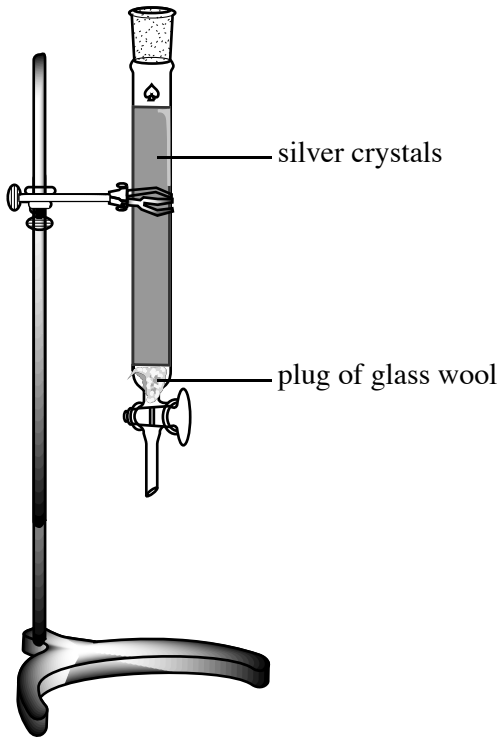
(a) Write two balanced ionic half-equations and a redox equation for the reaction between copper metal and a silver nitrate solution.

Oxidation Half-Equation:

Reduction Half-Equation:

Redox Equation:

Dendritic silver crystals can be utilised in a **silver reductor**. A silver reductor is used to reduce cations such as Fe^{3+}, Cu^{2+} and Mo^{6+} to lower oxidation states. A silver reductor consists of a tube in which a plug of glass wool supports a column of fine dendritic crystals of silver metal, as shown in the diagram below.



As a solution passes through the silver reductor, cations in solution are reduced while the silver metal is oxidised to solid silver chloride ($AgC\ell$).

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(b) Write a half-equation for the oxidation of silver metal to silver chloride in the presence of chloride ions.

A student is given a sample of hydrated ammonium molybdate by their teacher. The student is told that the formula of hydrated ammonium molybdate is of the form $(NH_4)_6Mo_xO_y.4H_2O$ **(where *x* and *y* are integers)** and that molybdenum has a +VI oxidation state. To determine the values of *x* and *y* the student carries out the following steps:

The student dissolves a sample (2.50 g) of the hydrated ammonium molybdate in a 250.0 mL volumetric flask and makes it up to the mark with distilled water. A 50.00 mL aliquot of this solution is diluted to 100 mL with 4 mol L^{-1} hydrochloric acid and heated to 80ºC. The hot solution is allowed to pass through a **silver reductor** and is collected in a 500 mL conical flask. The reductor is washed with hot hydrochloric acid several times to ensure that no molybdenum remains in the reductor column and these washings are also collected in the same 500 mL conical flask.

Molybdenum(VI) is reduced to molybdenum(V) by the silver reductor.

(c) Write a redox equation for the reaction that takes place in the silver reductor.

(d) Why is it necessary to add hydrochloric acid to the molybdate solution?

(e) Why is the molybdate solution heated?

The student notices that as the molybdate solution passes through the reductor, the upper part of the silver crystal column develops a dark coating.

(f) What causes the formation of the dark coating?

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To determine the chemical amount of molybdenum present in the reduced molybdate solution the student titrates the reduced molybdate solution with a solution of cerium(IV) ions. Over the course of the titration cerium(IV) ions are reduced to cerium(III) ions and molybdenum(V) is oxidised to moybdenum(VI). A titre of 24.41 mL was required to reach endpoint using a cerium(IV) sulfate solution standardised at 0.1160 mol L^{-1}.

(g) Calculate the chemical amount (in moles) of molybdenum in the original sample.

(h) In terms of *x* and *y*, write an equation for the formula weight of hydrated ammonium molybdate $[(NH_4)_6Mo_xO_y.4H_2O]$.

(i) Determine the values for *x* and *y* and hence the formula for ammonium molybdate.

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x:

y:

formula:

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17. In this question, the elements with atomic numbers 1 to 20 have had their symbols replaced by letters **A** to **T**. The letters **X**, **Y** and **Z** represent three elements with atomic numbers greater than 20. Unless otherwise stated, a temperature of 25°C and 100 kPa is assumed throughout this question.

Elements **I**, **O** and **P** are unreactive monatomic gases. **O** has the smallest atomic radius of the three, and **I** has a higher boiling point than **P**.

(a) Identify elements **I**, **O** and **P**.

The following elements exist as diatomic molecules: $\mathbf{E}_2$, $\mathbf{G}_2$, $\mathbf{J}_2$, $\mathbf{S}_2$, $\mathbf{Q}_2$, $\mathbf{Y}_2$, $\mathbf{Z}_2$.

$\mathbf{Y}_2$ is a liquid and $\mathbf{Z}_2$ is a solid; the other five being gases.

$\mathbf{S}_2$ forms compounds with each of the other six diatomic elements. Compounds of **S** with **E**, **G**, **Y** and **Z** result in diatomic gases that react with the liquid $\mathbf{S_2Q}$ to form acidic solutions. **E** has the highest electronegativity of these elements. The reaction of $\mathbf{J}_2$ and $\mathbf{S}_2$ is of immense industrial importance, the product being a gas that reacts with liquid $\mathbf{S_2Q}$ to form a basic solution.

(b) Identify elements **E**, **G**, **J**, **S**, **Q**, **Y** and **Z**.

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Elements **D**, **H**, **L** and **R** are metals that react vigorously with liquid $\mathbf{S_2Q}$ to produce $\mathbf{S_2}$ and a basic solution. **D** reacts more vigorously than **R**. The ions formed from **H** and **L** in this reaction have the same electron configuration.

1.00 g of element **H** reacts with excess $\mathbf{S_2Q}$ to produce 0.3115 L $\mathbf{S_2}$ at 20.00°C and 100.0 kPa.

(c) Identify elements **D**, **H**, **L** and **R**.

Elements **B**, **C** and **K** are also metals. They do not react with cold $\mathbf{S_2Q}$ but do react with $\mathbf{Q_2}$ to form **BQ**, $\mathbf{C_2Q_3}$ and **KQ** respectively. Of these, **KQ** contains the largest percentage of **Q** by mass.

(d) Identify elements **B**, **C** and **K**.

Elements **A**, **F**, **M**, **N** and **T** are solids at room temperature.

M reacts with $\mathbf{G_2}$ to produce $\mathbf{MG_3}$ whereas **A** reacts with $\mathbf{G_2}$ to produce $\mathbf{AG_3}$ and $\mathbf{AG_5}$, depending on the conditions.

F, **T** and **N** all react with react with $\mathbf{Q_2}$. Both $\mathbf{FQ_2}$ and $\mathbf{NQ_2}$ are gases that react with water to give acidic solutions; $\mathbf{TQ_2}$ on the other hand is a solid that is insoluble in water. $\mathbf{FQ_2}$ can further react with $\mathbf{Q_2}$ to form $\mathbf{FQ_3}$.

(e) Identify elements **A**, **F**, **M**, **N** and **T**.

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10.00 g of an unknown metal, **X**, reacts completely with 3.335 L of $\mathbf{Q}_2$ gas to form a compound of **X** and **Q**. 10.00 g of the metal can react with 6.670 L of $\mathbf{G}_2$ to form a compound of **X** and **G** or with 1.334 L of $\mathbf{Q}_2$ and 4.002 L of $\mathbf{G}_2$ to form a compound containing **X**, **Q** and **G**. Note that these gas volumes are all measured at 25°C and 100 kPa.

(f) Identify element **X** and calculate the empirical formula for these three compounds.

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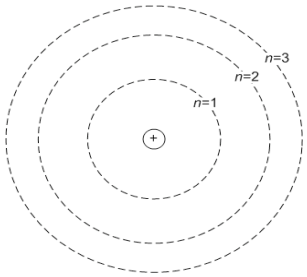
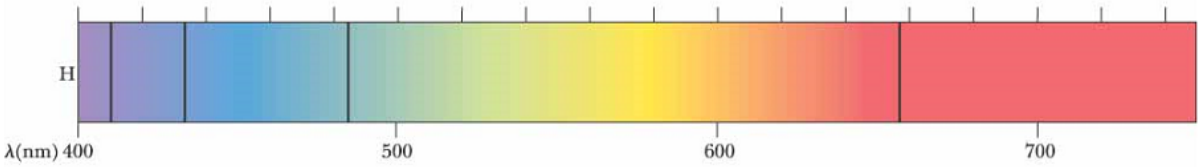
18. Spectroscopy is a useful analytical tool which involves examining the interaction of molecules with electromagnetic (EM) radiation in order to gain information about the structure and properties of the molecules. The technique relies on the fact that energy (where **energy** includes both the **kinetic motion** of the atoms in the molecule and the **potential energy states** of the electrons) is **quantised**, i.e. only certain discrete values of energy are allowed.

We are most familiar with this concept in relation to Bohr's model of the hydrogen atom. The potential energy states of electrons in Bohr atoms are quantised in circular orbits around the nucleus, which are indexed by a principal quantum number n (n = 1,2,3...). An atom can absorb EM radiation of a particular energy (in Joules, J) $E = \frac{hc}{\lambda}$ (where **λ** is the wavelength (in metres, m), **h** is Planck's constant (6.626×10^{-34} J s) and **c** is the speed of light (2.998×10^{8} m s^{-1}) which promotes an electron from one orbital to another orbital (e.g. from the n = 1 orbital to the n = 2).



These distinct energy levels are observed in atomic absorbance spectra as discrete black lines positioned at wavelengths (in nm) at which energy is absorbed, such as that for the hydrogen atom shown below.



Here, the wavelength corresponding to the each transition can be related by

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where $\mathbf{R_H}$ is the Rydberg constant ($R_H = 1.09678 \times 10^{7}$ m^{-1}), $\mathbf{n_1}$ is the principal quantum number of the lower energy orbital and $\mathbf{n_2}$ is the principal quantum number of the higher energy orbital.

(a) (i) Within the visible spectrum, one can observe lines corresponding to the transition from the n=2 to higher energy levels. Calculate the wavelength corresponding to each of the following transitions:

1. n = 2 → 3
2. n = 2 → 5

(ii) Circle and label these transitions on the above spectrum.

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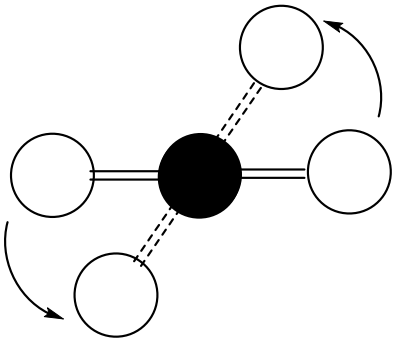
(iii) Determine the energy associated with **transition 1** (in J).

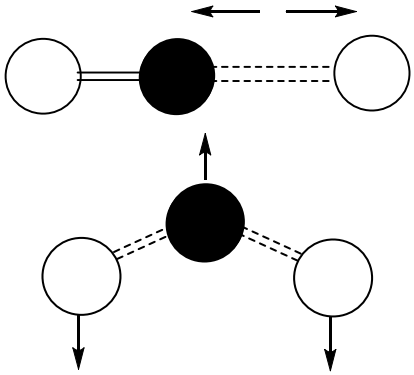
(iv) Qualitatively, how does the energy associated with the n + 1→ n ($\Delta n=1$) transition vary as n increases?

(v) Explain the spacing of the lines in the above spectrum.

As mentioned above, kinetic motion of nuclei in molecules is also quantised. Types of ***quantised*** kinetic motion include:

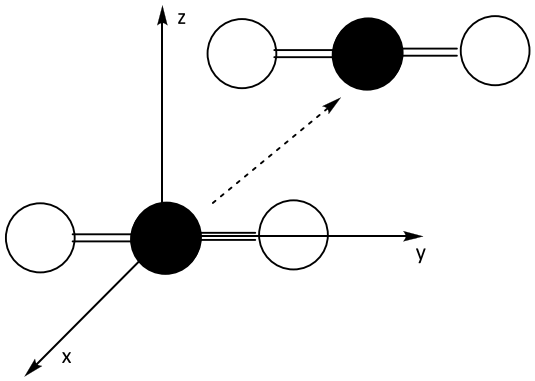


Rotations:
"spinning" a molecule about its centre of mass



Vibrations:
the stretching (top) or bending (bottom) of bonds

Translation is another form of molecular motion, however this form of motion is not quantised. It is described by the motion of the centre of mass of the molecule in space.



Whilst electronic transitions occur in the UV-Visible region of the EM spectrum, vibrations and rotations are excited in the IR and microwave regions respectively.

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Each independent motion of a molecule is called a degree of freedom (DoF). A molecule with N atoms in 3D requires 3 co-ordinates per atom for complete description and hence has 3N DoF. Generally, 3N-6 of these will be *vibrational* modes. However, in a **linear** molecule, 3N-5 of these will be *vibrational* modes as it has one fewer independent rotational mode.

(b) For each of the following molecules, draw a Lewis structure. Thus determine the number of DoF for each molecule and how many are associated with translation, rotation and vibration.

Molecule	**Ne**	**O_2**	**C_2H_4**
Lewis Structure			
Total DoF			
Vibrational			
Translational	3	3	3
Rotational			

A single vibration (between two atoms) can be approximated as experiencing a parabolic potential energy (like a spring). The allowed energy levels then become dependent on the characteristic vibrational frequency, **ω,** for that particular vibration, and a vibrational quantum number **v (**v = 0, 1, 2, …).

$$E_v = \left(v + \frac{1}{2}\right)h\omega \quad (\text{in J})$$

When the frequency of the radiation matches the resonant frequency of the bond(s), transitions between vibrational states occur. This frequency, **ω,** can be related to the following molecular properties: **k** is the force constant, or measurement of the stiffness of the bond (N m^{-1}), and **μ** is the reduced mass (in kg): $\mu = \frac{m_1 m_2}{m_1 + m_2}$, where m_1 is the mass of atom 1 and m_2 is the mass of atom 2.

$$\omega = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Note: 1 amu = 1.661×10^{-27} kg

(c) (i) Calculate the reduced mass of $^{1}H^{35}Cl$ (in kg).

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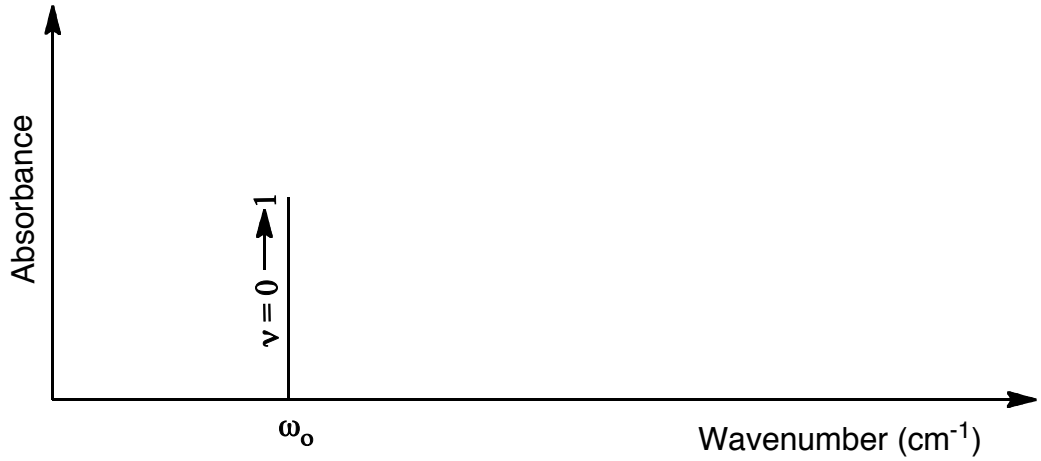
(ii) Determine the energy required for the v = 0→1 transition of $^{1}H^{35}Cl$, given that the force constant is 516 N m^{-1} (in J).

(iii) How does the energy emitted/absorbed in Δv= ±1 transitions vary as v increases?

(iv) Thus, sketch on the following IR spectrum where the following transitions will be found with respect to the v= 0 → 1 transition (remember a spectrum shows at what energies absorbances of radiation occur).

1. v = 1 → 3 2. v = 2 → 5 3. v = 3 → 4

Note that frequency is often reported in wavenumber, ṽ, which is the inverse of wavelength (in cm^{-1}).



One would naturally expect to observe a number of peaks in the spectrum equal to the number of vibrational degrees of freedom for each molecule. However, not all vibrations are IR active. Quantum mechanically, there **must be a change in dipole moment** within the molecule during the vibration which can interact with the EM radiation.

This dipole moment can be considered as a product of charge difference and distance of separation. It arises due to a difference in electronegativity of two atoms. The net dipole moment arises from the sum of all the individual bond dipole moments.

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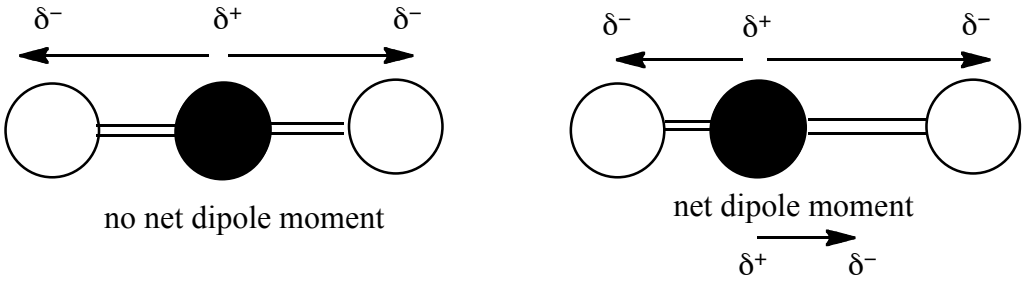
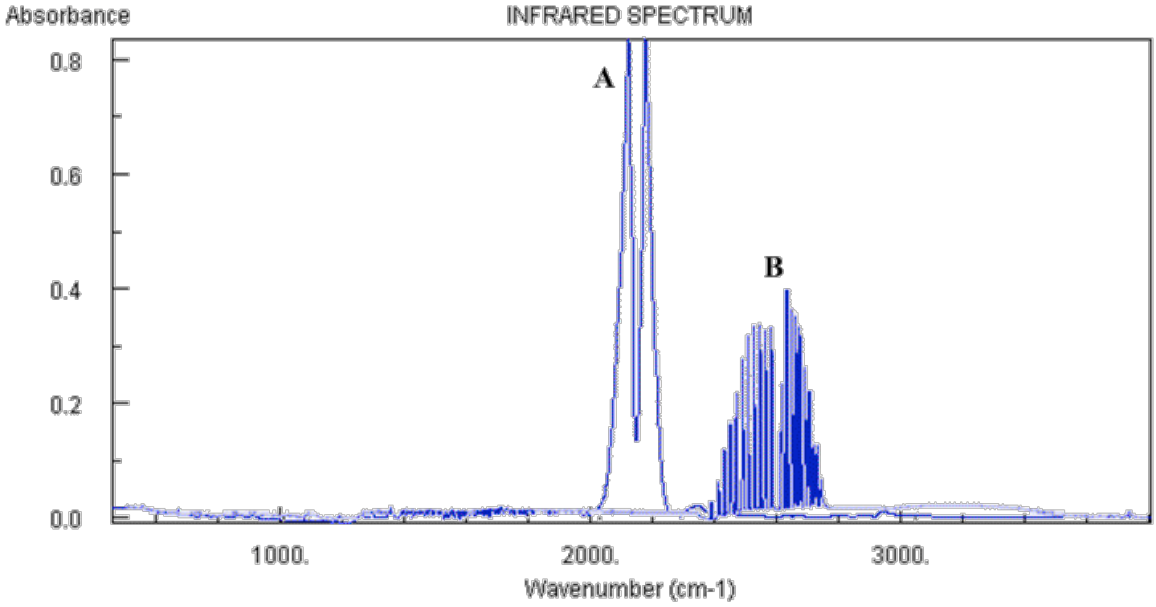
For example, the CO_2 molecule in a neutral state does not exhibit a dipole, however, as we lengthen a bond and shorten the other in an asymmetric-type stretch, we observe a change in dipole moment. The arrows points from the positive charge to the negative charge.



Let us consider the case of simple diatomic molecules first.

(d) Below is an infrared spectrum of a mixture of HBr, CO and N_2 and a table containing reduced mass and force constant data for each of these molecules**.** Note that spectral peaks do not appear as single sharp lines. We thus use the centre of the peak spread as a good indication of the numerical position of the peak.

k (HBr) = 410 N m^{-1}	k (CO) = 1860 N m^{-1}	k (N_2) = 2300 N m^{-1}
μ (HBr) = 0.99 amu	μ (CO) = 6.86 amu	μ (N_2) = 7.00 amu



Identify which peak (labeled as A or B on the above spectrum) corresponds to which molecule.

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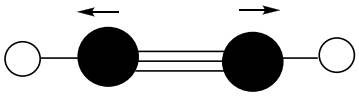
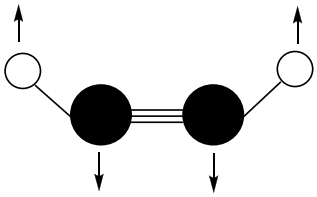
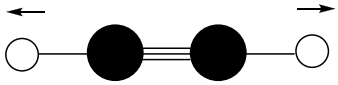
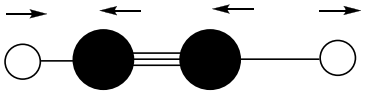
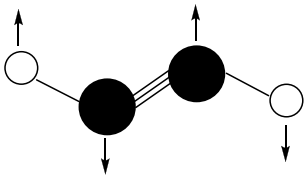
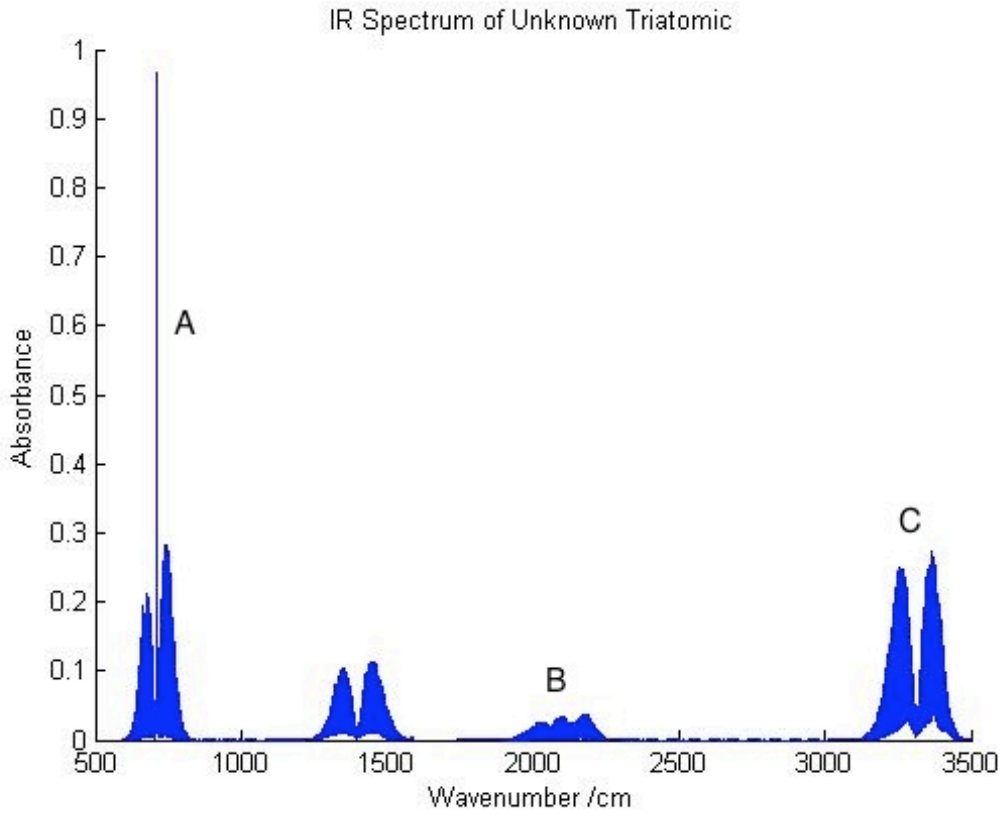
When molecules possess more than two atoms, the independent vibrational modes often involve more than just 2 atoms, but the same general rules and principles apply.

(e) Below are 5 of the vibrational modes of acetylene. Which of these modes will be IR active?

Mode			
Type	*Stretch #1*	*Bend #1*	*Stretch #2*
IR Active	□Yes □ No	□Yes □ No	□Yes □ No
Mode			
Type	*Stretch #3*	*Bend #2*	
IR Active	□Yes □ No	□Yes □ No	

Now we will put our knowledge together to attempt to identify a simple unknown molecule by infrared spectroscopy.

Below is the infrared spectrum for an unknown triatomic molecule with molecular mass 27. The force constant (**k**) of the two bonds are in a ratio of 3:1, implying the existence of one triple and one single bond.



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(f) (i) Suggest a molecular formula and draw the corresponding Lewis structure.

(ii) Determine the number of vibrational degrees of freedom for this molecule.

(iii) Describe/draw the vibrational modes corresponding to peaks A, B and C (labeled on the spectrum), explaining how you reached your answer.

(iv) Explain the appearance of the extra peak at approximately 1400 cm^{-1}.

The author thanks:

- USEPA and NIST for use of spectra.
- Keedy, C.R., (1992), J Chem Ed (69)11: pp A296-A298.

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If there is evidence of collusion or other academic dishonesty, students will be disqualified. Markers' decisions are final.

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