FIRST YEAR CHEMISTRY

SUBJECT INFORMATION

TUTORIAL WORKBOOK

Chemistry 1 – CHEM10003
Semester 2

THE UNIVERSITY OF
MELBOURNE

CONTENTS

Welcome

Knowledge of chemistry is essential for understanding and participating in all branches of technology and science that support modern society. Chemistry 1 (CHEM10003) provides an important basis for the study Chemistry, regardless of whether you intend to major in the subject, require the subject as a pre-requisite or you are just studying Chemistry because you enjoy it! The subject material is presented in a variety of ways reflecting the broad theoretical and practical aspects of the subject.

The theory is mainly presented in lectures that are supported by a tutorial program utilizing multi-media technology within the School of Chemistry's Learning Laboratory. Besides formal classes, students have access to ChemCAL - a web-based system that provides online tutorials and quizzes designed to assist students with their understanding of the subject and give ongoing feedback. The prescribed texts are excellent resources that give students an opportunity to consider the subject material in detail and independently.

The practical aspects of the subject are covered in laboratory activities that will run throughout the semester. While there is a loose association between theory and practical exercises in the subject, it should be remembered that the purpose of the practical program is to develop sound laboratory techniques and good report writing skills.

The University and the School of Chemistry are keen to ensure that our graduates are independent thinkers who are able to research a topic and discover information for themselves. In response to this, students will undertake independent learning tasks (ILT's) throughout the semester. These exercises are designed to complement both the theoretical and practical aspects of the subject and encourage students to become independent learners. The material in these tasks will not necessarily be referred to in the lectures, but is part of the course and will be examined in the semester examination.

Feedback, on a more formal basis, is provided by the feedback (mid-semester) tests. A short test (30 mins) will be delivered at or near the end of each of the three sections of the subject. Students should attempt all three tests and note that the grades obtained for these tests contribute 6% of the final mark. These tests will enable students to monitor their progress in the subject.

Many resources are available to our students, including the Learning Centre, where students can obtain help on a one-to-one basis or as part of a small group. These resources are in place to help students understand the subject. While good performance in exams is important the emphasis should always be on understanding the subject rather than developing strategies to obtain the best possible exam mark with the minimum amount of work. We discourage students from merely focusing on the final exam rather than understanding the subject.

The teaching staff you will encounter over the course of the year have a passion for the subject, with many of our staff having international reputations in various fields of chemical research. We hope you will share this passion and see Chemistry not just as a subject that you study for a few hours a week but rather as an area of modern science that is of fundamental importance to our lives and the way we live. Enjoy the semester!

Professor Muthupandian Ashokkumar

Director of First Year Studies (email: chemistry-first-year@unimelb.edu.au)

Subject Information

Contact

- 36 lectures (3 per week), six 3-hour practical sessions, 11 hours of tutorials, 9 hours of independent learning tasks (ILTs) and 9 hours of ChemCAL.
- Lectures begin in week 1 of semester.
- Tutorials begin in week 2 of semester.
- Practical work commences from week 1 of semester (refer to practical timetable on the LMS).
- Independent learning tasks will begin in week 2.
- The Labyrinth will be open from week 1 of semester.
- Mid-semester feedback tests at the end of weeks 4, 8 and 11.
- The Chemistry Learning Centre will operate from week 2 of semester on Wednesdays, Thursdays and Fridays and from Week 7 Monday to Fridays.

Tutorial and Practical Allocations

Lecture, tutorial and practical allocations are managed by Student Portal. You should select appropriate sessions when constructing your overall timetable using your Student Portal. (http://portal.unimelb.edu.au).

Assessment

- One 3-hour exam at the end of Semester 1 (74 % of the final assessment).
- Three mid-semester feedback tests (6 % of the final assessment).
- Continuous assessment of practical work that contributes 20 % to the final assessment.

Practical work is a "hurdle requirement" which means that you must pass the practical work component of the course to pass Chemistry CHEM10003. **Note that you must attend <u>ALL</u> practical sessions and must pass in at least four out of the six practical sessions in order to pass the practical component. What to do in the case of illness is described in detail in your practical manual.**

Independent learning tasks are also "hurdle requirements". You will need to complete these tasks on the LMS. The topics in these tasks will be examinable in the end of semester examination but will not be covered necessarily in lectures.

Tutorials

Tutorials for CHEM10003 are an integral part of the subject and provide a valuable opportunity for students to develop their knowledge and understanding of Chemistry. It is expected that students will attend tutorials. There is 1 tutorial per week for each student.

Please note that due to time constraints it is not possible to cover all tutorial problems in the class and as a result, tutors may select appropriate problems in order to meet the learning objectives presented in the introduction to each tutorial problem set.

Answers to tutorial questions will be provided in the tutorials. The answers will later be published on the LMS at the end of Weeks 4, 8 and 12.

Tutorial Schedule

Week 1	Weeks 2 – 5	Weeks 6 - 8	Weeks 9 - 12
No tutorial	Tutorials cover lecture content from weeks 1-4	Tutorials cover lecture content from weeks 5-8	Tutorials cover lecture content from weeks 9-12

Mid-semester feedback tests

The mid-semester tests are provided to give you **feedback on your progress** in CHEM10003. The tests will cover the content presented in lectures during weeks prior to the test according to the following program:

Test 1 will cover the Organic Chemistry lecture material in Weeks 1-4 and will be at the end of Week 4;

Test 2 will cover the Physical Chemistry lecture material in Weeks 5 – 8 and will be at the end of Week 8;

Test 3 will cover the Inorganic Chemistry lecture material in weeks 9-11 and will be held at the end of Week 11.

Details of the mid-semester tests will be available through the LMS. If you do not sit any of the tests and you have not been awarded special consideration, then your mark for this component of the assessment will be '0'. Further details regarding the arrangements for the mid-semester test will be available on the LMS (**www.lms.unimelb.edu.au**).

Practical Work Exemption

Students who have previously attempted this subject and have passed the practical component are eligible to apply for an *Exemption from Practical Work.* This is done by completing an application form, which is available from Student Enquires outside the first year laboratory. A list of students who have been granted an exemption will be placed on the First Year notice board outside the First Year Laboratory. If you have not been awarded an exemption, you must attend your practical classes. This is especially important for those who are in the process of applying – do not assume that you will automatically be granted an exemption simply because you have applied.

Illness or misadventure affecting your studies and assessment

Mid-semester tests: If you are unable to complete any of the mid-semester tests because of illness or for other reasons you must contact the First Year Coordinator as soon as possible (chemistry-first-year@unimelb.edu.au). If you are sick you must provide a medical certificate. If your request for Special Consideration is approved then your test result will be calculated based on the average of your other mid-semester results.

Practical sessions: In the event of missing a lab session because of illness or for other reasons you may apply for a make-up practical session by visiting Student Enquiries outside the first year laboratory (Room 187). It is recommended to investigate the possibility of doing a make-up practical session, so you do not miss the educational opportunity of completing the practical. Up to 2 make-up practical sessions can be organised in the case of illness, when a medical certificate is provided within 2 weeks. For other valid circumstances one make-up practical sessions may be scheduled, provided that the practical laboratory is still being run.

Special Consideration and Special Examinations

Applications for special consideration are made through the faculty (Eastern Precinct Student Centre) in which you are enrolled within 3 business days of the final examination (with the 3 days starting the day after the examination). Following an application for special consideration related to the CHEM10003 examination, you may be granted a special examination. **If you are awarded a special examination, you must be available to attend that examination at the University of Melbourne in the special examination period from 6-12 December 2018. Refer to your student portal (http://portal.unimelb.edu.au) for further details. Special examinations will NOT be held at any other time.**

Supplementary Examinations

Supplementary examinations are **NOT** awarded by the Faculty of Science**.** However, if you are awarded a supplementary examination by another faculty you must be available to attend that examination at the University of Melbourne in the supplementary examination period from **6-12 December 2018**. See your student diary for further details. Supplementary examinations will NOT be held at any other time.

Absences due to long term illness or other problems

Students experiencing long term health problems or other difficulties of a personal nature which may hamper progress are advised to discuss these matters with the Director of First Year Studies, Professor Muthupandian Ashokkumar, School of Chemistry, as soon as possible (chemistry-first-year@unimelb.edu.au)**.**

Resources to assist your learning

Learning Management System

Information regarding the subject is available through the University's Learning Management System (LMS). Access to the LMS is obtained through the following site:

http://www.lms.unimelb.edu.au

Important announcements are made through the LMS and it is essential that students regularly check the CHEM10003 subject page in the LMS and/or their @ugrad.unimelb.edu.au email account. In addition, students are able to obtain access to lecture notes (normally as pdf files), tutorial questions, independent learning tasks, mid-semester tests, handouts, answers to past exam questions, staff information and other useful resources through this site. There are also links to other web sites that students may find useful.

Chemistry Home Page

The web address of the chemistry home page is:

http://www.chemistry.unimelb.edu.au

The chemistry web site also contains useful resources and information relating to the School of Chemistry. In particular, details of special events, seminars and research activities are available through this site.

Computer aided learning (ChemCAL) modules

An important part of the **support and feedback** in your Chemistry course at Melbourne is the program of interactive computer aided learning modules. You should use these in combination with your lectures, lab course and problem-based tutorials throughout the Semester.

Use the CAL tutorials in a self-paced and flexible way. Different students take different times to complete them – you take as much time or as little as you decide that you need. You can use them over the web from home, from any of the public access areas on campus, or from the Labyrinth in the Chemistry School. Begin to use ChemCAL modules early in semester for **feedback** on your skills and knowledge and later for revision – but *you* set the pace. The tutorials have a range of information, explanations and problems specifically for your course, with immediate scores on your progress. Access to ChemCAL Online may be achieved directly through the URL: http://chemcal.chemistry.unimelb.edu.au

or via the link on our home page: http://www.chemistry.unimelb.edu.au
or by following the links in the LMS system: http://www.lms.unimelb.edu.au

To check that your home computer is set up appropriately, run the early screens of the *'Using ChemCAL Online*' Module on the ChemCAL Home Page. Your personal username and password for ChemCAL tutorials are the same as for your university email account. See the page in 'Using ChemCAL Online' with its link to ITS Computing Assistance to activate your email account if you have not done so already. There are 12 tutorials in the CHEM10003 CAL program. The Syllabus and References document also reference them to specific sections of the syllabus.

A recommended schedule to make sure you use the ChemCAL modules well is –

Weeks 1 to 4	Introducing ChemCAL Online
	Structure and Bonding in Alkanes
	Conformers, Stereochemistry and Cycloalkanes
	Alkenes, Benzene and Alkynes
	Organic Functional Groups
Weeks 5 to 8	Measurement and Stoichiometry
	Behaviour of Gases
	Chemical Energy and Calorimetry
	Chemical Equilibrium
Weeks 11 to 12	Acids and Bases
	Weak Acids and Bases
	Molecular Shape and Bonding
	Ionic Solids and Silicates

ChemCAL Online Feedback Tests

As well as the ChemCAL Online topic tutorials and prelab modules, the ChemCAL Online Feedback Tests are designed to give you practice and timely feedback about your progress as the subject develops. Tests are grouped by topic. The questions are typical of the multiple-choice questions you will encounter in your end-of-semester exam. At the end of semester the Syllabus Revision Tests provide a balanced mixture of topics for you to help with your end of semester revision.

First Year Chemistry Learning Centre

The Learning Centre is a room where students can drop in to seek help with their chemistry problems from the tutor on duty. The Learning Centre will be open from week 2 of semester. The Learning Centre (Room 156) is located on the ground floor of the Chemistry building. Enter the main doors and turn right. Opening hours are from **1 to 2 pm Wednesday to Friday from week 2 of semester and from Week 7 Mondays to Fridays.**

Text book

The prescribed textbook in CHEM10003:

Burrows *et al*, *Chemistry³,* 3rd edition, Oxford, 2016

You are strongly encouraged to read the text to improve your understanding of material presented in lectures and for general educational enrichment. The course syllabus refers to the appropriate sections of this text.

Independent Learning Tasks (ILT)

Your experience at the University of Melbourne should lead to the development of independent and critical thinking abilities in addition to the technical skills developed throughout your course. With the need to develop independent learning skills in mind we have developed a series of Independent Learning Tasks (ILTs). These tasks are designed to expand and enhance your Chemistry knowledge and help you to develop skills in independent learning. You will need to complete the ILTs on the LMS. ILTs are a hurdle requirement and the material covered in the ILTs is examinable. It will not necessarily be covered in lectures. Feedback will be provided. You will complete three independent learning tasks.

Suggested completion Dates for Independent Learning Tasks

ILT- 1	Wednesday 1 August
ILT- 2	Wednesday 15 August
ILT- 3	Wednesday 5 September

QR codes and the LabBytes

The LabBytes are short movies of lab procedures you will be using in your lab course. You can use them as you prepare for each experiment before the class. You can also call up a LabByte in the lab to check as you are about to carry out the procedure.

You need a QR reader app on your smart phone or tablet. There are many available. They are generally free. The app uses the camera on your phone to 'read' the QR code, like the samples here, and directs your phone browser to a website that then downloads that movie or website. You need internet access. You might use UniWireless or the data plan you have with your phone. Movies are typically a few MB and download in a few seconds. The download cost is low within most data plans, but you need to monitor your own traffic levels. Uniwireless access is free to student users on campus. This is a Test Byte. The LabDot QR code is a text message. Use it to test that your QR reader is working.

Syllabus and References

Lectures 1-12 (Organic Chemistry) Weeks 1-4

Professor Spencer Williams and Dr Anastasios Polyzos

Topics	No. of Lectures	References Burrows	CAL Modules
Structure and Bonding Alkanes (sp^3 Hybridisation) • Covalent bonding - H$_2$ • σ-bonding and sp^3 hybridisation in methane and ethane • Structural isomerism • Methane, ethane, nomenclature of saturated hydrocarbons • Conformational isomerism: ethane, butane • Cycloalkanes • Stereochemistry, Optical activity, enantiomers and their physical/chemical properties. • Racemates. • Designation of absolute configuration • Diastereoisomers • Meso compounds	5	2.1, 2.2, 5.2, 5.4 2.5 2.5 18.2 2.5 18.2 18.4 18.4 18.4 18.4	Structure and Bonding in Alkanes Conformers, Stereochemistry and Cycloalkanes
Structure and Bonding Alkenes (sp^2 Hybridisation) • sp^2 hybridisation, σ and π bonding in ethene • Nomenclature of alkenes • Geometrical isomerism • Conjugated alkenes	2	5.3, 5.4 2.5 18.3 2.5	Alkenes, Benzene and Alkynes
Benzene and its derivatives • Kekulé structures/resonance • Nomenclature of substituted benzenes	1	2.2 2.5	
Structure and Bonding of Alkynes (sp hybridisation) • sp hybridisation, σ and π bonding in ethyne • Nomenclature of alkynes	1	 5.2, 5.4 2.5	

Topics	No. of Lectures	References Burrows	CAL Modules
Functional Groups	1		
• Haloalkanes		2.6	Organic
• Alcohols		2.6	Functional
• Ethers		2.6	Groups
• Amines		2.6	
• Carbonyl compounds		2.7	
• Carboxylic acids and derivatives		2.7	
Spectroscopy and Determination of Structure	2		
• The EM Spectrum		3.2	
• Mass spectrometry / combustion analysis information available from molecular formulae		12.1	
• Infrared spectroscopy		12.2	
• Nuclear magnetic resonance spectroscopy: ^{1}H and ^{13}C		12.3	

Problems for lectures 1-12

Some exercises for the Organic Chemistry component of CHEM10003 are given as Problem Set 1 in the Appendix of this Tutorial Workbook

Solutions to Problem Set 1 will be made available on the LMS: http://www.lms.unimelb.edu.au

Further practice questions involving spectroscopy to determine structure are found in Appendix 2.

Lectures 13 - 24 (Physical Chemistry) Weeks 5-8
Professor Muthupandian Ashokkumar

Topics	References Burrows[3] 3rd Ed (& 2nd Ed)	Questions Burrows[3] 2nd Ed	Questions Burrows[3] 3rd Ed	CAL Modules

Gases (3 lectures)
  Gas Laws: an Empirical Approach:
  Boyle's Law, Charles's Law, and Avogadro's Law
  The Ideal Gas Equation
  Mixtures of Gases: Dalton's Law
  Kinetic Molecular Theory and the Gas Laws
  The Speeds of Molecules in a Gas
  Real Gases
	Chapter 8
	8.1 (8.1)
	8.1 (8.1)
	
	8.2 (8.2)
	8.3 (8.3)
	8.4 (8.4)
	8.5 (8.5)
	8.6 (8.6)
		Worked examples: 8.1, 8.2, 8.6, 8.7, 8.8, 8.11
		
		pp 374-376: 1, 3, 5, 6, 9, 10, 11, 15, 17, 21, 23
			Worked examples: 8.1, 8.2, 8.6, 8.7, 8.8, 8.11
			
			pp 378-380: 1, 3, 10, 11, 14, 15, 16, 21, 23, 27, 29
				Behaviour of Gases

Energy and Thermochemistry (3 lectures)
  Energy Changes in Chemistry: Heat and Work
  Enthalpy and Enthalpy Changes
  Enthalpy Changes in Chemical Reactions and Hess's Law
  Variation of enthalpy with temperature
  Internal Energy and the First Law of Thermodynamics
  Measuring Energy Changes
	Chapter 13
	13.1 (13.1)
	13.2 (13.2)
	13.3 (13.3)
	
	13.4 (13.4)
	13.5 (13.5)
	
	13.6 (13.6)
		Chapter 13
		13.3, 13.5, 13.7, 13.8
		13.9, 13.11, 13.13, 13.15, 13.16, 13.17, 13.21, 13.23, 13.25
			Chapter 13
			13.3, 13.5, 13.7, 13.8
			13.9, 13.11, 13.13, 13.15, 13.16, 13.17, 13.21, 13.23, 13.25
				Chemical Energy and Calorimetry

Spontaneity, Entropy and Free Energy (3 lectures)
  Spontaneous processes
  Entropy and The 2nd law of thermodynamics
  The 3rd Law and Absolute entropies
  Entropy changes in chemical reactions
  Gibbs energy
  Variations of Gibbs energy with conditions
	14.1(14.1)
	14.2 (14.1)
	14.3 (14.2)
	14.4 (14.5)
	14.5 (14.5)
	14.6(14.6)
		Ch 14:
		Qualitative: 1, 2
		Quantitative: 13, 15, 18		

Topics	References Burrows[3] 3rd Ed & 2nd Ed	Questions Burrows[3] 2nd Ed	Questions Burrows[3] 3rd Ed	CAL Modules
Chemical Equilibrium (3 lectures)		Worked examples: 15.1, 15.2, 15.3, 15.4, 15.6, 15.7, 15.9 pp 719 - 720: 1, 2, 3, 4, 6, 7, 8, 11, 12,15,17,25	Worked examples: 15.1, 15.2, 15.3, 15.4, 15.6, 15.7, 15.9 pp 721 - 724: 1, 2, 3, 4, 6, 7, 8, 11, 12,15,17, 25	Chemical Equilibrium
Gibbs energy and equilibrium	15.1 (15.1)			
The direction of a reaction: the reaction quotient	15.2 (15.1)			
Gibbs energy and equilibrium constants	15.3 (15.1)			
Calculating the composition of a reaction at equilibrium	15.4 (15.2)			
Effects of conditions on reaction yields and K	15.5 (15.5)			

Problems for the Physical Chemistry component of CHEM10003 are given in the course outline above. These exercises are from Burrows et al, *Chemistry³,* 3rd edition, Oxford, 2017. The student solution manual for *Chemistry³* is available from the OUP website

3rd edition: https://arc2.oup-arc.com/access/burrows3e-student-resources

2nd edition: http://global.oup.com/uk/orc/chemistry/burrows2e/student/solutions/

This is freely available to all students and provides fully worked examples to half the questions at the end of worked examples, boxes, and at the end of each chapter.

Lectures 25 - 36 (Inorganic Chemistry) Weeks 9-12

Associate Professor Guy Jameson and Associate Professor Brendan Abrahams

Topics	References Burrows[3] 3rd Ed (& 2nd Ed)	Questions Burrows[3] 2nd Ed	Questions Burrows[3] 3rd Ed	CAL Modules
Acids and Bases (2 lectures) The Nature of Acids and Bases Brønsted Lowry Theory Lewis Acids/Bases Dissociation of Carboxylic Acids Amine Basicity Acid Strength The pH Scale Calculating the pH of Strong Acid Solutions Calculating the pH of Weak Acid Solutions Bases Strategy for Solving Acid-Base Problems Buffers	7 (7) 7.1 (7.1) 7.8 (7.8) 7.2 (7.2) 7.2,7.4 (7.2,7.4) 7.4 (7.6, 7.7) 7.3 (7.3)	7.1-7.8 7.10, 7.12, 7.13	7.1-7.8 7.10, 7.12, 7.13	Acids and Bases Weak acids and bases
Molecular Structure and Bonding (4 lectures) Lewis structures Formal charge Resonance VSEPR – predicting the shapes of molecules Polarity of molecules Covalent Bonding Valence bond theory (Localized Electron model) Molecular orbital theory Metallic bonding	4.2 (4.2) 5.1 (5.1) 5.1 (5.1) 5.5 (5.5) 5.2 (5.2) 5.3 (5.3) 4.4, 4.5, 5.4 4.5, 5.4 (4.5,5.4) 4.6-4.12 (4.6,4.12) 6.3 (6.3)	4.1,5.1 5.2,5.15 5.3-5.6,27.18 5.7,5.8 4.5,5.10 4.7,4.10,4.11 6.1 1.19a & b,	4.1,5.1 4.5,5.2,5.15 5.3-5.6,27.18 5.7,5.8 4.6,5.10 4.8,4.11,4.12	Molecular Shape and Bonding Shape and Bonding in Molecules
Trends in the Periodic Table (1 lecture) Size, ionization energy, electron affinity, electronegativity, metallic character Ion size Intermolecular forces	3.7 (3.7) 4.3 (4.3) 6.5 (6.5) 27.1 (27.1) 1.8, 17.3 (1.8, 17.3)	3.16, 3.17 27.2 17.14	3.17, 3.18 27.2 6.1 1.19a & b, 17.18,17.19	
Solubility, Solubility Equilibria and Lattice Energy (1 lecture) Solubility - gases and solids Solubility equilibria and solubility products Lattice energy	Box 15.1 (Box 15.1) 6.5 (6.5), 6.6 (6.6)	Box 15.1 (c) and (d) 6.13	Box 15.1 (c) and (d) 6.13	

Topics	References Burrows[3] 3rd Ed & 2nd Ed	Questions Burrows[3] 2nd Ed	Questions Burrows[3] 3rd Ed	CAL Modules
Structures of Solids (2 lectures)				
X-ray diffraction	Box 6.4	6.4, 6.7	6.4, 6.7	
Sphere packing models	(Box 6.4)			Ionic Solids and Silicates
Structures of metals	6.2 (6.2)			
Structures of ionic compounds	6.4 (6.4)			
Silicates	6.5 (6.5)			
	27.3 (27.3)			
Main Group Chemistry (2 lectures)				
Structures of the elements	6.1 (6.1)			
Chemistry of main group compounds	27.2 - 27.6 (27.2 - 27.6)			

Problems for the Inorganic Chemistry component of CHEM10003 are given in the course outline above. These exercises are from Burrows et al, *Chemistry[3]*, 3rd edition, Oxford, 2017.

The student solution manual for *Chemistry[3]* is available from the OUP website

3rd edition: https://arc2.oup-arc.com/access/burrows3e-student-resources

2nd edition: http://global.oup.com/uk/orc/chemistry/burrows2e/student/solutions/

This is freely available to all students and provides fully worked examples to half the questions at the end of worked examples, boxes, and at the end of each chapter.

In Appendix 3 at the back of this workbook, there are some essential practice questions for Weeks 9-12 on Inorganic Chemistry. The answers will be provided on the LMS
http://www.lms.unimelb.edu.au

CHEM10003 – WEEK 2 - Alkanes and Cycloalkanes

Introduction

Representing the structures of organic molecules on paper is an important skill for a chemist. Newman projections are descriptive tools used by chemists to represent conformers of alkanes, on the page. They enable chemists to determine the differences in energy between the conformers of the molecule.

Perspective drawings of cycloalkanes also allow you to do this. The conformers of *cis-* and *trans-*isomers of substituted cyclohexane are also considered in this tutorial. The use of models is crucial in appreciating the two different chair conformers related to each other by ring flip. The models used in this tutorial also help to illustrate the underlying reasons for any differences in energy between these two chair conformers. The following exercises provide opportunities for you to practice these skills.

After this tutorial you should be able to:
- draw the conformer of an alkane in the form of a Newman projection
- generate and rank the energies of different alkane conformers
- represent clearly on paper the two chair conformers of a given *cis-* or *trans-*isomer of a substituted cyclohexane
- rank the relative energies of two conformers
- predict the number of structural isomers that are represented by a simple molecular formula

Question 2.1

Draw the three Newman projections constructed by looking down the C(1)-C(2) bond of the staggered conformations of 2-methylpentane. Repeat this process by looking down the C(2)-C(3) bond. In each case, indicate which conformations will be the most stable.

Question 2.2

Construct and draw chair conformations for *cis-* and *trans-*1,2-cyclohexanediol. For each of them convert the structure to the alternate chair conformation. Are all of these conformations of equal energy?

Question 2.3

Draw the most stable chair conformation for each of the following structures (you must clearly indicate whether the ring substituents are either axial or equatorial).
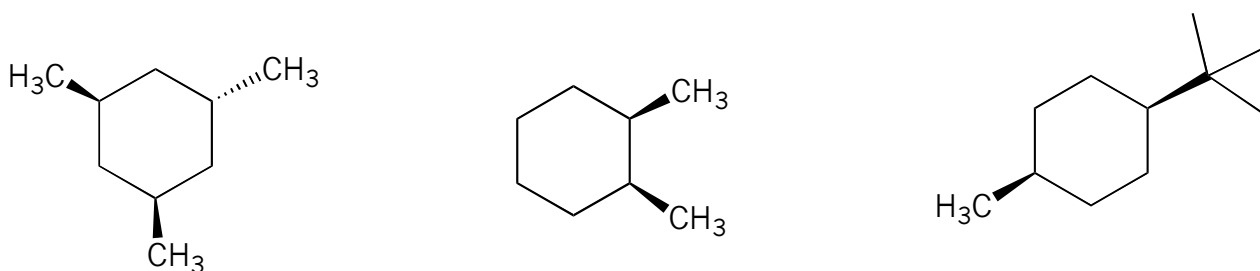
Homework question

Question 2.4

An unknown alkane was found to have a molecular mass of 86 g mol^{-1}.
(a) Determine the molecular formula of the alkane.
(b) Draw all possible structural isomers of the alkane.
(c) How many different monobromo derivatives can be formed from each of the alkane isomers?
(d) For the alkane isomer that can form two monobromo derivatives, how many dibromo derivatives can be formed?

Workspace

Introduction

In this tutorial you will continue your study of isomers. You know that isomers, in general, have the same molecular formula, but different structures.

Structural isomers have different connectivity between the atoms, whereas stereoisomers have the same connectivity but have a different orientation. These differences can be

- across the plane of a ring as you saw in Week 2 tutorial leading to cis and trans isomers
- across the plane of a double bond which gives us E and Z isomers (Week 4 tutorial)
- about an asymmetric centre which gives us R and S isomers. (Week 3 tutorial)

Asymmetry plays a large role in organic chemistry. Perspective drawings of asymmetric molecules (using dashes and wedges) are used to indicate stereochemistry in asymmetric molecules. In this tutorial you will learn how to determine an asymmetric or chiral centre as a carbon with four different groups bonded to it. The mirror image if this molecule will have the same connectivity, but it will not be superimposable and will be a different molecule. You will learn a way to tell the difference between for these molecules and assign them an absolute configuration.

After this tutorial you should be able to:

- identify asymmetric centres in an organic molecule
- represent the spatial arrangement of asymmetric molecules on paper
- assign asymmetric centres with the correct absolute configuration (*R* or *S*)

Question 3.1

Place an asterisk (*) by each of the asymmetric centres contained in molecule **D** shown below:

D

Workspace
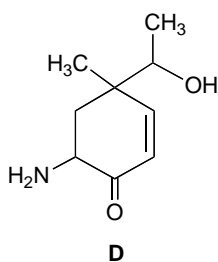
Question 3.2

Using the model-building kits provided, construct mirror images of $CH_3CH(OH)CH_2CH_3$.
Using the models, determine whether these mirror images are superimposable on the original molecules. Are these molecules optically active?

Reproduce these 3-D models on paper, labelling *R* or *S*.
[Draw tetrahedral three-dimensional diagrams for all models, using wedges (▬▬◼) for 'out of the plane' and dotted (dashed) lines (⋯⋯ⁱⁱⁱⁱ) for 'into-the plane' bonds.]

3-D diagram of a tetrahedral centre
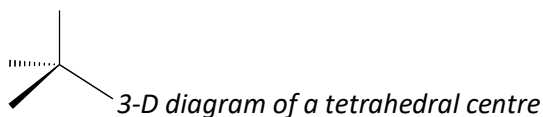
Homework Questions

Question 3.3

In the molecule you studied last week, *cis*- and *trans*-1,2-cyclohexanediol, you drew all the chair conformers for the cis and trans isomers.
Are any of these molecules asymmetric i.e. can they display optical isomerism? (If you are not sure, construct the mirror image and see whether it is superimposable on the original).

Question 3.4

Assign the absolute configuration (*R,S*) of all of the asymmetric or stereogenic centres in each of the following compounds.

i)

ii)

iii)

iv)

v)

vi)

Workspace
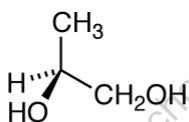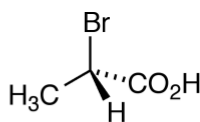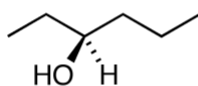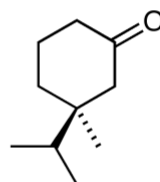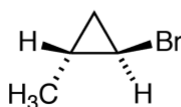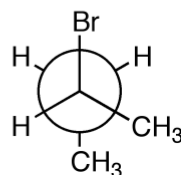
Question 3.5

Classify each of the pairs of structures (i)–(v) using one of the following descriptions:

(a) same compound

(b) structural isomers

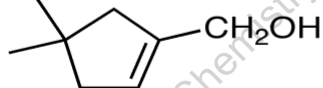(c) pair of enantiomers

(d) pair of diasterisomers

i)

ii)

iii)

iv)

Workspace
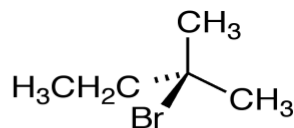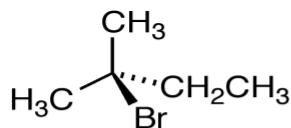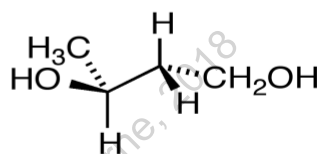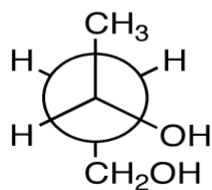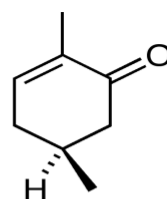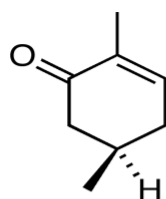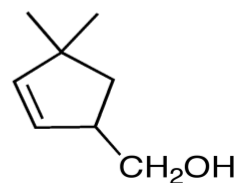
Introduction

This tutorial considers molecules that contain double bonds - alkenes. Because there is no rotation about a double bond, different geometric isomers are possible. These molecules have the same connectivity, but the orientation of the groups across the plane of the double bond is different. You will learn how to determine when geometric isomers can be formed and how to distinguish these stereoisomers by labeling them E and Z. You will also look at molecules containing more than one chiral or asymmetric centre, and define a meso compound and diastereoisomerism.

The hybridisation of carbon atoms is also considered in this tutorial. Hybridisation is a model that enables us to explain the way atoms in organic compounds bond to each other.

At the end of this tutorial you should be able to:

- name alkenes
- identify and label geometric isomers using the *E* and *Z* descriptors
- identify and name diastereoisomers
- identify and name a *meso*-compound
- recognize the type of hybridisation (*sp³*, *sp²* or *sp*) of all carbon atoms present in any molecule

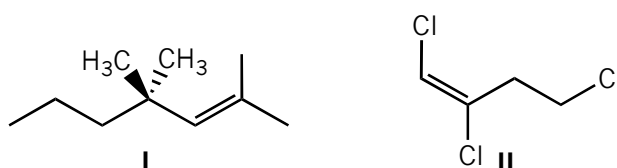**For Tutorials 2-4 there are more questions to be completed in Appendix 1 on page 89.**

Question 4.1 (Revision question)

Indicate the absolute (*R*, *S*) configuration of molecule E.

E
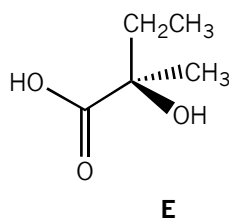
Question 4.2

Give the IUPAC name for compounds I and II (shown below). Each name should include stereochemical (*R*, *S*) or geometrical (*E*, *Z*) descriptors, if relevant
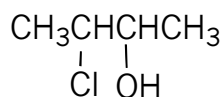

I   **II**

Question 4.3

What happens when we have more than one asymmetric centre in a molecule?
How many asymmetric atoms are in the following molecule?

$$CH_3CHCHCH_3$$
$$\quad\quad |\quad |$$
$$\quad\quad Cl\quad OH$$

How many stereoisomers do you expect for this compound? (Hint: 2^n isomers are possible, where n is the number of asymmetric atoms).
Draw and label all the stereoisomers for the above compound.

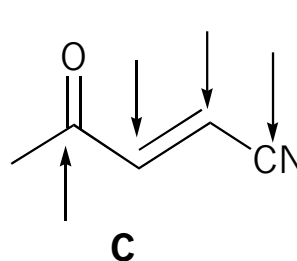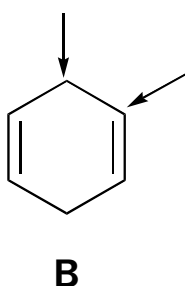**Question 4.4**

Identify all the asymmetric centres in the molecule below.
Draw all the possible stereoisomers of this molecule. Identify which of these are diastereoisomers and which of the stereoisomers would be <u>chiral</u>.
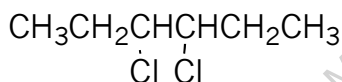
$$CH_3CH_2CHCHCH_2CH_3$$
$$\quad\quad\quad\quad |\quad |$$
$$\quad\quad\quad\quad Cl\quad Cl$$

Asymmetry plays a large role in organic chemistry. Perspective drawings of asymmetric molecules (using dashes and wedges), are used to indicate stereochemistry in asymmetric molecules. The following exercises provide opportunities for you to practice these skills.

Question 4.5

For the molecules **A**, **B**, **C** shown below indicate on the diagrams the hybridisation (*sp³*, *sp²* or *sp*) of the arrowed atoms (students will not have encountered sp hybridisation yet, so take time to work through it with them):

$$H-C\equiv C-CH_3$$
A

B

C
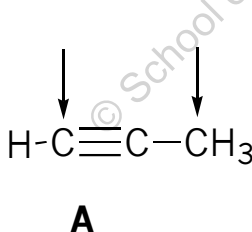
Homework question

Question 4.6

A substance of the formula C_7H_{14} is known to be a mono-substituted cycloalkane. Draw all possible structural isomers and indicate those (if any) that can exist as stereoisomers.

Workspace

CHEM10003 – WEEK 5 – Aromaticity and Spectroscopy

Introduction

This session focuses on the determination of aromaticity, the use of spectroscopy and the characterization of organic compounds by spectroscopic techniques.

At the end of this tutorial you should be able to:

- explain why a molecule is aromatic
- name substituted benzenes
- use elemental analyses to determine the empirical formula of a compound
- interpret the information presented in a mass spectrum
- use infrared spectroscopy to identify the presence of certain functional groups
- recall the infrared bands expected for selected functional groups
- interpret a ^{13}C NMR spectrum
- interpret a ^{1}H NMR spectrum
- calculate the expected number and type of ^{1}H and ^{13}C nmr peaks for simple organic molecules
- draw upon all the above information to determine the structure of a molecule.

Some extra exercises for this tutorial are provided in the Appendix 2 on page 93. The answers are in brackets at the end of the questions.

Also the free *CEA Chemical Detectives* app for iphones and ipads is available for useful practice.

Question 5.1

Ortho-Dimethylbenzene (*o*-xylene) is an example of an aromatic compound.
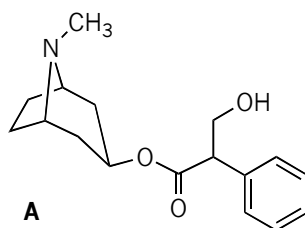Briefly explain why *o*-xylene is considered to be aromatic.
There are three other aromatic structural isomers of xylene (C_8H_{10}). Draw and provide IUPAC names for these three isomers.
Which of the structures you have drawn in part (b) are optically active? Briefly explain.
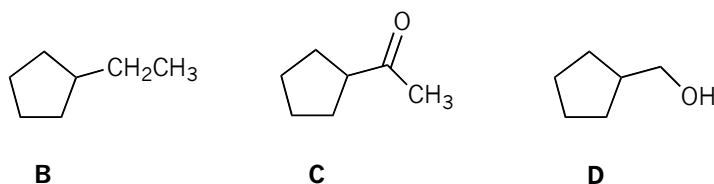
Question 5.2

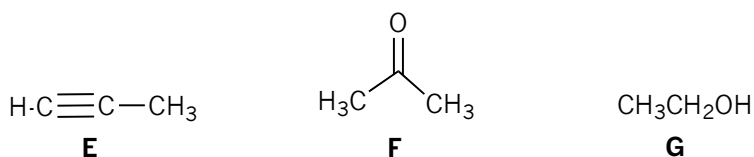Name all the functional groups present in atropine **A** (below).

A

Workspace

Question 5.3

Which of the three molecules **B-D** would you expect to exhibit an absorption band close to 3400cm^{-1}?

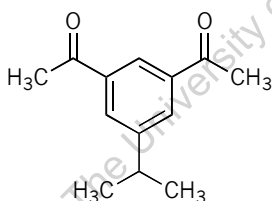|		
B	**C**	**D**

Question 5.4

Which of the three molecules **E-G** would you expect to exhibit a strong absorption band close to 1700cm^{-1} in the infra-red spectrum?
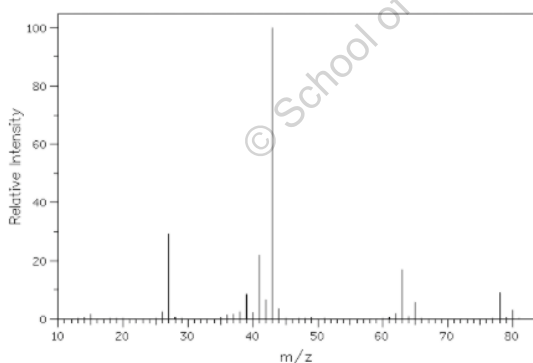
$$H\text{-}C\equiv C\text{-}CH_3$$

E

H_3C—C(=O)—CH_3

F

CH_3CH_2OH

G

Question 5.5

How many signals would you expect to see in the in the ^{13}C NMR spectrum of the compound shown below? Justify your answer by reference to the structure.

Question 5.6

The mass spectrum of 2-chloropropane is given below.

(a) Why does the mass spectrum show two molecular ion peaks at m/z = 78 and 80, rather than just one.

(b) Suggest a possible species that has the m/z values of 43.

(c) How many signals would you expect in a ^{13}C NMR spectrum?

(d) How many signals would you expect in a ^1H NMR spectrum? Would you expect any splitting?

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Workspace

Introduction to characterization

You have been introduced to some of the spectroscopic techniques that are routinely used by chemists to characterize compounds. Among these techniques are ^1H and ^{13}C NMR and infrared spectroscopy.

Elemental Analyses - Provides information for determining the empirical formula.

Mass Spectroscopy - The mass of the parent ion, combined with the results of the elemental analysis, allow for the determination of the molecular formula.

Infrared Spectroscopy - Provides information about the types of functional groups present.
[*Recall that the presence of an absorption band in a particular region indicates the presence of a particular kind of covalent bond. The table below contains selected characteristic IR absorptions of some functional groups.*]

Function Groups	Band Position	Intensity of absorption
$-NH_2$	$3600\text{-}3400 \text{ cm}^{-1}$	medium
$-OH$		strong, broad
$-C\equiv N$	$2300\text{-}2100 \text{ cm}^{-1}$	medium
$-C\equiv C-$		medium
$>C=O$	$1800\text{-}1540 \text{ cm}^{-1}$	strong
$>C=C<$		medium

NMR Spectroscopy - Provides the map of the carbon-hydrogen framework.

^{13}C NMR spectra

The number of lines present (split) = the number of different carbon environments present.

If the number of lines present is less than the number of carbon atoms in the molecular formula then some degree of symmetry exists in the molecule.

Resonance coupling uses the N + 1 rule: the number of lines observed for a signal = N + 1, where N = the number of protons on that carbon (CH_3- the peak due to a methyl carbon would be split into four).

^1H NMR spectra

The size of the peaks is related to the number of protons present.

The relative size of the peaks indicates how many protons are present on nearby atoms.

Resonance coupling uses the N + 1 rule: the number of lines observed for a signal = N + 1, where N = the number of protons at the adjacent nucleus (separation by 3 bonds).

Double Bond Equivalent Calculations

This is a concept that is likely to be unfamiliar to you, however for this tutorial the DBE calculation will provide you with useful structural information for characterizing molecules with a known molecular formula.

The DBE = (2n4 + n3 - n1 + 2)/2 where:

  n4 is the number of tetravalent atoms (*e.g.* C, Si, etc.)

  n3 is the number of trivalent atoms (*e.g.* N, etc.)

  n1 is the number of univalent atoms (*e.g.* H, F,Cl, Br etc.)

Note: a carbon-carbon triple bond, would count as two DBE's and a ring would count as one DBE.

  Example: Benzene C_6H_6 DBE = (12 - 6 + 2)/2 = 4

    i.e. 1 ring + 3 double bonds

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Workspace

Use the method provided in this information and your knowledge to determine the structure of the following compound. There are several more in Appendix 2 at the back of the book which you can complete for homework and revision.
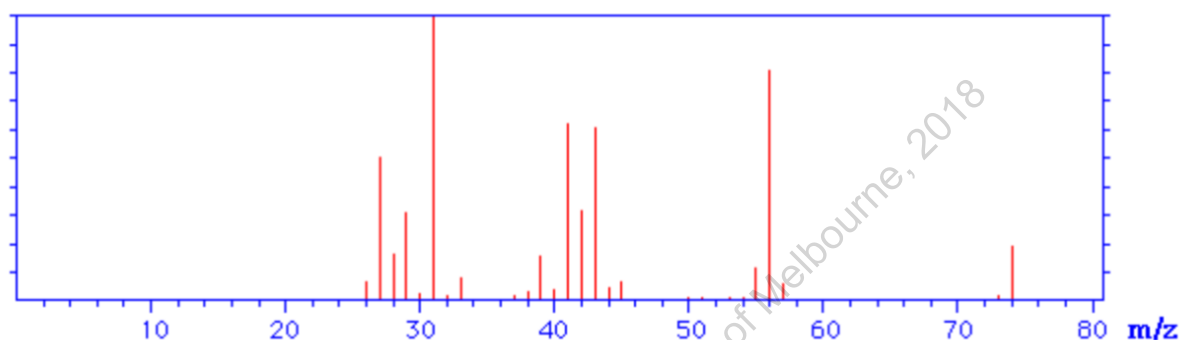
Question 5.7

(a) A small sample of an unknown compound was analysed yielding the following combustion analysis data:

%C 64.80; %H 13.61; %O 21.59

Use this data to determine the empirical formula.

The empirical formula of the compound is C_ H_O_

(b) The mass spectrum of the unknown compound is shown below.

Which peak corresponds to the molecular ion for this compound? Molecular ion m/z _____

What is the molecular mass of the compound? Molecular mass _____

What is the molecular formula of the compound? Molecular formula: _____
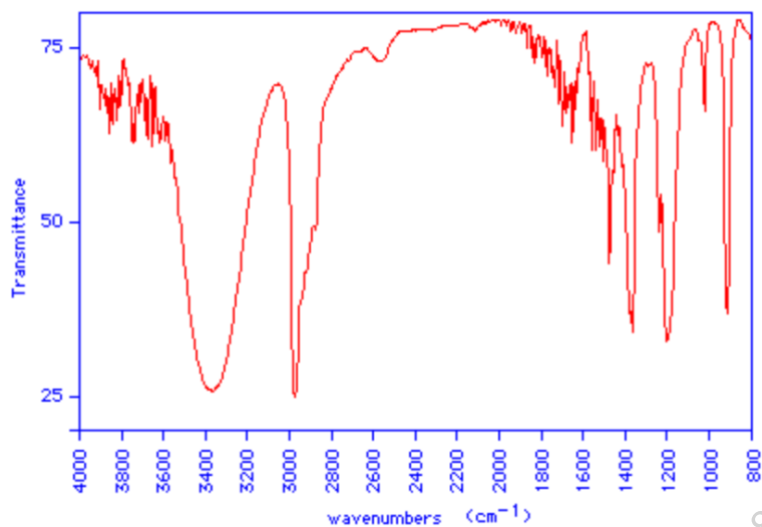
(Hint: remember the empirical formula of the compound).

(c) Determine the number of Double Bond Equivalents for the unknown compound.

DBE for unknown compound _____

Workspace

(d) The infrared spectrum of the unknown compound is shown below:

Examine this spectrum and decide which functional groups are present.

Functional groups present

☐ O—H   ☐ N—H   ☒ C—H

☐ C=C   ☐ C=O   ☐ C≡C   ☐ C≡N

(e) The ^{13}C NMR spectrum of the unknown is shown below.
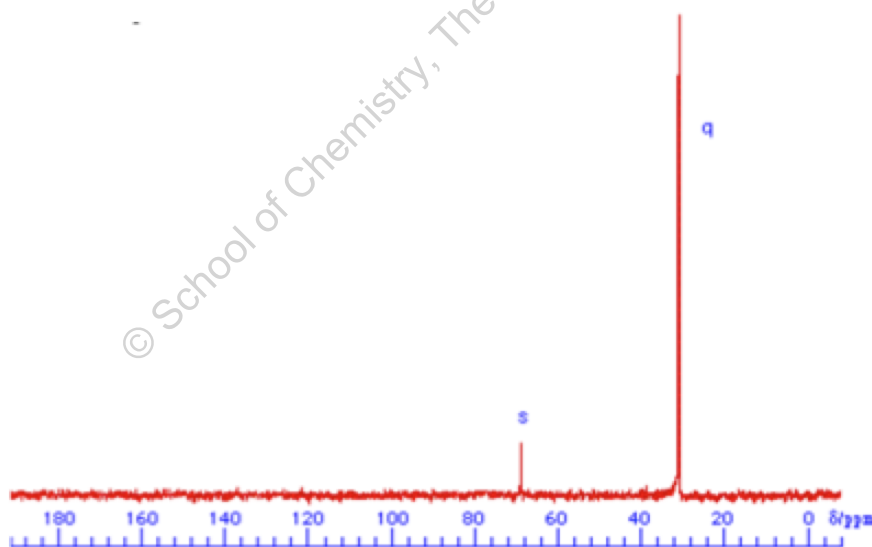
Examine this spectrum and then decide how many different carbon atoms (or carbon atom environments) are present in this molecule. Number of different carbon atoms _____

(f) Based on your conclusions to parts (a) – (e) propose a structure for the unknown compound.

Homework questions – see appendix

Workspace

Introduction

The gas equation, *PV=nRT*, represents the relationship between pressure, volume, temperature and the number of moles of gas particles for an "ideal gas". This tutorial includes questions involving gases and questions that explore the relationship between heat and temperature.

At the end of this session you should be able to:

* apply the gas laws in stoichiometric calculations.
* carry out unit conversions. These relationships will be useful:
    * $1\ Pa = 1\ N\ m^{-2}$
    * $1\ J = 1\ N\ m$
    * $1\ J = 1\ kg\ m^2\ s^{-2}$
* demonstrate an appreciation of the limitations of the ideal gas law model.
* understand that the speed of molecules is related to the molar mass.

Please note that the Table of Constants used in the exam is on the last page in this workbook.

Question 6.1

Consider the flasks shown below. What are the final partial pressures of H_2 and N_2 after the stopcock between the two flasks is opened? Assume the total volume is 3.00 L and there is no reaction between H_2 and N_2. What is the total pressure in torr, atm, and Pa? Note: 1 atm = 760 torr = 101.325 kPa
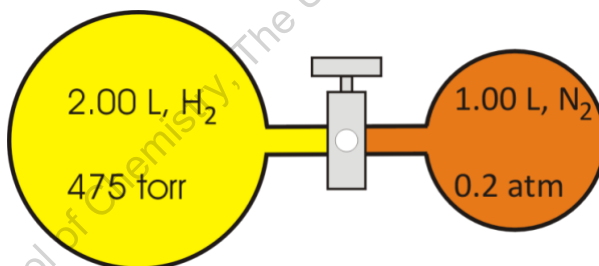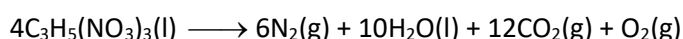

Question 6.2

The density of N_2 (M = 28 g mol^{-1}) in a sealed container is 1.2 mg mL^{-1}. What is the pressure of the gas inside the container at 20°C?

Question 6.3

Nitroglycerine (M = 227 g mol^{-1}) is a shock-sensitive liquid that detonates by the reaction,

$$4C_3H_5(NO_3)_3(l) \longrightarrow 6N_2(g) + 10H_2O(l) + 12CO_2(g) + O_2(g)$$

Calculate the total volume of product gas at 350 kPa and 80°C from the detonation of 0.50g of nitroglycerine.

Workspace

Question 6.4

Here are four statements about real gases:

1. The molecules of a real gas are in constant motion.
2. Molecules of real gases have volume.
3. Molecules of real gases collide with the walls of the container.
4. Molecules of real gases attract each other.

Real gases behave differently from ideal gases because of:

A   1 and 2
B   2 and 4
C   3 only
D   2, 3 and 4
E   1, 2, 3 and 4

Question 6.5

Which list shows the following five gases (H_2, N_2, CH_4, H_2O, CO_2) in the order of the smallest to greatest deviation from ideal gas behaviour at 300 K and 1 atmosphere?

A H_2, N_2, CH_4, CO_2, H_2O
B H_2O, CO_2, CH_4, N_2, H_2
C H_2, N_2, CH_4, H_2O, CO_2
D N_2, H_2, CO_2, CH_4, H_2O
E H_2, CH_4, H_2O, N_2, CO_2

Question 6.6

A 50 L cylinder is filled with 5 kg O_2 gas (M = 32 g mol^{-1}) and at a temperature of 10 ^{o}C.

a) Calculate the pressure in Pa assuming ideal-gas behaviour.
b) Calculate the pressure in Pa assuming real-gas behaviour by using the van-der-Waals equation.
Discuss the difference between the real- and ideal-gas solutions.
(van-der-Waals constants for O_2: a = 0.138 J m^3 mol^{-2}; b = 3.2 x 10^{-5} m^3 mol^{-1})

Question 6.7

Determine the average molecular kinetic energy and molar kinetic energy of neon gas at 150 ^{o}C.

Workspace

Homework questions

Question 6.8

What volume of N_2 is produced when 75.0 g of NaN_3 is decomposed? The reaction is carried out at 26 °C and 1 atm. Molar mass of NaN_3 = 65.01 g mol^{-1}.

$$2NaN_3(s) \rightarrow 2Na\ l) + 3N_2(g)$$
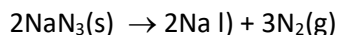
Question 6.9

Calculate the root mean square speed of ammonia gas at 17 °C. Give your answer in m s^{-1}.

Question 6.10

The pressure inside a 10.0 L cylinder containing 1.00 mole of helium at 20 °C is 2.40 atm. The cylinder valve is opened to reduce the pressure inside the cylinder to 0.30 atm. What is mass of helium left in the cylinder at this pressure? (Molar mass of helium is 4.003 g mol^{-1}).

Question 6.11

A 22.4 L cylinder contains 1 mole of fluorine gas at a pressure of 1 atm and 273 K. About 16 g of oxygen gas is injected into the cylinder through a valve and the pressure inside the cylinder increases to 1.5 atm. Which one of the following statements is correct following the injection of oxygen gas?

A   The mole fraction of fluorine increases causing an increase in the total pressure.

B   The mole fraction of fluorine decreases causing an increase in the total pressure.

C   The pressure inside the cylinder increases due an increase in the total number of moles of gases.

D   The partial pressures of fluorine and oxygen become equal causing an increase in the total pressure.

Question 6.12

A 5.00 L cylinder is filled with a mixture of nitrogen and oxygen gases to a total pressure of 26.8 atm at 298 K. The gas mixture contains 44% nitrogen and 56% oxygen.

(a) Calculate the partial pressures of nitrogen and oxygen.

(b) What is the total mass of the gases present in the cylinder?

Question 6.13

20.0 mL sample of an ideal gas exerts a pressure of 0.48 atm at -15 °C.

(a) What volume (in mL) does the sample occupy at 1 bar and 25°C?

(b) What pressure would it exert if it were transferred to a 12 mL flask at 20 °C?

(c) Calculate the temperature (in °C) needed for the ideal gas to exert a pressure of 500 Torr in the 12.0 mL flask.

Workspace

Introduction

The problems in this tutorial are designed to highlight the conventions used by chemists when dealing with the transfer of energy and to develop a quantitative understanding of the relationship between chemical reactions and energy.

After these problems you should be able to:

- recall the sign conventions in energy transfer
- recalculate ΔH values when there are changes in stoichiometry
- employ the relationship $\Delta U = q + w$
- determine the work done on (or to) a system using $w = -P\Delta V$
- calculate the changes in temperature after heat transfer between materials.
- calculate the heat transferred to (or from) a substance after a change in temperature.
- employ Hess's Law to determine the ΔH of a reaction
- understand that enthalpy changes with temperature
- use the Kirchoff equation $\Delta_r H^o_{T2} = \Delta_r H^o_{T1} + \Delta C_p(T_2 - T_1)$
- calculate ΔH of a reaction from ΔH_f (reactants and products)
- explain the spontaneity of simple physical process

Question 7.1

The temperature of one mole of a system is raised by heating it with 860 J of energy. The system expands and does 260 J of work. What is ΔU?

Question 7.2

The ΔH^o for the decomposition of $CaCO_3(s)$ is 178.3 kJ mol^{-1} at 25.0^{o}C and 1.000 atm. What is the ΔU for the decomposition process?

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$
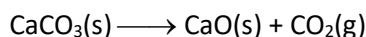
Workspace

Question 7.3

The heat of solution of KBr is 20.0 kJ mol^{-1}. If 0.0880 mol of KBr(s) is dissolved in 125 mL of water that is initially at 24.4°C, what will be the final solution temperature?
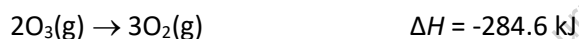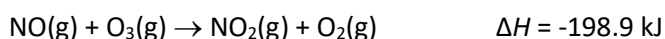
[Molar mass of KBr is 119.01 g mol^{-1}; Specific heat of water is 4.18 J g^{-1} K^{-1}; assume specific heat capacity of the final solution is 4.18 J g^{-1} K^{-1}; assume the density of water is 1 g cm^{-1}]
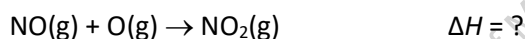
Question 7.4

A mixture of 150 g of lead and 335 g of water is heated from 22.7 to 67.6 °C. How much heat is absorbed by the lead-water mixture? [Specific heat capacities are 4.18 J g^{-1} °C^{-1} for water and 0.128 J g^{-1} °C^{-1} for lead]

Question 7.5

Given the following data:

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \qquad \Delta H = -198.9 \text{ kJ}$$
$$2O(g) \rightarrow O_2(g) \qquad \Delta H = -495.0 \text{ kJ}$$
$$2O_3(g) \rightarrow 3O_2(g) \qquad \Delta H = -284.6 \text{ kJ}$$

Calculate ΔH for the reaction of:

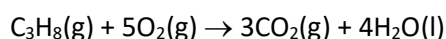$$NO(g) + O(g) \rightarrow NO_2(g) \qquad \Delta H = ?$$

Question 7.6

The enthalpy change for the complete combustion of ethane at 1 bar and 298 K is -1558.8 kJ mol^{-1}. Calculate $\Delta H°$ at 373 K, given the following molar heat capacities, C_p (J K^{-1} mol^{-1}): $C_2H_6(g)$ 52.5; $O_2(g)$ 29.4; $CO_2(g)$ 37.1; $H_2O(l)$ 75.1.

Question 7.7

Given the following heats of formation, determine the $\Delta H°_{reaction}$ for the reaction:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

Data: $\Delta H°_f (C_3H_8(g)) = -103.85$ kJ mol^{-1}; $\Delta H°_f (CO_2(g)) = -393.5$ kJ mol^{-1}; $\Delta H°_f (H_2O(l)) = -285.8$ kJ mol^{-1}

Homework Questions

Question 7.8

What is the final temperature of 50.0 g of water at 18.5°C after it absorbs 1.23 kJ of heat?
[The specific heat of water is 4.18 J g^{-1} °C^{-1}]

Question 7.9

Explain why the evaporation of water from clothes on an outside clothes line on a low humidity day is a spontaneous process.

Question 7.10

What is the change in internal energy, ΔU, when a system absorbs 15 J of heat and does 41 J of work?
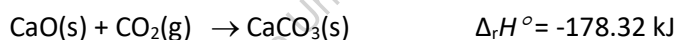
Question 7.11

A certain gas expands in volume from 2.0 L to 6.0 L at constant temperature. Calculate the work done (in J) by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 1 atm.
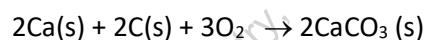
Question 7.12

Calculate enthalpy change **per mole** (of HCl) when 50.0 mL of 0.50 M aqueous HCl at 25 °C is added to 50 mL of 0.50 M aqueous NaOH at 25 °C, the temperature of the mixture rises to 28.2 °C? The specific heat capacity and density of the reaction mixture are equal to those of water.

Question 7.13

Use the following reactions and corresponding enthalpy changes

$$2Ca(s) + O_2(g) \rightarrow 2CaO(s) \qquad \Delta_rH^\circ = -1270.18 \text{ kJ}$$
$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta_rH^\circ = -393.51 \text{ kJ}$$
$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \qquad \Delta_rH^\circ = -178.32 \text{ kJ}$$

to calculate Δ_rH° for the reaction,

$$2Ca(s) + 2C(s) + 3O_2 \rightarrow 2CaCO_3(s)$$

Workspace

Introduction

The second law of thermodynamics states that the entropy (S) of the universe increases for all spontaneous processes. In this session you will consider the spontaneous directions of reactions and how this relates to the thermodynamic quantity known as the change in the system's free energy, ΔG. The relationship between free energy, enthalpy, entropy and temperature will be examined using the equation $\Delta G = \Delta H - T\Delta S$. You will also examine the relationship between free energy and equilibrium.

Many reactions do not go to completion, however, given time they will reach a point where the rate of the forward reaction equals the rate of the back reaction. At this point chemical equilibrium is reached.
After the questions in this session you should be able to:

- identify whether the entropy of the universe is increased or decreased of left unchanged by a process.
- predict the spontaneous direction of a reaction based upon its ΔG value
- perform calculations using the equation $\Delta G = \Delta H - T\Delta S$
- employ the relationship between free energy and equilibrium in calculations
- use the relationship between partial pressure and total pressure in equilibrium calculations
- use Le Chatelier's principle to determine the effect of the change of one quantity in a reaction, on another quantity
- perform calculations to determine equilibrium concentrations, understanding that you cannot always make assumptions (may need to solve a quadratic)
- perform calculations using the van't Hoff equation $\ln K = \Delta_r S^\circ/R - \Delta_r H^\circ/RT$

Question 8.1

Predict the sign of $\Delta S°$ for the transformation below and briefly explain your answer.
$$K(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow KCl(s)$$
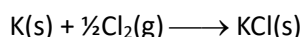
Question 8.2

For mercury the standard enthalpy of vaporization is 58.51kJ mol^{-1} and the standard entropy of vaporization is 92.92 J K^{-1} mol^{-1}.
What is the normal boiling point of mercury?
Is the free energy for vaporization positive or negative below the normal boiling point at standard pressure?
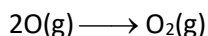
Question 8.3

The enthalpy change, ΔH, for the conversion of liquid water to steam is 40.67 kJ mol^{-1} at 100°C, the boiling point of water. What is the entropy change for vapourisation, ΔS_{vap} at the boiling point?

Workspace

Question 8.4

The standard free energy is related to the equilibrium constant: $\Delta G^o = -RT\ln K$.
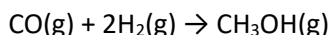For the reaction:

$$2O(g) \longrightarrow O_2(g)$$

Calculate the temperature when $K = 1$ given the following information $\Delta H^o = -498$ kJ mol^{-1} and the $\Delta S^o = -117$ J K^{-1} mol^{-1}. (assume ΔH^o and ΔS^o are independent of temperature).

Question 8.5

Calculate the standard Gibbs energy change, $\Delta_r G^o_{298}$ (kJ mol^{-1}), for the following reaction:

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$$

Use the following data: $\Delta_f G^o_{298}$ in kJ mol^{-1}: CO(g) -137.2; H_2(g) 0.0; CH_3OH -162.0

Question 8.6

Consider the reaction,

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$$
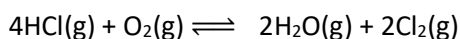
If this reaction is exothermic, predict the effect (increase, decrease, no change) on the quantity in the right hand column of the following table that would be caused by the change indicated in the left-hand column.

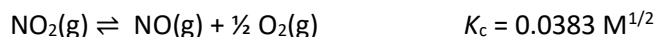| Change	Quantity	Effect
(a) adding O_2	$[Cl_2]$	
(b) adding O_2	$[HCl]$	
(c) decreasing volume of container	mole H_2O	
(d) increasing temperature	K	
(e) increasing temperature	$[O_2]$	

Question 8.7

Given that $K_p = 18$ atm^2 for the equilibrium below, calculate the total pressure, in atm, in a sealed vessel initially containing only NH_4I(s), that reaches equilibrium.
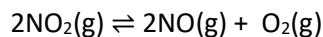
$$NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$$

Workspace

Question 8.8

For the equilibrium,

$$NO_2(g) \rightleftharpoons NO(g) + \tfrac{1}{2} O_2(g) \qquad K_c = 0.0383 \ M^{1/2}$$

What is K_c for the equilibrium:

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

Homework questions

Question 8.9

For each of the following conditions, state in terms of the algebraic signs of ΔH and ΔS the circumstances under which a change will be spontaneous.

(a)   at all temperatures.
(b)   at low temperatures but not at high temperatures.
(c)   at high temperatures but not at low temperatures.

Question 8.10

What is a thermodynamically reversible process? How is the amount of work obtained from a change related to thermodynamic reversibility?

Question 8.11

What is the maximum amount of useful work that could theoretically be obtained at 25°C and 10^5 Pa from the combustion of 48.0 g of natural gas, $CH_4(g)$, to give $CO_2(g)$ and $H_2O(g)$?

Question 8.12

At a certain temperature, $K_c = 0.18$ for the equilibrium:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$
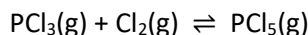
Suppose a reaction vessel at this temperature contained these three gases at the following concentrations:

[PCl_3] = 0.0420 M, [Cl_2] = 0.0240 M, [PCl_5] = 0.0050 M

(a)   Is the system in a state of equilibrium?
(b)   If not, in which direction will a spontaneous change occur to restore equilibrium?

Workspace

Question 8.13

Which one of the following statements is **CORRECT** for the following reaction?

$$R(g) \rightleftharpoons P(g)$$
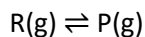
A. $\Delta H = \Delta U$

B. $\Delta H > \Delta U$

C. $\Delta H < \Delta U$

D.   There is insufficient information to predict the relationship between ΔH and ΔU.

Question 8.14

For which of the following processes below is ΔS negative? Explain your answers.

- Evaporating 1 mL of $CCl_4(l)$.
- Mixing 5 mL ethanol with 25 mL water.
- Compressing 1 L of Ne to 200 mL at constant T.
- Raising the temperature of 100 g of Cu from 275 K to 395 K.
- Grinding a crystal of KCL to powder.

Question 8.15

Which one of the following statements is **INCORRECT** for the following reaction?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
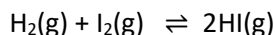
A   When $Q = K$ the concentration of hydrogen will remain constant.

B $K_p > K_c$

C   When $K > Q$, more HI would form.

D   When $Q > K$, more hydrogen would form.

Question 8.16

Ethanethiol (C_2H_5SH) is commonly added to natural gas to provide the "rotten egg" smell of a gas leak. The boiling point of ethanethiol is 308 K and its enthalpy of vaporisation is 27.5 kJ mol^{-1}. What is the entropy of vaporisation of this substance?

A 89.3×10^{-3} J K^{-1} mol^{-1}

B   89.3 J K^{-1}mol^{-1}

C   -89.3J K^{-1} mol^{-1}

D   27.5 kJ K^{-1} mol^{-1}

E   None of the above

Workspace

Question 8.17

The equilibrium below is established when a gaseous mixture of 0.0500 mol of hydrogen and 0.0500 mol of iodine are placed in a closed system of volume 500 mL. Given the equilibrium constant, K_c = 49.5, at the experimental temperature, calculate the equilibrium concentrations of $H_2(g)$, $I_2(g)$ and $HI(g)$.

$$H_2(g), + I_2(g) \rightleftharpoons 2HI(g)$$
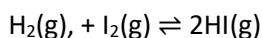
Question 8.18

The following gaseous mixture was allowed to come to equilibrium in a 10 L container at 460°C and the equilibrium constant, K_c = 85.0.

$$SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$$
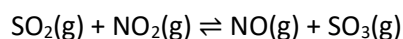
The initial amounts of each species are listed below:

- 0.120 mol $SO_2(g)$
- 0.0328 mol $NO_2(g)$
- 0.0913 mol $NO(g)$
- 0.159 mol $SO_3(g)$

What are the concentrations of the reactants and products when the system reaches equilibrium?
(Hint: Remember when solving a quadratic, you will not have your graphics calculator in the exam.)

Question 8.19

Consider the reaction:

$$PCl_3(l), + Cl_2(g) \rightleftharpoons PCl_5(s)$$
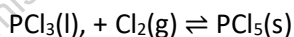
At equilibrium, the pressure of the Cl_2 gas is 0.4 bar. Calculate K_p and the dimensionless K assuming ideal conditions (Hint: K is expressed with thermodynamic activities).

Workspace

Acid/base reactions and the buffering of solutions play an essential role in our health and also our everyday life. An understanding of these processes is therefore important. Finding the pH of a strong acid is a simple process, whereas to determine the pH of a weak acid requires you to use the expression for K_a.

After the questions in this session you should be able to:

- rank acid/base strength using pK_a/pK_b values respectively
- use the expression $pK_a = -\log K_a$
- calculate the K_a of an acid from the K_b of its conjugate base according to $K_a \times K_b = 1.0 \times 10^{-14}$ at 25°C.
- calculate the pH of a weak acid solution
- indicate how a buffer may be prepared using three different approaches
- calculate pH in buffered solutions
- calculate pH in buffered solutions where a strong acid (or a strong base) has been added
- identify circumstances under which a buffer will fail.

Question 9.1

Given the following pK_a and K_a values, which list shows the acids in order of **decreasing** strength?

1. lactic acid, $K_a = 8.3 \times 10^{-4}$ 2. chlorous acid, $pK_a = 2.00$

3. boric acid, $K_a = 7.2 \times 10^{-10}$ 4. acetic acid, $pK_a = 4.74$

  (a)   2>1>4>3   (b)   4>1>2>3   (c)   3>4>1>2   (d)   2>4>1>3   (e)   3>2>1>4   (f)   1>2>3>4

Question 9.2

Indicate which of the following statements is/are true.

i.   The reaction of a strong acid with a strong base continues until the reaction is effectively complete.

ii.   The reaction of a weak acid with a strong base continues until the reaction is effectively complete.

iii.   The reaction of a strong acid with a weak base continues until the reaction is effectively complete.

iv.   In a titration of a weak acid with a strong base the pH at the equivalence point is greater than 7.

v.   In a titration of a weak base with a strong acid the pH at the equivalence point is greater than 7.

Question 9.3 (essential that all students complete and understand)

0.040 moles of propanoic acid ($K_a = 1.4 \times 10^{-5}$) is dissolved in water and the solution made up to 100 mL.
 (a) What is the pH of the solution?
  (b) What is the percentage dissociation of the propanoic acid?
Now, 0.020 moles of NaOH is added to the solution to form a buffer solution. *You may assume that the addition of NaOH occurs without a change in volume of the solution*.
  (c) What is the ratio of propanoate to propanoic acid?
  (d) What is the pH of the solution?
  (e) If the new solution is diluted by a factor of 10 what is the new pH?
  (f) Suggest two other ways of preparing a similar propanoic acid/propanoate buffer solution.

Question 9.4 (essential that all students complete and understand all parts)

  (a) Calculate the pH of a solution that is prepared by mixing 100 mL of 0.050 M ethanoic acid (CH_3COOH) and 100mL of 0.050 M sodium ethanoate ($NaCH_3COO$) which is in equilibrium according to:

$$CH_3COOH\ (aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$
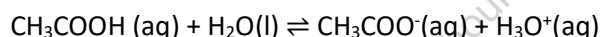
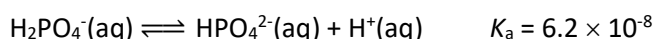 [K_a for ethanoic acid (acetic acid) is 1.8×10^{-5}. Remember Na^+ is a spectator ion.]

  (b) Calculate the pH of the mixture in 9.4(a) following the addition of 0.004 mol of gaseous HCl.
  (c) Calculate the pH of the mixture in 9.4(a) following the addition of 0.004 mol of solid NaOH.
  (d) Calculate the pH of the mixture in 9.4(a) following the addition of 0.04 mol of solid NaOH.

(In parts (b), (c) and (d) assume there is no change in volume, upon addition of the gas or solid.)

Homework Questions

Question 9.5

  (a) Phosphate buffers are important in regulating the pH of intracellular fluids at pH values generally between 7.1 and 7.2. What is the concentration ratio of $H_2PO_4^-$ to HPO_4^{2-} in intracellular fluid at pH = 7.15?
$$H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq) \qquad K_a = 6.2 \times 10^{-8}$$
  (b) Why is a buffer composed of H_3PO_4 and $H_2PO_4^-$ ineffective in buffering the pH of intracellular fluid? (Start by calculating the ratio of H_3PO_4 to H_2PO_4 at pH 7.15.) $K_{a1} = 7.5 \times 10^{-3}$

To enhance your understanding, please complete all homework questions at the back of the Tutorial Workbook on page 103. This is essential. Solutions will be provided on the LMS.

Workspace

Introduction

In this tutorial we examine the shapes of simple molecules and consider different ways of describing the bonding. We have three models which we use to determine shapes of molecules: VSEPR theory, hybridization and valence description and molecular orbital theory.

In this session you will be required to:

- use Lewis structures and the VSEPR approach to determine the electron pair geometry and molecular shape of simple molecules and polyatomic ions.
- determine whether a molecule is polar on the basis of its shape and symmetry
- describe the bonding of a molecule using the valence bond approach
- recognize the hybridization of a central atom from its electron pair geometry

Question 10.1

For each of the following molecules or ions draw a Lewis structure. Show formal charges where required.

$$NH_3 \qquad H_2CO \qquad SF_4 \qquad NO_2 \qquad NO_3^- \qquad CO_3^{2-}$$

Using the Lewis structure for the following species predict the electron pair geometry, molecular shape and bond angles using VSEPR. Show formal charges where required.

$$NH_3 \qquad H_2CO \qquad SF_4 \qquad NO_2 \qquad NO_3^- \qquad CO_3^{2-}$$

Which of these species is a radical?
Which of these species will have a dipole moment?
What conclusion might you draw concerning the structures of species that contain the same number of valence electrons?

Question 10.2

Provide a valence bond description for the NH_3 and H_2CO molecules based upon their VSEPR structures.

Workspace

Homework Questions

Question 10.3

Ozone, sulfur dioxide and sulfur trioxide are significant atmospheric pollutants. Draw Lewis structures and predict the electron pair geometry and shape of the molecules of these substances. Show formal charges where required. Which of these molecules will have a net dipole moment?

Question 10.4

For each of the following species, draw a Lewis structure, showing formal charges (if any), and use VSEPR to predict the electron pair geometry and molecular shape.

$$ClO_3^-, SO_3^{2-}, ICl_4^-, XeF_3^+, IF_3$$
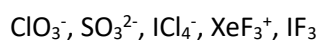
Indicate which of the above ions/molecules has a zero dipole moment.

To enhance your understanding, please complete all homework questions at the back of the Tutorial Workbook on page 105. Solutions will be provided on the LMS.

Workspace

CHEM10003 – WEEK 11- Molecular orbital theory, Intermolecular forces and Solubility products

Introduction

The first part of the tutorial is concerned with intermolecular interactions whilst the second half of the tutorial is focused on the formation of ionic solids.

At the end of this session you should be able to:

- recognise that the simple Lewis structure approach is not always able to account for the observed properties of molecules such as O_2.
- recognise the types and relative strength of intermolecular forces present in a substance
- calculate the solubility products from the concentrations of ions
- use solubility products to predict whether precipitation will occur
- account for the relative differences in lattice energies of simple ionic solids

Question 11.1

Draw a Lewis structure for oxygen, O_2.

(a) How many unpaired electrons are predicted in this model?

(b) What does the term paramagnetic mean?

(c) O_2 is paramagnetic. Is the paramagnetic behaviour consistent with the simple Lewis structure?

(d) Which theory can account for the paramagnetism?

(e) Draw the molecular orbital diagram of O_2.

Question 11.2

Arrange the following species in order of increasing size: O^{2-}, F^-, Na^+, Al^{3+}, S^{2-}
Which of the species has the highest ionization energy?

Question 11.3

Identify the most important intermolecular forces present in the solids of each of the following substances.

| (a) | Ar | (b) | HCl | (c) | HF | (d) | CH_4 | (e) | HNO_3 |
| (f) | $CHCl_3$ | (g) | NH_3 | (h) | SO_2 | (i) | C_{60} (buckminsterfullene) | | |

Question 11.4

For which molecule, in each of the following pairs, would you expect the stronger intermolecular interactions?
a) HF or HBr   b) CH_3CH_2OH or CH_3OCH_3

Workspace

Question 11.5

The concentration of Pb^{2+} in a solution saturated with $PbBr_2$ is 2.14×10^{-2} M. Use this information to calculate K_{sp} for $PbBr_2$.

Question 11.6

A solution contains 1.0×10^{-5} M Na_3PO_4. What is the minimum concentration of $AgNO_3$ that would cause precipitation of solid Ag_3PO_4 ($K_{sp} = 1.8 \times 10^{-18}$)?

Question 11.7

Write a thermochemical equation, for which ΔH is the lattice energy of CaSe.

Provide an explanation for the variation in the following lattice energy values.

Compound	ΔH / kJ mol^{-1}
CaSe	2862
Na$_2$Se	2130
CaTe	2721
Na$_2$Te	2095

Homework Questions

Question 11.8

(a) Draw the energy level (band) diagram of an insulator, semiconductor and metal.

(b) Briefly explain why regular arrays of atoms in solids can form bands.

Question 11.9

Complete the table, then calculate the lattice energy for LiF based upon the following information.

Process	Energy Change / (kJ·mol^{-1})	Name of Process
Li(s) $\longrightarrow$ Li(g)	161	
Li(g) $\longrightarrow$ Li$^+$(g) + e$^-$	520	
F$_2$(g) $\longrightarrow$ 2 F(g)	154	
F(g) + e$^-$ $\longrightarrow$ F$^-$(g)	-328	
Li(s) + ½ F$_2$(g) $\longrightarrow$ LiF(s)	-617	

Workspace

Question 11.10

Teeth are mainly composed of $Ca_3(PO_4)_2$ and $Ca_5(PO_4)_3(OH)$. Calculate the solubility of $Ca_3(PO_4)_2$ in water in gL^{-1} given that $K_{sp} = 1.2 \times 10^{-26}$. Explain why the excess consumption of carbonated drinks (some of which have a pH as low as 3) is likely to lead to an increase in the incidence of dental decay.

To enhance your understanding, please complete all homework questions at the back of the Tutorial Workbook on page 106. Solutions will be provided on the LMS.

Workspace

Introduction

The properties of solids are determined by the arrangement and interaction of atoms and ions. In this session you will examine a number of sphere packing models and relate these to some simple inorganic structures. At the end of this session you should be able to:

- recognise the similarity and differences between hexagonal close-packing (HCP) and cubic close packing (CCP)
- Identify the octahedral and tetrahedral interstitial sites in close-packed structures
- calculate and recall the ratio of 2 tetrahedral sites : 1 octahedral site : 1 sphere in close-packed structures
- recognise the similarities and differences that exist between the following pairs of structures:
  zinc blende and wurtzite   and   NaCl and zinc blende
- determine the formula of an ionic compound from inspection of its unit cell
- calculate the ionic radii of ions, from unit cell dimensions
- represent finite and infinite silicate structures using simple tetrahedra
- determine the charge on finite and infinite silicate structures

Tutor demonstration using models: Exercise A: HCP and CCP and tetrahedral and octahedral holes

From the model kits available identify the close packed rafts of spheres. Place two of these close packed rafts together so that each sphere from the second layer settles down into hollows of the first layer [Fig 1.1]. Note that only *half* the hollows in the first layer contain atoms from the second layer. Identify the octahedral and tetrahedral sites between these two layers.
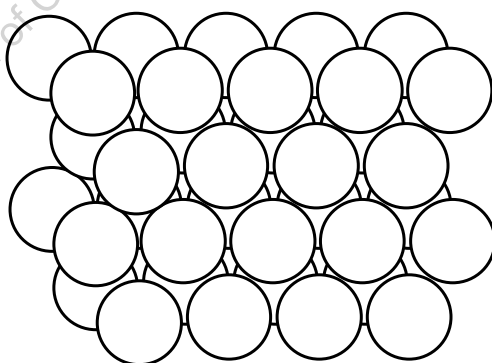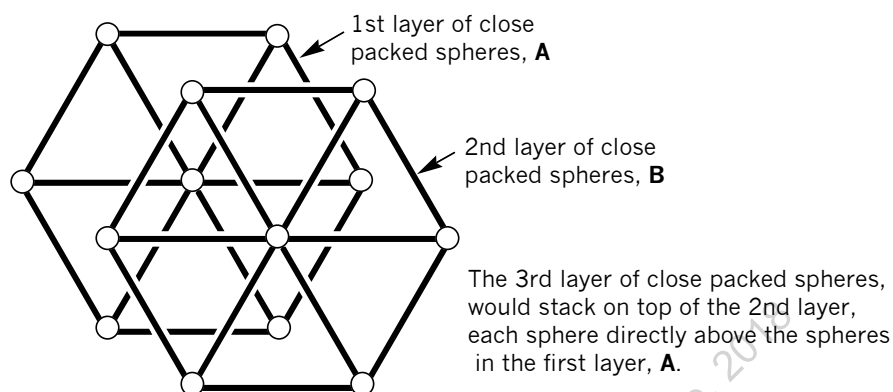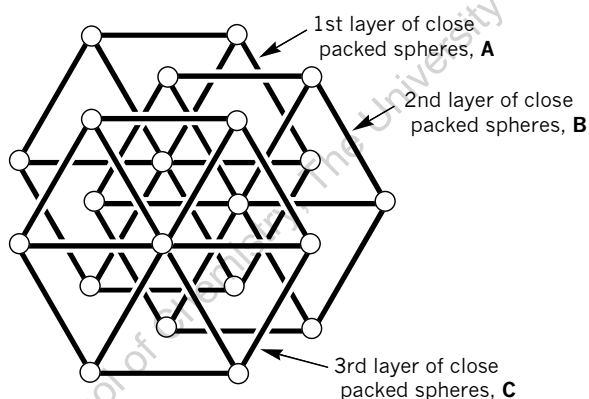

Figure 1.1 Layers of Spheres

Workspace

There are two distinct ways in which a third layer can be added to the first two:

i.   The spheres of the third layer can be directly above the spheres of the first layer so that a sequence of alternate layers ABAB builds up the lattice. This is referred to as a Hexagonal Close Packed (HCP) arrangement.

1st layer of close packed spheres, **A**

2nd layer of close packed spheres, **B**

The 3rd layer of close packed spheres, would stack on top of the 2nd layer, each sphere directly above the spheres in the first layer, **A**.

ii. The spheres of the third layer can be placed so that they lie above the unfilled hollows in the first layer. The packing sequence in this case is referred to as ABCABC and is referred to as Cubic Close Packing (CCP).


1st layer of close packed spheres, **A**

2nd layer of close packed spheres, **B**

3rd layer of close packed spheres, **C**

Using the rafts of spheres convince yourself of the two different ways of adding the third layer of close-packed spheres.

Workspace

Interstitial Sites in Close Packed Layers

The tetrahedral site is the vacancy
at the centre of the diagram below.

● First layer of atoms
○ Second layer of atoms
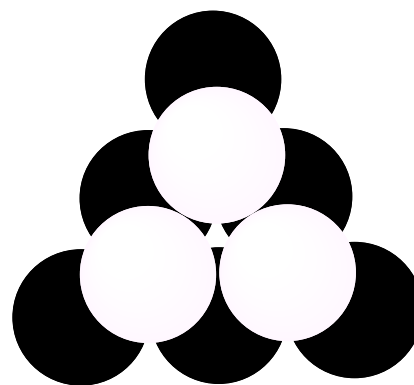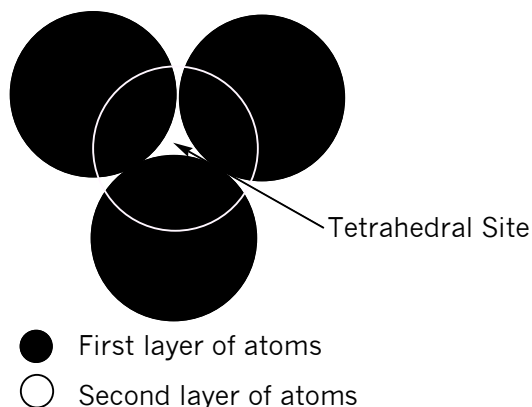
The octahedral site is the vacancy
at the centre of the above diagram.

Tetrahedral Sites: The space enclosed by these four spheres is called a tetrahedral site.

Octahedral Sites: The space enclosed by a bottom triangle of spheres on which is situated another triangle of spheres.

Student centered activity with completed tutor model on the document camera: Exercise B

Using the layer containing one blue sphere as the middle layer, make a close packed sequence of three layers. [*The blue sphere is typical of any sphere (metal atom or ion) in this arrangement.*]
  i.   Place the small black spheres in the octahedral sites of which the blue sphere is part.
  ii.   Place the small red spheres in the tetrahedral sites of which the blue sphere is part. (Hint: Keep them in place with the blue-tac provided).

Having completed exercise B you should now be able to answer Question 12.1

Question 12.1

  i.   How many octahedral sites directly surround any single sphere?
  ii.   How many tetrahedral sites directly surround any single sphere?
  iii. How many spheres surround any octahedral site?
  iv.   How many spheres surround any tetrahedral site?
  v.   What is the ratio of octahedral sites to spheres?
  vi.   What is the ratio of tetrahedral sites to spheres?
  vii. Would it matter, to the atom to site ratio, if the layering of spheres you created was CCP or HCP?
  viii. What is the total number of interstitial sites around each atom in a close - packed structure?

Exercise C: Tutor explanation using large models.

Ionic Crystalline Solids: - The NaCl structure

movie of the structure of NaCl: http://www.metacdn.com/r/m/ukhcnnyr/ej9qPNz

On the basis of what is observed in Exercise C complete question 12.2

Question 12.2

    (a) What occupies the tetrahedral sites in this structure?

    (b) What occupies the octahedral sites?

    (c) For each of the ions in the NaCl structure, what is the coordination number and the coordination geometry?

    (d) Look at the unit cell to determine the ratio of Na^+:Cl^- ions.

Ionic Crystalline Solids: - The ZnS structures

Exercise D: Tutor explanation using large models.

Ionic Crystalline Solids: - The zinc blende structure

movie of the structure of zinc blende: http://www.metacdn.com/r/m/ukhcnnyr/gosCJmX

On the basis of what is observed in Exercise D complete question 12.3.

Question 12.3

Zinc Blende consists of a close-packed structure of sulfide ions with zinc ions in the interstitial sites.

    (a) Name the type of close-packing in zinc blende (CCP or HCP)?

    (b) What proportion of the tetrahedral sites is filled by zinc in the zinc blende structure?

    (c) What is the coordination geometry of the S^{2-} ion?

    (d) What is the coordination geometry of the Zn^{2+} ion?

    (e) Look at the unit cell to determine the ratio of Zn^+:S^{2-} ions.

Exercise E: Tutor explanation using large models.

Ionic Crystalline Solids: - The Wurzite structure

movie of the structure of wurtzite: https://www.metacdn.com/r/v/ukhcnnyr/HWPG1Crb

On the basis of what is observed in Exercise E complete question 12.4.

Question 12.4

Wurtzite, like zinc blende, consists of a close-packed structure of sulfide ions with zinc ions in the interstitial sites.

What is the *essential* difference between zinc blende and wurtzite?

Workspace

Question 12.5

NaCl adopts a fcc structure with the Na^+ ions occupying all the octahedral holes. Given that the edge length of the unit cell is 563 pm calculate the radius of the Na^+ ion. Assume Cl^- ions just contact one another.

Question 12.6

    (a)   Draw the structure and determine the charge on the silicate anion $[Si_2O_7]^{n-}$.

    (b)   Draw the structure and determine the charge on the cyclic silicate anion $[Si_3O_9]^{n-}$.

    (c)   Describe the structure of the SiO_3^{n-} ion in Jadeite. The formula of Jadeite is $NaAl(SiO_3)_2$.

   In each case represent the SiO_4 unit using the following shorthand notation.

SiO_4^{4-}
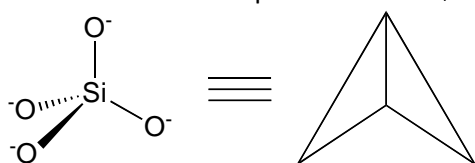
Jadeite – movie showing structure: http://www.metacdn.com/r/m/ukhcnnyr/ZzPq84e

Homework Questions

Question 12.7

The unit cell for a pure compound formed between xenon and fluorine is shown in the following diagram. Xe - large blue, F - small green

a) What is the formula of the compound?

b) The unit cell of this compound has a height of 702 pm and the edge of the square base has a length of 432 pm. Calculate the density of the compound. (Molar masses in g mol^{-1}: Xe is 131.3 and F is 19.0)

Workspace
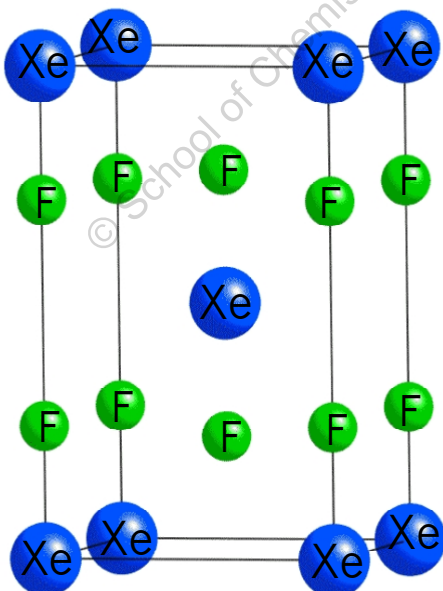
Question 12.8

Perovskite is a mineral containing barium, titanium and oxygen. The following diagram represents the unit cell. What is the formula of Perovskite?
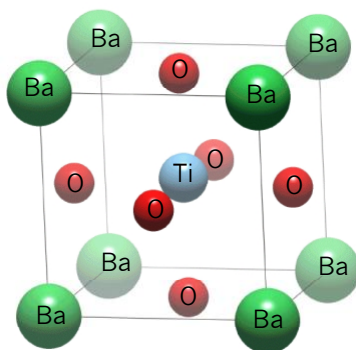
Ba - large green spheres
Ti - medium blue sphere
O - small red spheres

To enhance your understanding, please complete all homework questions at the back of the Tutorial Workbook on page 107. Solutions will be provided on the LMS.

Workspace

CHEM10003- Independent Learning Tasks (ILTs)

Introduction

In our chemistry subjects we encourage students to be independent, informed and critical thinkers. The Independent Learning Tasks are designed to expand and enhance your chemistry knowledge and help you develop an independent style of learning. **The material in these tasks will not necessarily be referred to in the lectures, but is part of the course and will be examined in the semester examination.**

Each Chemistry CHEM10003 student will be required to complete **three** Independent Learning Tasks (ILTs) Updates regarding these ILTs will be posted on the LMS.

Important information about ILTs

- Each Independent Learning Task is to be undertaken **independently**.
- You are encouraged to do your own research to obtain the answers for your unique set of questions in each ILT.
- These tasks do not have to be completed in one sitting you can take your time, as long as it is completed before the generous deadline.
- Independent Learning Tasks are hurdle requirements - *i.e.* they **must** be attempted in order to pass Chemistry CHEM10003.
- The score you achieve for ILTs does not contribute to your overall mark, however, material presented in ILTs may be **examined**.

Please make sure that you click on "**Submit**" when you have completed the ILT otherwise your attempt will not be recorded!

Suggested completion dates for Independent Learning Tasks
ILT 1: Wednesday 1 August
ILT 2: Wednesday 15 August
ILT 3: Wednesday 5 September

CHEM10003 ILT-1 - SciFinder

The aim of this Independent Learning Task is to introduce you to the database SciFinder.

SciFinder is a sophisticated chemistry database that provides access to references, substances and reactions relevant to chemistry and related sciences.

A basic understanding of how this database works will support further study at undergraduate and graduate level.

By working through these questions and related support resources you should understand

- how to register and set up an account in SciFinder
- how to search for an author
- how to search for co-authors
- how to search for articles and access the full text
- how to draw molecular structures and find related information

In order to answer the questions successfully you need to work through the Subject Research Guide CHEM10003 ILT

Note: In order to fully complete this hurdle task, press **SUBMIT** in the online test not just SAVE.

Complete:

Date completed:

Score obtained:

CHEM10003 ILT- 2 – Isotopes and stoichiometry

ALL students enrolled in CHEM10003 are required to attempt this test. On submission you will be given answers and feedback. The questions will change on each attempt of the ILT. We strongly advise all students to have their FIRST attempt at this test by the deadline given below.

The questions in this ILT **are not related to topics you have been taught in Lectures.** This **independent learning tasks** should mainly be revision of topics taught to you at secondary school.

This independent learning task deals with the concepts associated with:

• Isotopes

• Stoichiometry/composition, including empirical formula from composition (and visa versa), reactions (relative quantities of reactants and products)

Note: In order to fully complete this hurdle task, press **SUBMIT** in the online test not just SAVE.

Complete:

Date completed:

Score obtained:

CHEM10003 ILT-3 – Significant figures

Significant figures are crucial when working in a laboratory as they indicate the accuracy of a measurement. For instance:

- A measurement of 4 kg is accurate within the range of 1kg,
- a measurement of 4.0 kg is accurate within a range of a tenth of a kilogram
- a measurement of 4.00 kg is accurate within a range of a hundredth of a kilogram.

Being able to convert between different units is also important when working in a laboratory. For example in an experiment a volume may have been measured in dm^3, however the calculation requires the volume to be in cm^3. Or a wavelength may have been measured at 490 nm, however the calculation requires it to be in m.

In ILT 3 you will revise identifying significant figures and applying them to calculations as well as practicing converting between various scientific units.

All students are required to attempt the Independent Learning Tasks as a hurdle requirement for passing the subject. The suggested attempt dates are given to assist you in pacing your studies through the semester.

Note: In order to fully complete this hurdle task, press **SUBMIT** in the online test not just SAVE.

Complete:
Date completed:
Score obtained:

Appendix 1

Problem Set No 1 (lectures 1 - 12) - Organic Chemistry

Solutions to Problem Set 1 will be made available on the LMS website: **http://www.lms.unimelb.edu.au**

1. Draw structural formulae for each of the following hydrocarbons. Where stereoisomers are possible, draw all possibilities.

(i)	2,2,3,3-tetramethylpentane	(vi)	2,5-dimethylhexane
(ii)	2,3-dimethylbutane	(vii)	3-ethyl-2-methylpentane
(iii)	3,4,4,5-tetramethylheptane	(viii)	2,2,4-trimethylpentane
(iv)	4-ethyl-3,4-dimethylheptane	(ix)	4-ethyl-2,4-dimethylheptane
(v)	3,3-diethylhexane	(x)	4-ethyloctane

2. Draw the Newman projections of all the possible staggered conformations of:
   (i) 2-methylbutane [about the 2,3-bond];
   (ii) 3-ethyl-2-methylpentane [as seen looking from C3 to C2].

3. Draw structures for each of the following compounds showing clearly all stereochemical details:
   (i) (*S*)-2-methylbutanoic acid
   (ii) (*R*)-2-chloro-2-bromobutane
   (iii) (*R*)-2-methylcyclopentanone
   (iv) (*S*)-3-methyloctane
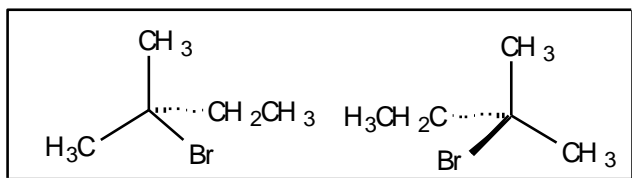   (v) (2*R*,3*R*)-2,3-dibromobutane

4. Assign the absolute configuration (*R,S*) of all of the chiral carbon atoms in each of the following compounds.
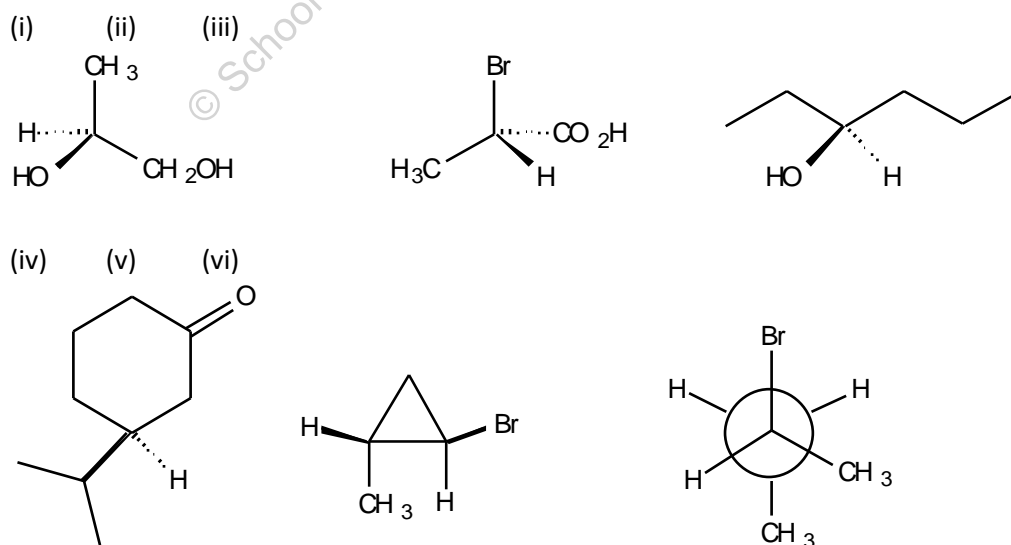
(i)   (ii)   (iii)

(iv)   (v)   (vi)

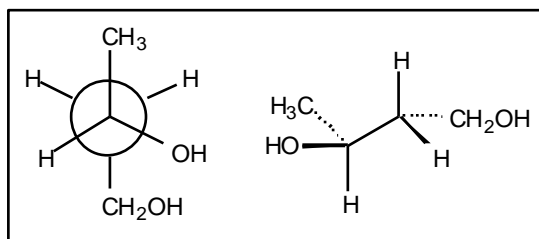

5. Classify each of the pairs of structures (i)-(x) using one of the following descriptions:

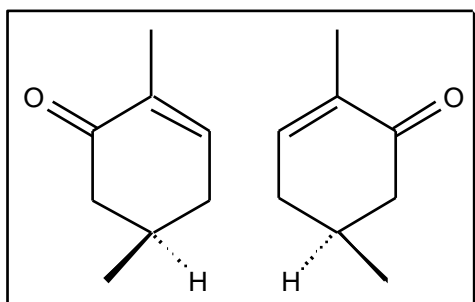(a) same compound
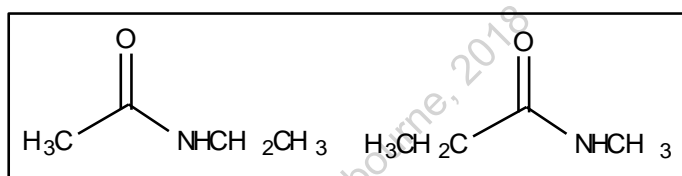
(b) structural isomers

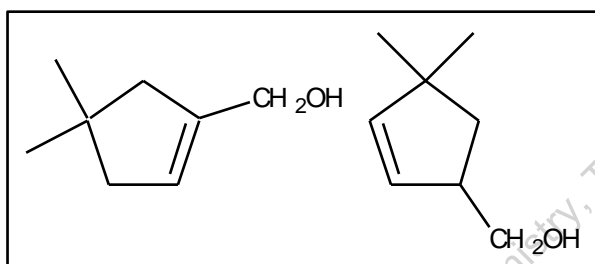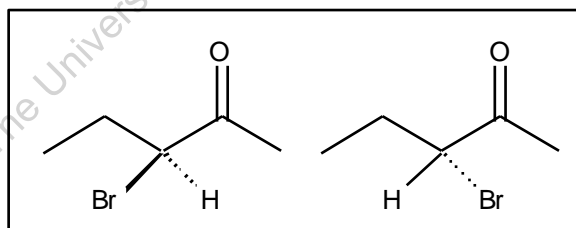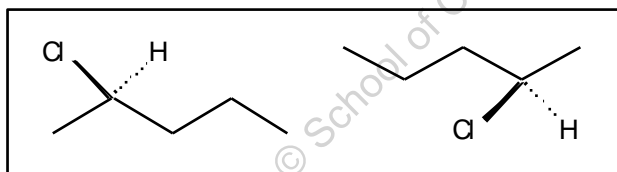(c) pair of enantiomers

(i)

(ii)

(iii)

(iv)

(v)

(vi)


(vii)

6.   Draw structural formulae for each of the following alkenes:

(i)	4-methyl-1-pentene	(v)	(Z)-3-methyl-2-pentene
(ii)	2-bromo-1-hexene	(vi)	(E)-2-bromo-3-chloro-2-pentene
(iii)	(Z)-1,2-dichloroethene	(vii)	(2E,5E)-2,5-heptadiene
(iv)	(E)-2-bromo-2-butene	(viii)	(Z)-1,3-pentadiene

7. Draw the lowest energy (most stable) conformations for each of the following structures (i) - (iv). Indicate whether the ring substituents are either *axial* or *equatorial* in the conformations that you have drawn.
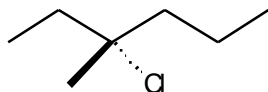
(i)   (ii)   (ii)   (iv)
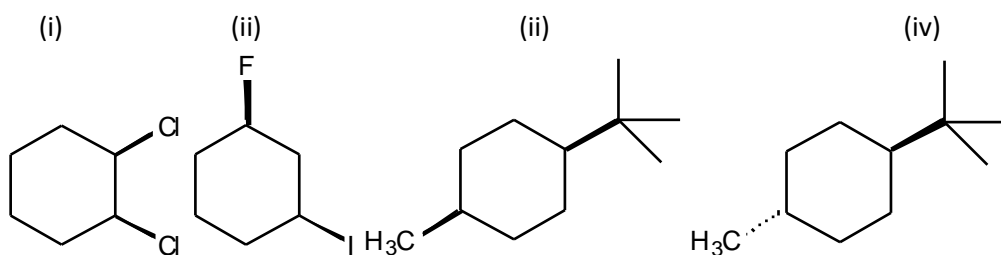
8. Indicate the hybridisation (sp, sp^2, sp^3) of each atom (excluding H) in the following compounds:

(i)	propane	(ii)	2-methylpropene
(iii)	1-butyne	(iv)	cyclobutene
(v)	anisole	(vi)	methyl 3-butenoate
(vii)	2-cyclopentenone	(viii)	benzamide
(ix)	propanenitrile	(x)	carbon dioxide
(xi)	propanol	(xii)	diethyl ether
(xiii)	pyridine		

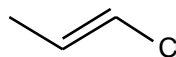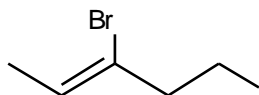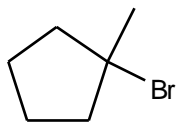9. Provide a systematic name (IUPAC) for each of the following compounds:
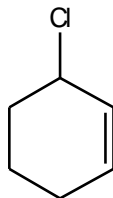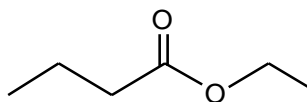
(i)

(ii)
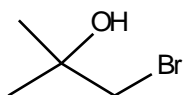
(iii)

(iv)

(v)
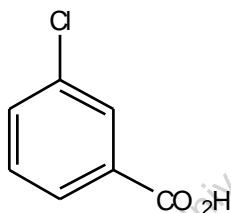

(vi)

(vii)

(viii)

(ix)

(x)

94
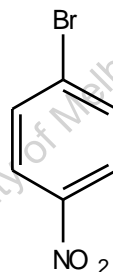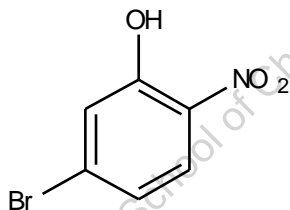
Appendix 2

Practice problems - using spectroscopy to determine structure Week 5

Question 1

(a) A small sample of an unknown compound was analysed yielding the following combustion analysis data:

%C 85.62; %H 14.38

Use this data to determine the empirical formula.

The empirical formula of the compound is C_ H_?

(b) The mass spectrum of the unknown compound is shown below.

Which peak corresponds to the molecular ion for this compound? Molecular ion m/z _____

What is the molecular mass of the compound? Molecular mass _____

What is the molecular formula of the compound? Molecular formula: _____

(Hint: remember the empirical formula of the compound).

(c) Determine the number of Double Bond Equivalents for the unknown compound.

The DBE = (2n4 + n3 - n1 + 2)/2 so the DBE for unknown compound _____

(d) The infrared spectrum of the unknown compound is shown below.

Examine this spectrum and decide which functional groups are present. (Hint: focus attention on the functional group region above about 1600 cm^{-1} and remember the molecular formula and result from the DBE calculation). Functional groups present:

☐ O—H   ☐ N—H   ☐ C—H

☐ C=C   ☐ C=O   ☐ C≡C   ☐ C≡N

(e) The ^{13}C NMR spectrum of the unknown is shown below.

Examine this spectrum and then decide how many different carbon atoms (or carbon atom environments) are present in this molecule. Number of different carbon atoms _____

(f) The ^1H NMR spectrum of the unknown is shown below.

Examine this spectrum and then decide how many different hydrogen atoms (or hydrogen atom environments) are present in this molecule. Number of different hydrogen atoms _____

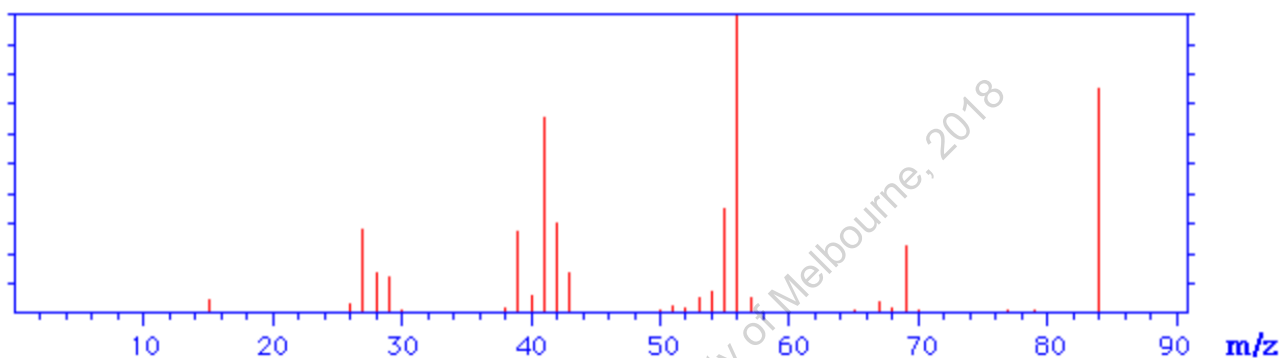(g) Based on your conclusions to parts (a) – (f) propose a structure for the unknown compound.

{Answer: cyclohexane}

Question 2
(a) A small sample of an unknown compound was analysed yielding the following combustion analysis data:

%C 60.95; %H 15.35; %N 23.70

The empirical formula of the compound is C_ H_ N_ ?

(b) The mass spectrum of the unknown compound is shown below.
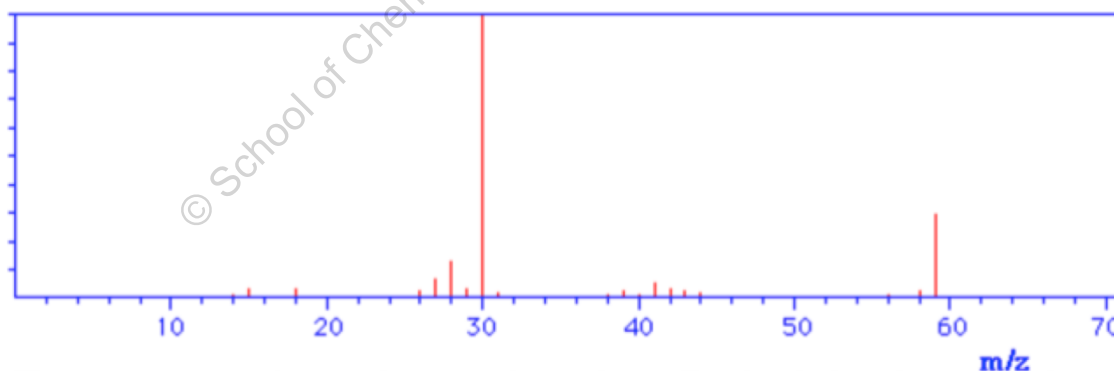
Which peak corresponds to the molecular ion for this compound? Molecular ion m/z ____

What is the molecular mass of the compound? Molecular mass ____
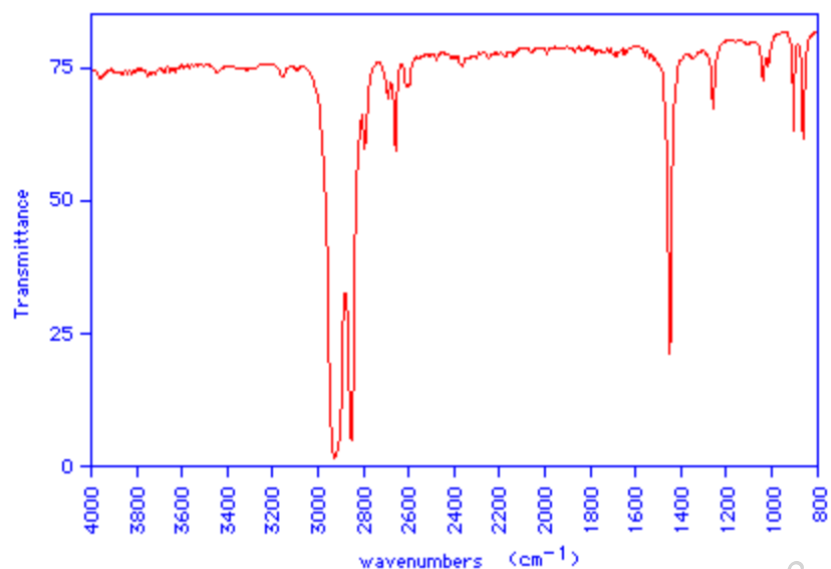
What is the molecular formula of the compound? Molecular formula: _____

(Hint: remember the empirical formula of the compound).

(c) Determine the number of Double Bond Equivalents for the unknown compound.   The DBE calculation provides information about the number of double bonds and or rings present in a compound.
The DBE = (2n4 + n3 - n1 + 2)/2 so the DBE for unknown compound ____
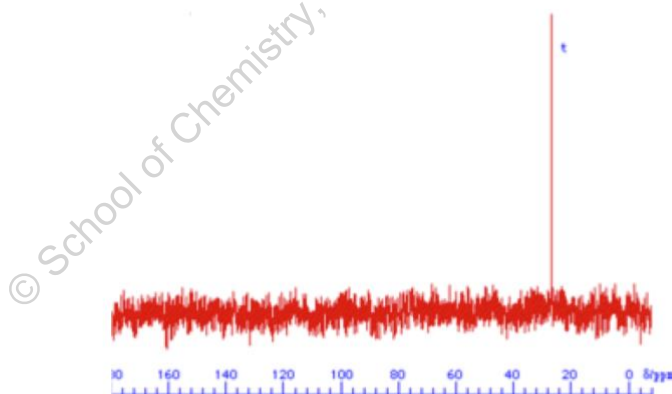
97

(d) The infrared spectrum of the unknown compound is shown below.
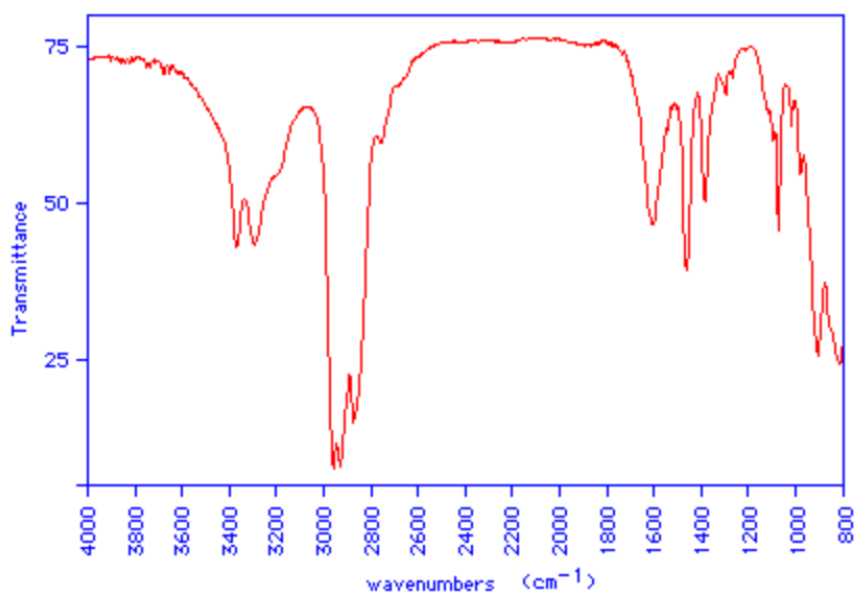
Examine this spectrum and decide which functional groups are present. (Hint: focus attention on the functional group region above about 1600 cm^{-1} and remember the molecular formula and result from the DBE calculation). List the functional groups present.
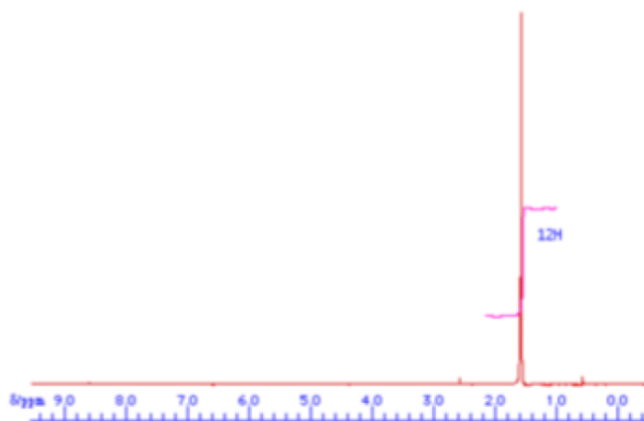
(e) The ^{13}C NMR spectrum of the unknown is shown below.
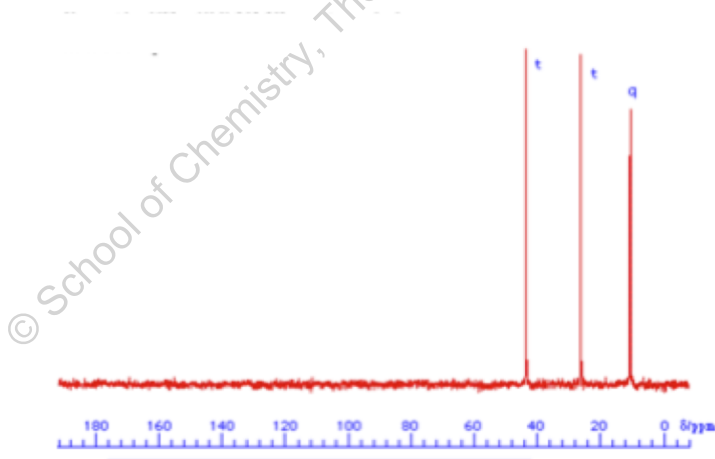
Examine this spectrum and then decide how many different carbon atoms (or carbon atom environments) are present in this molecule. Number of different carbon atoms _____

(f) The ^{1}H NMR spectrum of the unknown is shown below.
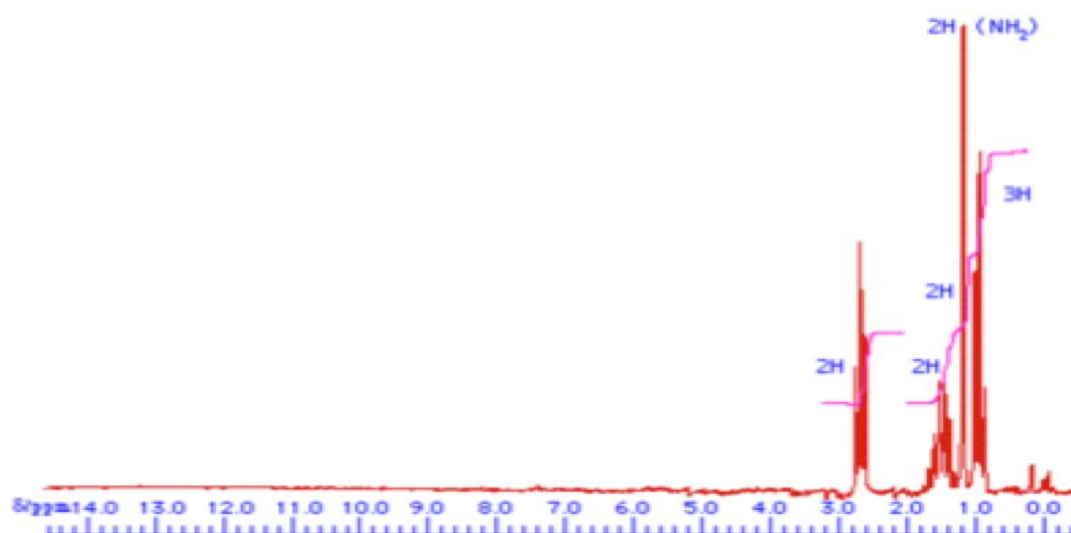
Examine this spectrum and then decide how many different hydrogen atoms (or hydrogen atom environments) are present in this molecule. (This spectrum shows coupled resonances which leads to multiplicity in the peaks associated with each group of protons. In your analysis focus on how many sets of peaks are observed in the spectrum). Number of different hydrogen atoms _____

(g) Based on your conclusions to parts (a) – (f) propose a structure for the unknown compound.

{Answer: propylamine}

Question 3

(a) A small sample of an unknown compound was analysed yielding the following combustion analysis data:

%C 91.24; %H 8.76

The empirical formula of the compound is C_ H_

(b) The mass spectrum of the unknown compound is shown below.

Which peak corresponds to the molecular ion for this compound? Molecular ion m/z ____

What is the molecular mass of the compound? Molecular mass ____

What is the molecular formula of the compound? Molecular formula: _____

(Hint: remember the empirical formula of the compound).

(c) Determine the number of Double Bond Equivalents for the unknown compound.

The DBE = (2n4 + n3 - n1 + 2)/2 so the DBE for unknown compound ____

(d) The infrared spectrum of the unknown compound is shown below.

Examine this spectrum and decide which functional groups are present.

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☐ O–H ☐ N–H ☐ C–H

☐ C=C ☐ C=O ☐ C≡C ☐ C≡N

(e) The ^{13}C NMR spectrum of the unknown is shown below.

Examine this spectrum and then decide how many different carbon atoms (or carbon atom environments) are present in this molecule. (There are 5 lines in this spectrum because 2 of the carbon atoms are in very similar environments). Number of different carbon atoms _____

(f) The ^{1}H NMR spectrum of the unknown is shown below.

Examine this low resolution spectrum and then decide how many different hydrogen atoms (or hydrogen atom environments) are present in this molecule. (In higher resolution this spectrum shows coupled resonances which leads to multiplicity in the peaks associated with each group of protons. In your analysis focus on how many sets of peaks are observed in the spectrum). Number of different hydrogen atoms _____
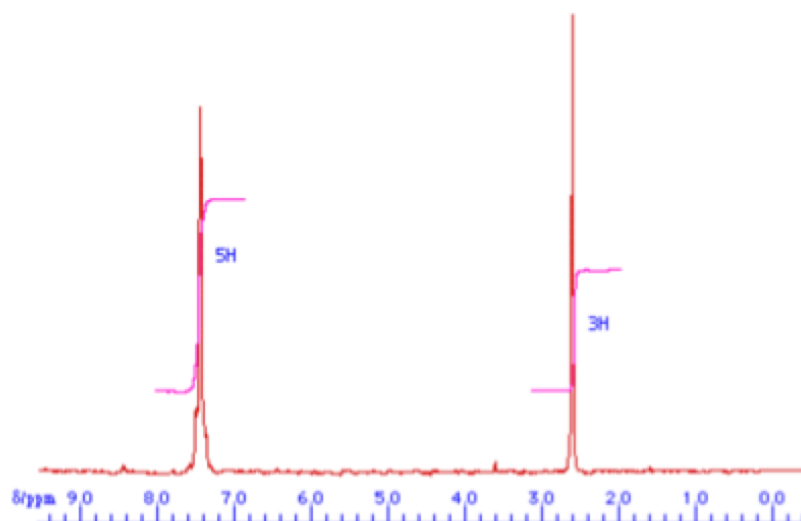
(g) Based on your conclusions to parts (a) – (f) propose a structure for the unknown compound.
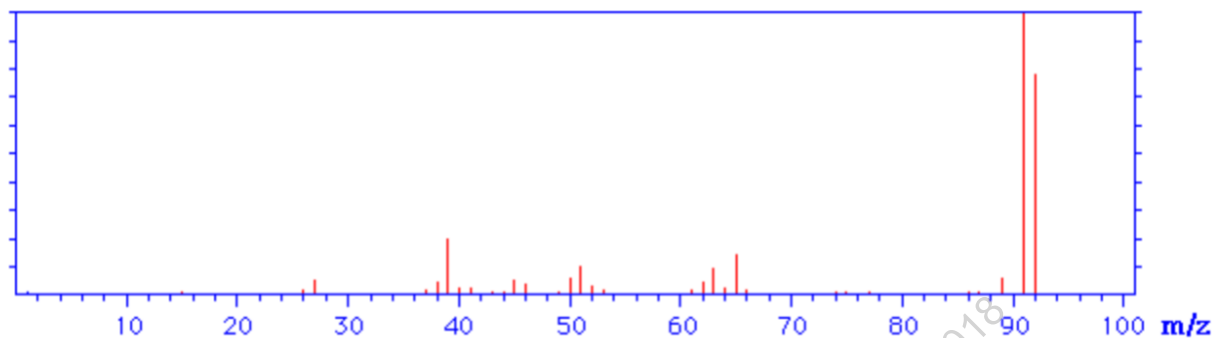
{Answer: toluene (methylbenzene)}

Characteristic Ranges for Infrared Absorption Bands

Bond	Wave number (cm^{-1})
C–Cl	700–800
C–C	750–1100
C–O	1000–1300
C=C	1610–1680
C=O	1670–1750
O–H (acids)	2500–3300
C–H	2850–3300
O–H (alcohols)	3200–3550
N–H (primary amines)	3350–3500

Appendix 3
Practice problems Weeks 9 -12 Inorganic Chemistry

> **Solutions** to Week 9 and 10 additional problems will be made available on the LMS website:
> **http://www.lms.unimelb.edu.au**

CHEM10003 Week 9 – Extra Problems

1. Give the pH and pOH of the following solutions

   (a) A 0.100 M solution of HCl

   (b) A 0.00010 M solution of HCl

   (c) A 200 mL aqueous solution that contains 0.02500 moles of HNO_3.

   (d) A 15 mL aqueous solution that contains 0.00100 moles of NaOH.

   (e) A solution prepared by adding 25.0 mL of 0.0200 M NaOH to 50.0 mL of 0.00800 M HCl.

   (f) A solution prepared by adding 25.0 ml of 0.050 M HCl to 25 mL of 0.0200 M $Ba(OH)_2$.

2. Give the pH and pOH of the following solutions:

   (a) A 0.100 M solution of acetic acid (CH_3COOH) (K_a (CH_3COOH) = 1.8 x 10^{-5})?

   (b) A 0.00010 M solution of CH_3COOH

   (c) A 200 mL aqueous solution that contains 0.02500 moles of HCOOH.

   (K_a (HCOOH) = 1.7 x 10^{-4})?

   (d) A 15 mL aqueous solution that contains 0.00100 moles of sodium acetate ($NaOOCCH_3$).

   (e) A 25 mL aqueous solution that contains 0.00400 moles of ammonia (NH_3).

   ($K_b(NH_3)$ = 1.8 x 10^{-5})

   (f) A 25 mL aqueous solution that contains 0.00400 moles of ammonium chloride (NH_4Cl).

3. A 0.150 M nitrous acid (HNO_2) solution has a pH of 2.11.

   (a) What is the concentration of nitrite (NO_2^-)?

   (b) What is the pK_a for nitrous acid?

   (c) What is the pK_b for nitrite?

4. Consider a 0.150 M solution of sulfurous acid (H_2SO_3)

   (For H_2SO_3 K_{a1} = 1.5 x 10^{-5}; K_{a2} = 1.0 x 10^{-7})

   (a) What is the pH of the solution?

   (b) What is the concentration of hydrogen sulfite (HSO_3^-)?

   (c) What is the concentration of sulfite (SO_3^{2-})?

5. A solution is prepared by adding 0.002 moles of sodium acetate to a 100 mL of 0.03 M acetic acid.

   (K_a (CH_3COOH) = 1.8 x 10^{-5})

(a) Assuming that no volume change occurs upon addition of the sodium acetate what is the pH of the solution?

(b) What is the concentration of the acetate ion?

(c) What is the concentration of the acetic acid?

6.   0.0020 moles of ammonia is added to 200 mL of a 0.010 M solution of ammonium chloride.

$(K_b(NH_3) = 1.8 \times 10^{-5})$

(a) Assuming no volume change, what is the pH of the solution?

(b) What is the concentration of the ammonium ion?

(c) What is the concentration of the ammonia?

7.   100 mL of 0.050 M NaOH is added to a 400 mL solution of 0.030 M formic acid solution.

$(K_a (HCOOH) = 1.7 \times 10^{-4})$

(a) What is the pH of the resulting solution?

(b) What is the concentration of the formate ion in the resulting solution?

(c) What is the concentration of the formic acid in the resulting solution?

8.   15.0 mL of a 0.040 M solution of ammonia is added to 10.0 mL of a 0.030 M nitric acid solution.

$(K_b(NH_3) = 1.8 \times 10^{-5})$

(a) What is the pH of the solution?

(b) What is the nitrate ion concentration?

(c) What is the concentration of the ammonia?

(d) What is the ammonium ion concentration?

9.   A student requires a buffer solution with a pH of 4.9.

(a) Select from the following buffer mixtures the best buffer for making a solution with a pH of 4.9.

Acetic acid/acetate $(K_a(CH_3COOH) = 1.8 \times 10^{-5})$

Formic acid/formate $(K_a(HCOOH) = 1.7 \times 10^{-4})$

`Ammonia/ammonium $(K_b(NH_3) = 1.8 \times 10^{-5})$

(b) For the buffer you select describe a method for making a buffer with a pH of 4.9.

10.   A propanoic acid/propanoate buffer solution of pH 4.3 has a propanoic acid concentration of 0.0150M.

pK_a (propanoic acid = 4.87)

(a) What is the propanoate ion concentration?

(b) What is the K_b of propanoate?

(c) The buffer solution is diluted by a factor of 10. What is the new pH?

11.   A 10.00 L metal drum contains 2.50 L of water and methane gas that has a partial pressure of 1.50 atm. Assuming the system is at equilibrium what is the mole fraction of methane in the water at 298 K?

$(k_H = 4.13 \times 10^2$ atm at 298 K)

12.   The mole fraction of O_2 in an aqueous solution is 5.50×10^{-5}. What is the partial pressure of O_2 above the solution at 298 K? ($k_H = 4.34 \times 10^4$ atm at 298 K)

13.   In regards to the Periodic Table describe the general trend in

(a) size in atomic going down a group.

(b) ionization energy going down a group

(c) size going across a period

(d) ionization energy across a period

(e) electronegativity across a period

(f) electronegativity down a group

14.   Which of the following species are isoelectronic with Cl^-?

Na, K, K^+, Al, Al^{3+}, S, S^-, S^{2-}, N, Ca, Ca^{2+}, Sc, Sc^{3+}, P, P^{3-}, V^{4+}, Ti^{4+}, Ar

15.   Arrange the following species in order of i) increasing size and ii) increasing ionization energy

(a) Li^+, Na^+, Na

(b) O^{2-}, Al^{3+}, S^{2-}

(c) Cl, Si, K

(d) B, Al, C

(e) C, Ga, Sr

CHEM10003 Week 10 – Extra Problems

1.   Give the number of valence electrons in the following species

a) NH_3 b) H_2O c) HF   d) SF_4 e) PF_5 f) BrF_3

2.   Give the number of valence electrons in the following ionic species

a) NH_4^+ b) H_3O^+ c) H_2F^+ d) SF_3^+ e) PF_6^- f) BrF_4^-

3.   Draw Lewis structures for

a) O_3 b) SO_2 c) SO_3 d) NO_2 e) NO_2^- f) ICl_3

4.   For the following list divide the species into groups that contain isoelectronic species:

ClO^-, NO_2^-, ClO_4^-, CO_2, NO_3^-, XeF_4, ClF, ClO_3^-, O_3, IF_4^-, CH_4, Ne, SO_4^{2-}, SO_3^{2-}, N_2O, CO_3^{2-}, TeF_4, PO_4^{3-}, H_2O

5.   Describe the electron pair geometry at the central atom for the following species

e.g. SF_4 – Trigonal bipyramidal with a lone pair in an equatorial site

a) NH_3 b) BeH_2 c) H_2O d) CH_4

6.   Give the Lewis structure, electron pair geometry and molecular shape of each of the following species.

a) BH_4^- b) SCl_2 c) BrF_3

7.   Give the Lewis structure, electron pair geometry and molecular shape of each of the following species.

a) NH_4^+ b) H_3O^+ c) H_2F^+ d) SF_3^+ e) BrF_4^-

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8. Give the Lewis structure, electron pair geometry and molecular shape of each of the following species. Also indicate if the species is polar.

   a) SO_3 b) NO_2^- c) ICl_3

9. Xenon is a noble gas element and as such is normally considered unreactive. Nevertheless it will form compounds with fluorine and oxygen. Give the Lewis structure, electron pair geometry and molecular shape of each of the following species. Also indicate if the species is polar.

   a) XeF_2 b) XeO_3

10. Indicate which of the following species are polar.

    PF_5, BeH_2, KrF_2, IF_4^-, SeF_4

11. Indicate the type of hybridization of the central atom in the following species

    a) NH_3 b) BeH_2 c) H_2O d) CH_4 e) BH_4^- f) SCl_2 g) SF_4 h) PF_5 i) BrF_3 j) Cl_2CO

12. Using the Valence Bond model provide a description of the bonding in methanal (formaldehyde). You answer should include a description of the orbitals involved in the σ-bonding framework and the π-bonding (if present).

CHEM10003 Week 11 – Extra Problems

1. Draw MO energy level diagrams for He_2^+, Li_2 and F_2.

2. Use the diagrams from question 1 to calculate the bond order for He_2^+, Li_2, and F_2.

3. The boiling points of the hydrogen halides reflect the strength of the intermolecular interactions. The boiling points for HF, HCl, HBr and HI are 19, -85, -66 and -34 °C. Provide an explanation for the variation in boiling points for HF, HCl, HBr and HI. In your answer identify the important intermolecular forces for each compound.

4. Identify three factors that have a significant impact on lattice energy.

5. What is the lattice energy for MgF_2?

   1st ionization energy of Mg = 735 kJ/mol; 2nd ionization energy of Mg = 1445 kJ/mol; Electron affinity of F = -328 kJ/mol; Bond energy of F_2 = 154 kJ/mol; Enthalpy of sublimation (Mg) = 150 kJ/mol; $\Delta H_f°$ (MgF_2) = -1124 kJ/mol.

6. Calculate the $\Delta H_f°$ for NaCl.

   1st ionization energy of Na = 495 kJ/mol; Electron affinity of Cl = -349 kJ/mol; Bond energy of Cl_2 = 239 kJ/mol; Enthalpy of sublimation (Na) = 109 kJ/mol; Lattice energy (NaCl) = 786 kJ/mol.

   Provide an explanation for the large difference in lattice energy between MgO (3916 kJ/mol) and NaCl (786 kJ/mol) despite the fact they have similar structures.

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7. The K_{sp} for PbI_2 is 1.4 x 10^{-8}.

   a) What is the concentration of Pb^{2+} and I^- in a saturated PbI_2 solution?

   b) An excess of PbI_2 is added to a 0.050 M KI solution. What is the concentration Pb^{2+}?

8. A crystal of silicon gives an X-ray diffraction reflection at a theta angle of 14.22°. If the wavelength of the radiation (λ) is 154 pm and it is a first order reflection what is the corresponding separation of the crystal planes.

9. Indicate the number of spheres, tetrahedral sites and octahedral sites per unit cell in a face-centred cubic arrangement of spheres.

10. It is not possible to pack spheres together without leaving space between the spheres. The fraction of space occupied by spheres divided by the unit cell volume is known as the packing efficiency, commonly expressed as a percentage. Consider the sphere packing arrangements for cubic close packing, body centred cubic packing and simple (primitive) cubic packing. For each of these three packing arrangements calculate the packing efficiency.

    The packing efficiency for hexagonal close packing is the same as what other type of packing?

    Hint: As a starting point, calculate the number of spheres in each unit cell and the volume of the unit cell in terms of the sphere radius.

11. Crystals of elemental calcium are face-centred cubic (cubic close packed). The Ca atom has a radius of 197 pm. Calculate the density of crystalline calcium in units of g cm^{-3}.

12. In regards to the face-centred cubic structure of calcium what is the radius of the largest sphere that will fit into an octahedral site.

CHEM10003 Week 12 – Extra Problems

1. Li_2O possesses a structure known as the anti-fluorite structure. The anti-fluorite structure has the same structure as fluorite (CaF_2) except that the locations of the cations and anions in the structure are reversed.

   a) What is the coordination number and geometry of the Li^+ ion?

   b) What is the coordination number and geometry of the O^{2-} ion?

   c) What fraction of the tetrahedral sites are occupied in the FCC lattice?

   d) What fraction of the octahedral sites are occupied in the FCC lattice?

   e) What is the ratio of Li^+ ions to O^{2-} ions to octahedral sites to tetrahedral sites.

2. Wurtzite and zinc blende are different forms of zinc sulfide (ZnS)

   a) What are the coordination numbers of Zn^{2+} in i) wurtzite and ii) zinc blende?

   b) What are the coordination numbers of S^{2-} in i) wurtzite and ii) zinc blende?

   c) Describe the arrangements of S^{2-} ions in i) wurtzite and ii) zinc blende.

   d) Describe the arrangements of Zn^{2+} ions in i) wurtzite and ii) zinc blende.

e) Considering the arrangement of S^{2-} ions, what fraction of the octahedral sites is occupied in

                i) wurtzite and ii) zinc blende.

f) Considering the arrangement of S^{2-} ions, what fraction of the tetrahedral sites is occupied in

 i) wurtzite and ii) zinc blende.

g) How many Zn^{2+} and S^{2-} centres are in each FCC unit cell?

3.   CsCl has a cubic structure in which the Cs^+ ion lies at the centre of cube that has Cl^- ions at the corners of the unit cell. Is the structure best described as simple cubic, body-centred cubic or face-centred cubic? Explain your choice of answer.

4.   What is the hydridisation at the carbon centres in a) diamond, b) Lonsdaleite, c) graphite, d) C_{60} and e) carbon nanotubes?

5.   Boron has a large number of allotropes that have unusual structures not seen with other elements. What factors contribute to the formation of these unusual structures?

6.   Nitrogen and phosphorus are both group 15 elements but there are significant differences in their structures that impacts upon their reactivity e.g. N_2 is very stable whereas white phosphorus, P_4, is extremely reactive. Why do nitrogen and phosphorus have different structures in their common allotropic forms?

7.   Based on the Lewis structure/V.S.E.P.R. approach what is the hybridisation of

     a) the nitrogen atoms in hydrazine?

     b) the oxygen atoms in hydrogen peroxide?

8.   What are the bond angles at the phosphorus atoms in

     a) white phosphorus?

     b) H_3PO_4

     c) H_3PO_3

9.   Using V.S.E.P.R. estimate the approximate bond angles at the sulfur atoms in

     a) SO_3

     b) SO_3^{2-}.

Appendix 4: Selected physical constants, useful quantities and conversion factors

Avogadro constant (N_A)	6.0221×10^{23} mol^{-1}
1 Atomic mass unit (u)	1.6605×10^{-27} kg
Gas constant (R)	8.314 J K^{-1} mol^{-1} or 0.08206 L atm K^{-1} mol^{-1}
Speed of light (c)	2.9979×10^{8} m s^{-1}
Planck constant (h)	6.6261×10^{-34} J s photon^{-1}
Rydberg constant (￼)	3.29×10^{15} Hz
Mass of an electron (m_e)	9.109×10^{-31} kg
Bohr radius (a_O)	53 pm
1 Atmosphere (atm)	101 325 Pa = 760 mm Hg
1 Bar	100 kPa = 0.987 atm
Faraday constant (F)	9.6485×10^{4} C mol^{-1}
RT/F (at 298 K)	0.0257 V
2.303 RT/F (at 298 K)	0.0592 V
Absolute zero, 0 K	-273.15 °C