

CHEM1011/CHEM1031/CHEM1051

TUTORIAL PROBLEMS AND NOTES

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It is assumed that you will have attempted all of the problems in each tutorial set before the end-of-semester examination. The examinable material is as detailed in the syllabus, the exercises in the tutorial sets, and in the laboratory assignments.

IMPORTANT NOTE: *No written answers will be provided for these questions. You are expected to attempt the relevant questions BEFORE tutorial class, and use the time in class to ask questions and record the correct written method for any questions with which you are having difficulty. For this reason, attendance at tutorials is compulsory.*

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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1 H 1.008	The Periodic Table																2 He 4.003
3 Li 6.941	4 Be 9.012																9 F 19.00
11 Na 22.99	12 Mg 24.31																17 Cl 35.45
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98.91)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210.0)	85 At (210.0)	86 Rn (222.0)
87 Fr (223.0)	88 Ra (226.0)	89 Ac (227.0)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264.1)	108 Hs (269.1)	109 Mt (268.1)	110 Ds (281)	111 Rg (272.1)	112 Cn (285)	113 Nh (284)	114 Fl (289)	115 Mc (288)	116 Lv (292)	117 Ts (294)	118 Og (294)

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (144.9)	62 Sm 150.0	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa (231.0)	92 U 238.0	93 Np (237.0)	94 Pu (239.1)	95 Am (243.1)	96 Cm (247.1)	97 Bk (247.1)	98 Cf (252.1)	99 Es (252.1)	100 Fm (257.1)	101 Md (256.1)	102 No (259.1)	103 Lr (260.1)

KEY

Atomic No.	6
Symbol	C
At. weight	12.01

For radioactive elements the relative atomic mass of the most common isotope is given in parentheses, and the mass number for that isotope is given as a superscript

NOTES ON UNITS

1. Two conventions are in common use for the *graphical* and *tabular* representation of data:

(a) The physical quantity is followed by the unit in parentheses:

e.g. mass (g), pressure (Pa), ΔH (kJ mol⁻¹), k (10⁻⁵ L mol⁻¹ s⁻¹)

(b) The better method is to divide the physical quantity by the unit, thus giving a *number*:

e.g. mass/g, pressure/Pa, ΔH /kJ mol⁻¹, $k/10^{-5}$ L mol⁻¹ s⁻¹ or $10^5 k$ /L mol⁻¹ s⁻¹

Both conventions are used in chemistry.

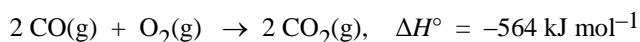
2. Although the SI unit of *volume* is m³, the units more often used in chemistry are dm³ (or litre, L) and cm³ (or mL). In these tutorial notes a variety of units has purposely been used.

3. The SI unit of *pressure* is the pascal (1 Pa = 1 N m⁻²). However, 1 Pa is a very small pressure and multiples such as kPa (*i.e.* 10³ Pa), MPa (*i.e.* 10⁶ Pa) are often used. Other units in common use are:

- the *bar* (1 bar = 10⁵ Pa). A pressure of 1 bar is the standard state pressure for thermochemical data, and is used in some books, *e.g.* SI Chemical Data;
- the standard *atmosphere* (atm, 1 atm = 1.013 × 10⁵ Pa). A pressure of 1 atm is the pressure used in defining the *normal* boiling temperature of a liquid and *normal* melting point of a solid.
- the *mmHg* or *Torr*. These are defined differently but are practically identical (both equal 133.3 Pa or 1 atm/760).

4. The use of *mol⁻¹* in thermochemical statements.

Many thermochemical data relate to a property of a particular substance with a specified formula. ΔH or ΔE would be given per mole of the specified formula, *e.g.* formation of CaCO₃(s) or vaporization of H₂O(l). A similar convention should be used for a balanced chemical equation. mol⁻¹ means per mole of reactants or products in the stoichiometric mixture as given by the specified equation, eg:



per mole of 2 CO(g) + O₂(g) reacting or per mole of 2 CO₂(g) being formed.

(This indicates that $\Delta H^\circ = -564$ kJ per mole of O₂(g) consumed or per 2 moles of CO(g) consumed or per two moles of CO₂ produced.)

NAMES, FORMULAE AND CHARGES OF SOME COMMON IONS

POSITIVE IONS (CATIONS)

H^+	hydrogen	Be^{2+}	beryllium	Al^{3+}	aluminium
Li^+	lithium	Mg^{2+}	magnesium	As^{3+}	arsenic(III)
Na^+	sodium	Ca^{2+}	calcium	Sb^{3+}	antimony(III)
K^+	potassium	Sr^{2+}	strontium	Bi^{3+}	bismuth
Rb^+	rubidium	Ba^{2+}	barium	Fe^{3+}	iron(III)
Cs^+	caesium	Zn^{2+}	zinc	Cr^{3+}	chromium(III)
NH_4^+	ammonium	Cd^{2+}	cadmium		
Ag^+	silver	Ni^{2+}	nickel	Sn^{4+}	tin(IV)
Cu^+	copper(I)	Co^{2+}	cobalt		
Hg_2^{2+}	mercury(I)	Pb^{2+}	lead		
		Fe^{2+}	iron(II)		
		Mn^{2+}	manganese(II)		
		Cu^{2+}	copper(II)		
		Hg^{2+}	mercury(II)		
		Sn^{2+}	tin(II)		

NEGATIVE IONS (ANIONS)

H^-	hydride	NO_3^-	nitrate	O^{2-}	oxide
F^-	fluoride	NO_2^-	nitrite	O_2^{2-}	peroxide
Cl^-	chloride	ClO^-	hypochlorite	S^{2-}	sulfide
Br^-	bromide	ClO_2^-	chlorite	CO_3^{2-}	carbonate
I^-	iodide	ClO_3^-	chlorate	$\text{C}_2\text{O}_4^{2-}$	oxalate
OH^-	hydroxide	ClO_4^-	perchlorate	SO_4^{2-}	sulfate
HCO_3^-	hydrogencarbonate	IO_4^-	periodate	SO_3^{2-}	sulfite
HSO_3^-	hydrogensulfite	BrO_3^-	bromate	CrO_4^{2-}	chromate
HSO_4^-	hydrogensulfate	MnO_4^-	permanganate	$\text{Cr}_2\text{O}_7^{2-}$	dichromate
H_2PO_4^-	dihydrogenphosphate	CN^-	cyanide	HPO_4^{2-}	monohydrogenphosphate
CH_3CO_2^-	ethanoate (acetate)	BiO_3^-	bismuthate	$\text{S}_2\text{O}_3^{2-}$	thiosulfate
$\text{CH}_3\text{CH}(\text{OH})\text{CO}_2^-$	lactate			PO_4^{3-}	phosphate
$\text{CH}_3\text{COCO}_2^-$	pyruvate				

Note: When naming an isolated cation or anion then the name of the ion must be followed by the word "ion",
e.g. Cl^- would be written or said as "chloride ion" or "chloride anion".

TIPS FOR REPORTING YOUR ANSWERS TO THE CORRECT SIGNIFICANT FIGURES

The concept of “significant figures” (or “significant digits”) is considered assumed knowledge for this course. Taking care with significant figures is part of a professional approach to data recording and handling, and is extremely important in the study and practice of Chemistry.

In science, if you record too few significant figures, you risk creating an error because you have dropped digits which were part of the original measurement. If you record too many significant figures, you are overstating the accuracy of your measurements. Hence, when you compare your results to values in the scientific literature, differences may seem significant when they are not.

This section is designed as a quick guide to assist you in your studies. *Please read the entire section carefully.*

Improper use of significant figures in assignments, lab reports, or exams may result in deducted marks.

Identification

Here are some example numbers and how they are classified in terms of their decimal places and significant figures.

Note that zeroes which only show the size of a value are not considered significant.

Number	Decimal Places	Significant Figures
1200	0	2 (maybe*)
1200.0	1	5
12.0	1	3
0.12	2	2

Number	Decimal Places	Significant Figures
0.120	3	3
0.012	3	2**
0.0012	4	2**
1.0012	4	5

* Zeroes which occur just before a decimal point (such as in the example above) are ambiguous: they may or may not be significant. Unless otherwise stated, assume they are not significant.

** Zeroes which occur just after a decimal point and are not preceded by any significant figures (such as in the examples above), are also NOT considered significant.

Calculations

When performing a calculation, consider the following steps:

- Check the number of significant figures and decimal places in each value you are given (either in the question or in the data available).
- When **adding or subtracting** values, your answer must have the same number of **decimal places** as the value above with the *fewest* decimal places.
- When **multiplying or dividing** values, your answer must have the same number of **significant figures** as the value above with the *fewest* significant figures.
- When applying a **logarithm**, the number of **decimal places** in the answer needs to match the number of **significant figures** in the value we applied (see the example below for more detail).
- Do not round any of intermediate values until the very end of your calculation.
 - If you are using the resulting number in a further calculation, use the un-rounded value in your next calculation.

The most reliable way to determine the number of significant figures in a value is to convert it into scientific notation.

NOTE: Some numbers in a calculation are “exact” numbers (eg: 2 sodium atoms in Na_2CO_3 , 1000 g in a kg, an $n=3$ energy level, etc). Whilst an exact number of 2 can be written in the form “2”, this actually means “2.000000000...” with an infinite number of significant figures. Therefore, exact numbers should **NOT** affect the number of significant figures in your calculation.

Example Questions

Here are a few examples, increasing in level of difficulty:

Question 1 – Adding/Subtracting Values 2.347 g of solid calcium carbonate is added to a beaker containing 20.0 g of calcium carbonate. How much calcium carbonate is now in the beaker?
Working $2.347 \text{ g} + 20.0 \text{ g} = 22.347 \text{ g}$ (based on the calculator display). Now let's look at the decimal places (since we're adding values): <ul style="list-style-type: none">• 2.347 g has <u>3</u> decimal places• 20.0 g has <u>1</u> decimal place• Therefore our answer needs to be expressed to <u>1</u> decimal place 22.347 expressed to 1 decimal place is 22.3.
Answer Hence our final answer to this question should be written as “22.3 g”.

Question 2 – Multiplying/Dividing Values A sample of solid CaCO_3 (1.65 mol) is added to 12 L of water until completely dissolved. Calculate the concentration of CaCO_3 .
Working Using the equation $C = n/V$, we see that $1.65 \text{ mol}/12 \text{ L} = 0.1375 \text{ mol L}^{-1}$ (based on the calculator display). Now let's look at the significant figures (since we're dividing values): <ul style="list-style-type: none">• $1.65 \text{ mol} \rightarrow 1.65 \times 10^0 \text{ mol}$. There are 3 digits in this scientific notation, so the value has <u>3</u> significant figures• $12 \text{ L} \rightarrow 1.2 \times 10^1 \text{ L}$. There are 2 digits in this scientific notation, so the value has <u>2</u> significant figures.• Therefore, our answer needs to be in <u>2</u> significant figures. $0.1375 \text{ mol L}^{-1} \rightarrow 1.375 \times 10^{-1} \text{ mol L}^{-1}$. Expressed to 2 significant figures is $1.4 \times 10^{-1} \text{ mol L}^{-1}$.
Answer Hence our final answer to this question should be written as “0.14 mol L ⁻¹ ”.

Question 3 – Multiplying/Dividing Values (Harder)

Calculate the number of moles of potassium ions in 33.0 mL of 0.1444 mol L⁻¹ K₂SO₄ (aq).

Working

Using the equation $C=n/V$, we rearrange the formula to find $n_{\text{solute}} = C_{\text{solution}}V_{\text{solution}}$.

Therefore $n_{\text{solute}} = 0.1444 \text{ mol L}^{-1} \times 0.0330 \text{ L} = 0.0047652 \text{ mol}$ (from the calculator).

$n_{\text{K}^+} = 2 \times n_{\text{solute}} = 2 \times 0.0047652 \text{ mol} = 0.0095304 \text{ mol}$ (from the calculator).

Now let's look at the significant figures (since we're multiplying values):

- 0.1444 mol L⁻¹ → 1.444 x 10¹ mol L⁻¹. This has 4 sig fig.
- 33.0 mL = 3.30 x 10¹ mL **OR** 3.30 x 10⁻² L. Whether you consider the value in mL or L, the value still has only 3 sig fig.
- The 2 in our “2 x n_{solute}” expression is an **exact value** (exactly 2 K⁺ ions per K₂SO₄)
- Therefore, our answer needs to be in 3 significant figures.

0.0095304 mol → 9.5304 x 10⁻³ mol. Expressed to 3 significant figures is 9.53 x 10⁻³ moles.

Answer

Hence our final answer to this question should be written as “0.00953 mol”.

Question 4 – Applying Logarithms

Calculate the pH of a 0.095 mol L⁻¹ solution of HCl (aq).

Working

$\text{pH} = -\log_{10}[\text{H}^+]$. Therefore $\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}[0.095] = 1.022276395$ (from the calculator).

Now let's look at the significant figures of the values (since we're applying a logarithm):

- 0.095 mol L⁻¹ → 9.5 x 10⁻² mol L⁻¹. This has 2 sig fig.
- Since there are 2 sig fig in the value, our final answer needs to be expressed to **2 decimal places**.

1.022276395 expressed to 2 decimal places is 1.02.

Answer

Hence our final answer to this question should be written as “1.02”.

The justification behind why logarithms behave like this is slightly complicated. However, if you are really interested in finding out the answer to this mathematical subtlety, please ask your tutors or approach the Duty Tutor in the Chemistry Student Study Area (see Moodle for details). For more information, you can also see the following resources:

- Uncertainties and Significant Figures: Blackman (*et al.*) Chemistry, 2nd edition. Wiley & Sons. (Page 30-32)
- Significant Figures in Calculations: Morris Hein, Susan Arena (2012) Foundations of College Chemistry, 14th edition. Wiley & Sons. (Page 18-21)
- Rounding and Significant Figures: <http://www.purplemath.com/modules/rounding2.htm>
- Significant Figure Rules: <http://chemistry.bd.psu.edu/jircitano/sigfigs.html>
- Rules (and tips for logarithms/antilogarithms): <http://www.ndt-ed.org/GeneralResources/SigFigs/SigFigs.htm>
- Sig Figs and Logs: <http://www2.chemistry.msu.edu/courses/cem262/sigfigsandlogs.pdf>

Rounding Errors

A common source of error in calculations can come about when students round their values too early. To avoid this source of error, you should follow two simple rules:

- Only round a value to the correct number of significant figures at the FINAL STEP of the calculation (just before you report your answer)
- If you are performing a calculation and need to use a value that you gave as an answer to a previous question, always use the UNROUNDED value in your calculation (not the rounded value that you reported).

Here is a quick example to illustrate these points:

Question 5 – Rounding Errors 1 (CORRECT) Calculate the molar mass of Compound A if 2.45 g of the solid dissolved in 100 mL of water produces a 0.1535 M solution
Working (CORRECT) <i>First we can calculate the number of moles of Compound A in the solution using $C=n/V$:</i> <ul style="list-style-type: none">• $C = n/V \rightarrow 0.1535 \text{ M} = n / 0.100 \text{ L} \rightarrow n = 0.01535 \text{ mol}$ <i>Now we can find the molar mass of Compound A using $n = m/M$:</i> <ul style="list-style-type: none">• $n = m/M \rightarrow 0.01535 \text{ mol} = 2.45 / M \rightarrow M = 159.6091205... \text{ g/mol}$ <i>Using our rules of significant figures, this should be expressed to 3 significant figures.</i> <i>159.6091205... expressed to 3 significant figures is 160</i>
Answer <i>Hence our final answer to this question should be written as “160 g/mol”.</i>

Here you can see that the rounding did not occur until the final step – after the correct answer was obtained, but before reporting the answer. Now let's see what happens if, instead, we round too early:

Question 6 – Rounding Errors 2 (INCORRECT) Calculate the molar mass of Compound A if 2.45 g of the solid dissolved in 100 mL of water produces a 0.1535 M solution
Working (CORRECT) <i>First we can calculate the number of moles of Compound A in the solution using $C=n/V$:</i> <ul style="list-style-type: none">• $C = n/V \rightarrow 0.1535 \text{ M} = n / 0.100 \text{ L} \rightarrow n = 0.01535 \text{ mol}$ <i>What happens if we decided to (incorrectly) round our value at this point? We would see that, based on the values used, the number of moles should be expressed to 3 significant figures. This would give us a value of “0.0154 mol”.</i> <i>Now we can find the molar mass of Compound A using $n = m/M$:</i> <ul style="list-style-type: none">• $n = m/M \rightarrow 0.0154 \text{ mol} = 2.45 / M \rightarrow M = 159.0909091... \text{ g/mol}$ <i>Using our rules of significant figures, this should be expressed to 3 significant figures.</i> <i>159.0909091... expressed to 3 decimal places is 159</i>
Answer <i>Hence our final answer to this question would be written as “159 g/mol”.</i>

Here you can see that rounding the value too early has produced an error in our final value. Therefore, in any calculation, rounding should only be done when reporting your answer; not when using a value in a calculation.

NAMING OF CHEMICAL COMPOUNDS – A 'DIY' TUTORIAL

Compounds are formed when two or more atoms of different elements combine together as the result of a chemical change. Facility in naming chemical compounds and in writing the chemical formulae corresponding to these names is important to an understanding of chemistry, because the names and the formulae given to the compounds store much information, such as the relative numbers of each different kind of atom each compound contains, and sometimes information about the arrangement in which the constituent atoms are held together.

Although certain rules are adopted in the naming of compounds (*i.e.* nomenclature) there is not just one universally accepted system used to name all compounds. The most common system of nomenclature is that laid down by I.U.P.A.C (International Union of Pure and Applied Chemistry). Even this system has found it necessary to recognize certain exceptions. Remnants of some of the older systems still remain in the chemical language.

Some of the simple rules for naming compounds are illustrated in the following self-instruction ('do it yourself' or 'DIY') tutorial. This tutorial assumes a familiarity with the names and symbols of the elements and their periodic classification. Each section of the tutorial begins with an informative statement, S, and the frames which follow it contain questions relevant to that statement. In using the tutorial, you should **cover the answers, attempt to answer the questions and then immediately check your answer by uncovering the next line**. If your answer is wrong you should not proceed with the tutorial until you know why your answer is wrong, what remedial action you should take in order to get the correct answer, and what you should do so as not to make the same error in the future.

S-1 Some of the elements have names which are derived from the Latin; others have been Anglicized, but the symbol for them is derived from the Latin; others have Greek or other origins. Most of the new synthetic elements are named after famous scientists or scientific establishments. Some of the elements whose names are of Latin origin (which remains only in their symbol) are given below:

Gold	Aurum	Au	Tin	Stannum	Sn
Silver	Argentum	Ag	Lead	Plumbum	Pb
Copper	Cuprum	Cu	Iron	Ferrum	Fe
Sodium	Natrium	Na	Antimony	Stibium	Sb
Potassium	Kalium	K	Tungsten	Wolfram	W
Mercury	Hydrargyrum	Hg			

	Q.1 What is the symbol for copper?
A.1 Cu	Q.2 What is the symbol for fluorine?
A.2 F	Q.3 Au is the symbol for which element?
A.3 Gold	Q.4 What are the symbols for (a) strontium , (b) nickel, (c) bromine?
A.4 (a) Sr (b) Ni (c) Br	

S-2 Atoms combine with themselves or with one another owing to the operation of an electrostatic attraction (i.e. bond) between them. Some atoms have a tendency to become positively charged by losing electrons, others to become negatively charged by gaining electrons while some may become either positively or negatively charged depending on the nature of the other atoms to which they are bonded. Atoms acquire a charge by gaining or losing electrons to become ions.

A positively charged ion is called a *cation*; a negatively charged ion is called an *anion*. Metals, especially those elements on the left hand side of the Periodic Table form cations; those in Group 1 (Li → Cs), lose 1 electron, show a charge of +1 (oxidation state) and those in Group 2 (Be → Ba) of +2. Nonmetals on the right hand side in Group 17 (F → I), gain 1 electron, form anions of -1 charge and those in Group 16 (O → Te) of -2. The *nonmetals* in groups 13 → 15, i.e. B, C and N groups and the transition metals, as well as a few others, show several oxidation states.

When two different elements combine, a binary compound is formed. Such compounds are named by stating first the name of the cation (or less negative of the two atoms) and then the name of the anion (or more negative atom). The names of the anions end in *-ide* if the anions are formed from the elements. A vowel preceding the last syllable is dropped, i.e. oxygen becomes oxide (not oxyde). Some elemental names drop more than one syllable, e.g. nitrogen and phosphorus become nitride and phosphide (not nitrogeide and phosphoride).

A summary of the common oxidation states of the elements in the main groups in the Periodic Table is given below.

Combining Capacities of the Elements							
Group 1	Group 2	Group 13	Group 14	Group 15*	Group 16	Group 17	Group 18
+1	+2	+3	+4	-3 or +3	-2	-1	zero
H							
Li	Be	B	C	N	O	F	
Na	Mg	Al	Si	P	S	Cl	
K	Ca		Ge	As		Br	
Rb	Sr		Sn**	Sb		I	
Cs	Ba		Pb**	Bi			

* The elements in Group 15 show several variations.

** The elements tin (Sn) and lead (Pb) in Group 14 show an oxidation state of +2 or +4.

For Pb, +2 is the common oxidation state.

For the purposes of nomenclature it is necessary to decide which of two elements is the more negative. For *nomenclature purposes ONLY*, the following order of negativity is used:

B, C, P, H, N, Se, I, Br, Cl, O, F.

	<p>Q.5 Name the binary compounds corresponding to:</p> <p>(a) NaBr (b) K_2S (c) MgO</p> <p>(d) $BaCl_2$ (e) Li_3N (f) AgI</p>
<p>A.5 (a) sodium bromide</p> <p>(b) potassium sulfide</p> <p>(c) magnesium oxide</p> <p>(d) barium chloride</p> <p>(e) lithium nitride</p> <p>(f) silver iodide</p>	<p>Q.6 What would be the formula for binary compounds formed from:</p> <p>(a) calcium and phosphorus</p> <p>(b) strontium and fluorine</p> <p>(c) silicon and carbon</p> <p>(d) hydrogen and sulfur</p> <p>(e) potassium and hydrogen</p> <p>(f) boron and nitrogen</p>
<p>A.6 (a) calcium phosphide Ca_3P_2</p> <p>(b) strontium fluoride SrF_2</p> <p>(c) silicon carbide SiC</p> <p>(d) hydrogen sulfide H_2S</p> <p>(e) potassium hydride KH</p> <p>(f) boron nitride BN</p>	

S-3 A few common binary compounds containing hydrogen are known by their common or trivial names. These are given in Q.7.

When more than one binary compound is possible between two nonmetal elements, the prefixes mono-, di-, tri-, tetra-, penta- and hexa- are used to indicate 1, 2, 3, 4, 5 or 6 atoms.

	<p>Q.7 Name the following compounds:</p> <p>(a) NH_3 (b) H_2O (c) CH_4</p> <p>(d) AsH_3 (e) PH_3 (f) SiH_4</p>
<p>A.7 (a) ammonia</p> <p>(b) water</p> <p>(c) methane</p> <p>(d) arsine</p> <p>(e) phosphine</p> <p>(f) silane</p>	<p>Q.8. What would be the formula for</p> <p>(a) carbon monoxide</p> <p>(b) sulfur dioxide</p> <p>(c) phosphorus pentachloride</p> <p>(d) sulfur trioxide</p>
<p>A.8 (a) CO</p> <p>(b) SO_2</p> <p>(c) PCl_5</p> <p>(d) SO_3</p>	<p>Q.9 Name the following:</p> <p>(a) CO_2 (b) SO_3 (c) PCl_3 (d) SF_6</p>

S-4	<p>A.9 (a) carbon dioxide (b) sulfur trioxide (c) phosphorus trichloride (d) sulfur hexafluoride</p>	
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Polyatomic ions are groups of atoms which have acquired a positive or negative charge and behave as if they were a single unit. The most common polyatomic cation is the ammonium ion, NH_4^+ . The names of some common anions are:

OH^- hydroxide NH_2^- amide
 O_2^{2-} peroxide CN^- cyanide

	<p>Q.10 Name the following: (a) $\text{Ca}(\text{OH})_2$ (b) KCN</p>
<p>A.10 (a) calcium hydroxide (b) potassium cyanide</p>	<p>Q.11 What is the formula for (a) hydrogen peroxide (b) sodium amide (sodamide)</p>
<p>A.11 (a) H_2O_2 (b) NaNH_2</p>	

S-5 Some elements can combine with other elements to form more than one compound (*i.e.* show more than one oxidation state). The compound formed depends upon the conditions used for its preparation. In order to distinguish between these compounds, their names have to indicate the ratio in which the elements have combined. One of the ways in which this is done is to use the prefix di-, tri-, etc. The prefix mono- is frequently omitted. This system is especially suitable for binary compounds of nonmetals and is sometimes used for those of metals as well. This system is being superseded although it is still retained completely in the names of some very common compounds such as sulfur dioxide and sulfur trioxide.

	<p>Q.12 Name the following (a) N_2O_3 (b) Fe_3O_4 (c) P_2S_5</p>
<p>A.12 (a) dinitrogen trioxide (b) tri-iron tetraoxide (c) diphosphorus pentasulfide</p>	<p>Q.13 What is the formula for: (a) dinitrogen oxide (b) dinitrogen tetraoxide (c) triuranium octaoxide</p>
<p>A.13 (a) N_2O (b) N_2O_4 (c) U_3O_8</p>	

S-6 The modern system uses a Roman numeral immediately following the element to indicate its oxidation state. Notice especially that the numeral is used only when the possibility of ambiguity exists.

	Q.14 Name the following: (a) NO (b) N ₂ O ₅ (c) PCl ₃ (c) SbCl ₅
A.14 (a) nitrogen(II) oxide (b) nitrogen(V) oxide (c) phosphorus(III) chloride (d) antimony(V) chloride	Q.15 Name the following (a) SrI ₂ (b) PCl ₅ (c) NaF (d) CO (e) BaCl ₂ (f) BiCl ₃
A.15 (a) strontium iodide (b) phosphorus(V) chloride (c) sodium fluoride (d) carbon monoxide (e) barium chloride (f) bismuth(III) chloride	Q.16 What is the formula for: (a) dichlorine heptaoxide (b) tin(IV) bromide (c) selenium dioxide (d) lead(IV) iodide (e) arsenic(III) oxide
A.16 (a) Cl ₂ O ₇ (b) SnBr ₄ (c) SeO ₂ (d) PbI ₄ (e) As ₂ O ₃	

S-7 Oxygen forms polyatomic anions with all other nonmetals, except fluorine, and with some metals, *e.g.* manganese, chromium, etc. Oxyanions can be formed between oxygen and the second row elements boron, carbon and nitrogen. These atoms are small atoms and the maximum number of oxygen atoms able to be located around any one of these is three. Oxyanions BO₂⁻, BO₃³⁻, CO₃²⁻, NO₂⁻ and NO₃⁻ are formed. (Notice there is no CO₂⁻ or CO₂²⁻).

Oxyanions between oxygen and the elements in the third and higher rows have a maximum of four oxygen atoms arranged around the central atom, *e.g.* PO₃³⁻, PO₄³⁻, SO₃²⁻, SO₄²⁻. When the maximum number of oxygen atoms surrounds an element in groups 13, 14, 15 or 16, the oxyanion has the ending **-ate** added usually to the stem of the name of the element. When one oxygen less is bonded to the central atom, the ending is **-ite** (except for BO₂⁻ which is a metaborate). The system of naming compounds containing these polyatomic anions is similar to that used for naming binary compounds. The formulae and names of the common oxyanions and the anion of the elements in Groups 14, 15 and 16 are given below.

Group 16	SO ₄ ²⁻ sulfate	SO ₃ ²⁻ sulfite	S ²⁻ sulfide	(Note: All are 2- anions)
Group 15	NO ₃ ⁻ nitrate	NO ₂ ⁻ nitrite	N ³⁻ nitride	
	(Note: Nitride is 3- BUT nitrate and nitrite are 1-)			
	PO ₄ ³⁻ phosphate	PO ₃ ³⁻ phosphite	P ³⁻ phosphide	
	(Note: All are 3-)			
	AsO ₄ ³⁻ arsenate	AsO ₃ ³⁻ orthoarsenite		
Group 14	CO ₃ ²⁻ carbonate	SiO ₃ ²⁻ silicate		
	(Note: no -ite oxyanion for Group 14)			

	<p>Q.17 Name the following anions</p> <p>(a) PO_3^{3-} (b) SO_3^{2-} (c) CO_3^{2-}</p> <p>(d) NO_3^- (e) BO_3^{3-} (f) NO_2^-</p>
<p>A.17 (a) phosphite ion</p> <p>(b) sulfite ion</p> <p>(c) carbonate ion</p> <p>(d) nitrate ion</p> <p>(e) borate ion</p> <p>(f) nitrite ion</p>	<p>Q.18 What would be the formula for</p> <p>(a) nitride ion (b) phosphate ion</p> <p>(c) sulfate ion (d) arsenate ion</p>
<p>A.18 (a) N^{3-} (b) PO_4^{3-}</p> <p>(c) SO_4^{2-} (d) AsO_4^{3-}</p>	<p>Q.19 Name the following:</p> <p>(a) CaSO_3 (b) MnSO_4 (c) FePO_4</p> <p>(d) Ag_2CO_3</p>
<p>A.19 (a) calcium sulfite</p> <p>(b) manganese(II) sulfate</p> <p>(c) iron(III) phosphate</p> <p>(d) silver carbonate</p>	<p>Q.20 What would be the formula for:</p> <p>(a) potassium sulfate</p> <p>(b) aluminium phosphate</p> <p>(c) strontium sulfite</p> <p>(d) lead nitrite</p> <p>(e) ammonium carbonate</p>
<p>A.20 (a) K_2SO_4 (b) AlPO_4</p> <p>(c) SrSO_3 (d) $\text{Pb}(\text{NO}_2)_2$</p> <p>(e) $(\text{NH}_4)_2\text{CO}_3$</p>	

S-8 Oxyanions containing the halogens (except fluorine) follow a slightly different pattern of nomenclature to that in S-7 in order to allow oxyanions containing 1, 2, 3 or 4 oxygen atoms to be named systematically. The ending -ate added to the stem name is given to the anion containing 3 oxygen atoms and -ite to that containing 2. The prefix per- (a contraction of hyper, meaning over or higher) is given to that containing 4 oxygen atoms and the prefix hypo- (meaning under or lower) to that containing one oxygen atom. Notice that all of them, like the simple anion, X^- , have a charge of -1.

hypo	ite	XO^-	where	$\text{X} = \text{Cl, Br or I}$	
	ite	XO_2^-	<i>e.g.</i>	ClO^-	is hypochlorite ion
	ate	XO_3^-		BrO_2^-	is bromite ion
per	ate	XO_4^-		IO_3^-	is iodate ion
				ClO_4^-	is perchlorate ion

	Q.21 Name the following (a) IO^- (b) BrO_3^- (c) ClO_2^- (d) IO_4^-
A.21 (a) hypoiodite ion (b) bromate ion (c) chlorite ion (d) periodate ion	Q.22 What would be the formula for: (a) sodium hypobromite (b) magnesium perchlorate (c) potassium iodate (d) calcium hypochlorite
A.22 (a) NaOBr or NaBrO (b) $\text{Mg}(\text{ClO}_4)_2$ (c) KIO_3 (d) $\text{Ca}(\text{ClO})_2$	

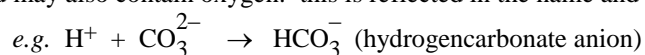
S-9 If the neutral hydrogen compound of these oxyanions dissolves in water to form an acidic solution, the -ite ending of the anion is changed to -ous and the -ate ending becomes -ic, and the word acid is added.

	Q.23 What is the name of an aqueous solution of (a) HClO (b) HIO_4 (c) HBrO_2
A.23 (a) hypochlorous acid (b) periodic acid (c) bromous acid	Q.24 What would be the formula for: (a) nitrous acid (b) phosphoric acid (c) silicic acid (d) boric acid (e) hydrofluoric acid (f) chloric acid
A.24 (a) HNO_2 (b) H_3PO_4 (c) H_2SiO_3 (d) H_3BO_3 (e) HF (f) HClO_3	

S-10 As stated in S-7, oxygen forms anions with some metals. The commonest of these oxyanions are the permanganate ion, chromate ion, and dichromate ion. In all oxyanions, the oxidation state of oxygen is -2. The oxidation state of manganese in MnO_4^- is therefore +7 in order for MnO_4^- to be -1 (*i.e.* Mn (+7), 4(O) = 4 x 2 = -8, overall +7 - 8 = -1). In ClO_4^- the oxidation state of chlorine is +7 and the anion is called 'perchlorate'; in MnO_4^- the oxidation state of the central atom is +7 and the anion is called 'permanganate'. Similarly, the oxidation state of sulfur in SO_4^{2-} is +6; this is the same as the oxidation state of chromium in the chromate ion, CrO_4^{2-} .

	Q.25 What is the formula for: (a) sodium permanganate (b) ammonium chromate (c) permanganic acid (d) potassium dichromate
A.25 (a) NaMnO_4 (b) $(\text{NH}_4)_2\text{CrO}_4$ (c) HMnO_4 (d) $\text{K}_2\text{Cr}_2\text{O}_7$	

S-11 Another important kind of polyatomic anion is formed from polyprotic acids. These type of anions are formed when one or two protons (but not all the available protons) are reacted with bases. The resulting anions then contain hydrogen and may also contain oxygen: this is reflected in the name and formula



	Q.26 Write the formula for (a) hydrogensulfite ion (b) (mono)hydrogenphosphate ion (c) dihydrogenphosphate ion (d) hydrogensulfide ion
A.26 (a) HSO_3^- (b) HPO_4^{2-} (c) H_2PO_4^- (d) HS^-	Q.27 Name the following (a) Na_2HPO_4 (b) NaH_2PO_4 (c) NH_4HSO_4
A.27 (a) sodium (mono)hydrogenphosphate (b) sodium dihydrogenphosphate (c) ammonium hydrogensulfate	Notice that the formula in (c) is NH_4HSO_4 (not NH_5SO_4). Written this way, the ammonium ion and the hydrogen-sulfate ion are clearly and distinctly represented.

S-12 Water of crystallisation may be indicated by (Greek prefix) hydrate or by numbers to indicate the relative numbers of each formula: *e.g.* $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ is sodium sulfate decahydrate or sodium sulfate– ten–water.

S-13 Binary acids are called hydro-acids, *e.g.*

HCl hydrochloric acid

H_2S hydrosulfuric acid

HF hydrofluoric acid

Having completed this programme, you should go through it again to reinforce the knowledge you have gained. Below are presented the names of some compounds and their corresponding formulae. You should go through these by covering the names and attempting to write the formula and then go through them again the reverse manner. If you make a mistake at any stage, you should return to the appropriate part of the programme, find out how to correct your error and take the necessary remedial action.

Chemical Name	Chemical Formula
potassium chloride	KCl
beryllium fluoride	BeF ₂
tin(II) bromide	SnBr ₂
mercury(I) nitrate	Hg ₂ (NO ₃) ₂
chromium(III) sulfate	Cr ₂ (SO ₄) ₃
manganese(II) sulfate	MnSO ₄
ammonium perchlorate	NH ₄ ClO ₄
phosphorus pentachloride	PCl ₅
aluminium oxide	Al ₂ O ₃
cobalt nitrate	Co(NO ₃) ₂
barium sulfite	BaSO ₃
lead chromate	PbCrO ₄
nickel carbonate	NiCO ₃
strontium iodide	SrI ₂
phosphoric acid	H ₃ PO ₄
calcium hypoiodite	Ca(IO) ₂
sodium dichromate	Na ₂ Cr ₂ O ₇
lithium periodate	LiIO ₄
iron(III) sulfate	Fe ₂ (SO ₄) ₃
copper(I) cyanide	CuCN
potassium hydrogensulfite	KHSO ₃
silver nitrite	AgNO ₂
magnesium hydrogencarbonate	Mg(HCO ₃) ₂
ammonia	NH ₃
iron(II) chloride	FeCl ₂
calcium carbide	CaC ₂
copper(II) sulfate pentahydrate	CuSO ₄ ·5H ₂ O
iron(III) bromide hexahydrate	FeBr ₃ ·6H ₂ O

In any study of chemistry it is essential that you can write chemical names and formulae correctly and almost automatically. This is an important first step in being able to use one aspect of the vocabulary of chemistry. Without this proficiency, you are “chemically illiterate” and your difficulties in trying to master other topics in chemistry will be compounded.

PROBLEM SET 0: REVISION OF ASSUMED KNOWLEDGE (not covered in class)

References: Blackman, *et al.* 'Chemistry': 1.2 – 1.4, 3.1 – 3.6, 6.1 – 6.6

NOTE: This problem set is for you to do in Week 1 in your own time and will not be covered in your tutorial classes. These questions are considered some of the easier revision concepts from HSC level chemistry. All students should attempt these questions to ensure you are up to speed on all topics discussed. In addition, you are expected to know the names and symbols of at least the first 36 elements and the symbols for other common elements such as tin, lead, gold, silver, and mercury. You should also have completed the 'Naming of Chemical Compounds' self-instruction tutorial earlier in this course pack.

Useful conversion factors:

Pressure units:	1 atm	=	760 mmHg = 760 Torr = 1.013×10^5 Pa.
	1 bar	=	1.000×10^5 Pa
Temperature units:	0 °C	=	273.15 K
Ideal gas constant:	R	=	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ (or $\text{m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}$ or $\text{L kPa K}^{-1} \text{ mol}^{-1}$)
		=	$0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$

Atoms, moles, and chemical calculations

1. Explain clearly the meaning of the following terms:

- | | | |
|-------------------|----------------------|-----------------------|
| (a) atomic number | (d) atomic mass | (g) a compound |
| (b) mass number | (e) atomic mass unit | (h) a binary compound |
| (c) an isotope | (f) a mole of atoms | (i) molar mass |

2. (a) Complete the following table of neutral atoms.

	Symbol	Atomic number	Mass number	Number of protons	Number of neutrons	Number of electrons
(i)	$^{40}_{20}\text{Ca}$					
(ii)			55			25

- (b) Naturally occurring boron is composed of only two isotopes $^{10}_5\text{B}$ and $^{11}_5\text{B}$ with isotopic masses of 10.0129 and 11.00931 respectively. To account for the atomic mass of 10.811, what must be the percentage abundance of each isotope?

3. (a) Complete the following table.

	Symbol	Atomic Number	Mass Number	Number of Protons	Number of Neutrons	Number of Electrons
(i)	$^{52}_{24}\text{Cr}$					
(ii)			80		46	36
(iii)	$^{81}\text{Br}^-$					
(iv)		25	55			23

- (b) Protium, deuterium and tritium are isotopes of hydrogen. Write the symbols which identify atoms of these isotopes and comment on any expected differences in their physical and chemical properties.

- (c) Calculate the average atomic mass of sulfur from this data for its four naturally occurring isotopes:

isotopic mass number	percent abundance	isotopic mass
32	95.0	31.97207
33	0.760	32.97146
34	4.22	33.96786
36	0.0140	35.96709

4. (a) Write the chemical formula for each of the following:

- | | | |
|--------------------------------|-----------------------------|--------------------------------------|
| (i) sodium chlorate | (v) periodic acid | (ix) mercury(I) chloride |
| (ii) lithium hydrogencarbonate | (vi) copper(II) oxide | (x) iron(III) phosphate |
| (iii) potassium permanganate | (vii) chromium(III) sulfate | (xi) cobalt(II) acetate tetrahydrate |
| (iv) sodium oxalate | (viii) acetic acid | (xii) lead(II) chromate |

- (b) Provide an unambiguous chemical name for each of the following:

- | | | |
|--|--|-------------------------------|
| (i) FeI_2 | (v) Cu_2S | (ix) K_2CrO_4 |
| (ii) NaCN | (vi) HNO_2 | (x) SF_6 |
| (iii) HClO_3 | (vii) $(\text{NH}_4)_2\text{HPO}_4$ | (xi) HNO_3 |
| (iv) $\text{Na}_2\text{S}_2\text{O}_3$ | (viii) $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ | (xii) MnO_2 |

5. (a) Write the chemical formula for each of the following:

- | | | |
|---------------------|------------------------|--------------------------|
| (i) sodium chloride | (ii) magnesium bromide | (v) copper(I) chloride |
| (ii) carbon dioxide | (iv) magnesium oxide | (vi) copper(II) chloride |

- (b) Write the chemical formula for each of the following:

- | | | |
|--------------------------------|-------------------------------------|--------------------------------------|
| (i) sodium chlorite | (v) barium carbonate | (ix) mercury(II) cyanide |
| (ii) lithium hydrogencarbonate | (vi) magnesium nitrate | (x) iron(III) phosphate |
| (iii) potassium permanganate | (vii) chromium(III) sulfate | (xi) cobalt(II) acetate tetrahydrate |
| (iv) calcium oxalate | (viii) strontium iodide hexahydrate | (xii) lead(II) chromate |

- (c) Provide an unambiguous chemical name for each of the following:

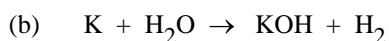
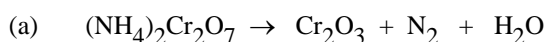
- | | | | |
|--------------------|----------------------------|---------------------|--------------------------------|
| (i) SiO_2 | (iii) MnO_2 | (v) SF_6 | (vii) FeO |
| (ii) KBr | (iv) Cu_2S | (vi) CCl_4 | (viii) Fe_2O_3 |

- (d) Provide an unambiguous chemical name for each of the following:

- | | | | |
|-------------------------------|-----------------------------------|------------------------------------|---|
| (i) NaOH | (iv) $\text{Al}_2(\text{CO}_3)_3$ | (vii) KBrO_3 | (x) $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ |
| (ii) KCN | (v) LiNO_3 | (viii) KMnO_4 | (xi) $\text{K}_2\text{Cr}_2\text{O}_7$ |
| (iii) Sb_2O_5 | (vi) NaNO_2 | (ix) $(\text{NH}_4)_2\text{HPO}_4$ | (xii) $\text{Na}_2\text{S}_2\text{O}_3$ |

6. One of the hydrides of boron has molar mass = $122.22 \text{ g mol}^{-1}$ and is 11.55 % by mass hydrogen. Determine its molecular formula.

7. Balance the following equations – the final equation should show the lowest whole number coefficients of reactants and products.



8. (a) Calculate the number of oxygen atoms that are contained in 1.10 moles of copper(II) sulfate pentahydrate.
 (b) Determine the number of moles of chromium atoms in 25.0 g of sodium chromate.
 (c) Determine the mass of 2.52 moles of oxygen gas.
 (d) How many grams of methanol (CH_3OH) must be added to 50.0 g water to make a solution containing equal numbers of methanol and water molecules?
9. (a) Calculate the molarity of the cation in each of the following solutions.
 (i) 2.30 M MgCl_2 (ii) 2.30 M MgSO_4 (v) 1.50 M Na_3PO_4
 (iii) 1.50 M NaCl (iv) 1.50 M Na_2SO_4
10. Briefly explain the meaning of the following terms.
 (a) solute (c) concentrated (e) dilute (a verb)
 (b) solvent (d) dilute (an adjective) (f) aliquot
11. (a) Determine the number of oxygen atoms contained in 1.10 mol of aluminium chlorate hexahydrate.
 (b) Determine the amount (mol) of chromium atoms in 140.0 g chromium(III) oxide.
 (c) Determine the mass of 1.16 moles of calcium phosphate.
 (d) Calculate the mass of copper(I) sulfide which contains 4.6×10^{23} copper atoms.
 (e) How many grams of ethanol ($\text{C}_2\text{H}_5\text{OH}$) must be added to 90.0 g water to make a solution containing equal numbers of ethanol and water molecules?
12. Write the unambiguous chemical name for each of the following acids in aqueous solution.
 (a) HClO (d) HClO_4 (g) HNO_2 (j) HF
 (b) HClO_2 (e) HIO_4 (h) CH_3COOH
 (c) HClO_3 (f) HNO_3 (i) HI

Solution stoichiometry and properties of gases

13. A water solution containing 50.0 g ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, per litre of solution has a density of 0.989 g cm^{-3} at 25°C . Calculate:
 (a) the molarity of $\text{CH}_3\text{CH}_2\text{OH}$, and
 (b) the mole fraction of $\text{CH}_3\text{CH}_2\text{OH}$ in this solution.
14. (a) Calculate the mass of solute required to make:
 (i) 250 cm^3 of 0.100 M potassium sulfate
 (ii) 50.0 mL of 0.100 M copper(II) sulfate pentahydrate
 (iii) 5.0 L of 0.020 M potassium permanganate
 (b) Calculate the volume of concentrated reagent required to make the following dilute solutions:
 (i) 18.0 M H_2SO_4 , to make 2.5 L of 2.0 M H_2SO_4 .
 (ii) 15 M NH_3 , to make 250 mL of 1.2 M NH_3 .

15. Balance the following equations – the final equation should show the lowest whole number coefficients of reactants and products.
- $\text{C}_4\text{H}_9\text{OH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
 - $\text{FeS}_2 + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2$
 - $\text{Ca}_3(\text{PO}_4)_2 + \text{SiO}_2 + \text{C} \rightarrow \text{CaSiO}_3 + \text{CO} + \text{P}_4$
16. (a) Calculate the volume of concentrated reagent required to make the following dilute solutions:
- 18.0 M H_2SO_4 , to make 5.0 L of 5.0 M H_2SO_4 .
 - 15 M NH_3 , to make 500 cm^3 of 1.2 M NH_3 .
- (b) Calculate the mass of solute required to make:
- 250 cm^3 of 0.050 M sodium carbonate
 - 10.0 cm^3 of 0.100 M $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
- (c) How many litres of 0.200 M NaOH solution may be prepared from 50.0 g of NaOH pellets?
- (d) What is the minimum volume of 0.1060 M AgNO_3 must be reacted with 125 mL of 0.0862 M K_2CrO_4 to precipitate all the chromate ions as Ag_2CrO_4 ?
- (e) It is desired to prepare 250.0 mL of a standard solution having a concentration of 0.1000 M AgNO_3 . How many grams of a sample of AgNO_3 of 98.8 % purity are required for this purpose?
- (f) A 20.0 mL sample of 0.15 M calcium chloride (CaCl_2) solution was pipetted into a 100.0 mL volumetric flask, which was made up to the 100.0 mL mark by adding water. What is the concentration of chloride ions in the final, mixed, solution?
- (g) It is desired to make 250.0 mL of 0.010 M sulfuric acid solution, by diluting the 0.100 M solution provided in the lab. What volume of 0.100 M sulfuric acid needs to be measured out and diluted to the 250.0 mL final volume?
17. Hydrogen at 1200 Torr pressure is in a constant volume, constant temperature container and nitrogen is introduced until the total pressure is 2100 Torr. The formation of ammonia is started by adding a catalyst, the whole process taking place at constant temperature. Calculate the partial pressure of (i) hydrogen, and (ii) ammonia, in the container when the partial pressure of nitrogen is 650 Torr.

NUMERICAL ANSWERS

- (b) $19.902\% \frac{10}{5} \text{ B}$;
- (c) 32.1
- $\text{B}_{10}\text{H}_{14}$
- (a) 5.962×10^{24} , (b) 0.154, (c) 80.64 g, (d) 88.89 g
- (a) (i) 2.30 M (ii) 2.30 M (iii) 1.50 M (iv) 3.00 M (v) 4.50 M
- (a) 9.93×10^{24} ; (b) 1.842; (c) 360 g; (d) 61 g; (e) $2.30 \times 10^2 \text{ g}$
- (a) 1.08 mol L^{-1} , (b) 0.020
- (a) (i) 4.358 g (ii) 1.249 g (iii) 15.80 g, (b) (i) 278 mL (ii) 20 mL
- (a) (i) 1.4 L; (ii) 0.040 L (b) (i) 1.3 g; (ii) 0.392 g (c) 6.25 L (d) 203 mL; (e) 4.30 g; (f) 0.06 M; (g) 25.0 mL.

PROBLEM SET 1: REVISION OF ASSUMED KNOWLEDGE (covered in Week 2 class)

References: Blackman, *et al.* 'Chemistry': 1.2 – 1.4, 3.1 – 3.6, 6.1 – 6.6

CHEM1011 and **CHEM1031/1051** may proceed at different rates through this problem set.

Useful conversion factors:

Pressure units:	1 atm	=	760 mmHg = 760 Torr = 1.013×10^5 Pa.
	1 bar	=	1.000×10^5 Pa
Temperature units:	0 °C	=	273.15 K
Ideal gas constant:	R	=	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ (or $\text{m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}$ or $\text{L kPa K}^{-1} \text{ mol}^{-1}$)
		=	$0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$

CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

- Briefly explain what is meant by the term "limiting reagent".
 - Magnesium reacts with nitrogen to form Mg_3N_2 .
 - Write a balanced equation;
 - Will a mixture of 30.0 g Mg and 20.0 g N_2 have sufficient magnesium to react with all the nitrogen?
 - Calculate the maximum mass of magnesium nitride which can be formed.
 - If, instead of the maximum yield from this reaction, you produced 28.3g of magnesium nitride, calculate the percentage yield.
- Teaspoons made from a certain alloy containing the elements bismuth, lead, tin and indium are not recommended for stirring sugar into hot coffee, as the alloy melts at 58 °C. A sample of the alloy, weighing 5.038 g, was treated in such a way as to convert the tin to 0.742 g SnO_2 , the lead to 1.298 g PbSO_4 and the bismuth to 2.780 g Bi_2O_3 .
What is the percentage, by mass, of each of the four elements in the alloy sample?
- Calculate the percentage composition, by mass, of each element in $\text{C}_2\text{H}_5\text{OH}$ (ethanol).
 - The composition of caffeine is 49.48 % carbon, 5.15 % hydrogen, 16.49 % oxygen, and 28.87 % nitrogen by mass. The molar mass of caffeine is 194.2 g mol^{-1} . Determine the empirical formula and the molecular formula of caffeine.
- Lithium hydroxide is used to absorb carbon dioxide from the atmosphere in space craft. The products of this reaction are lithium carbonate and water.
 - Write a balanced equation for this reaction;
 - Calculate the mass of CO_2 which can be absorbed by 1.00 kg of lithium hydroxide.

5. (a) A sample of concentrated hydrochloric acid was prepared by passing HCl gas into distilled water. The resultant acid solution had a density of 1.18 g cm^{-3} at 25°C . Analysis showed that 20.0 g of the concentrated acid contained 8.16 g of HCl.
- How many grams of HCl are contained in 100.0 g of the concentrated acid?
 - What is the percent by mass, of water in the concentrated acid?
 - Calculate the mass of HCl contained in 1.00 L of the concentrated acid.
 - How many moles of HCl are contained in 1.00 L of the acid solution?
- (b) An aqueous solution containing 100.0 g of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, per litre of solution has a density of 0.984 g cm^{-3} . Calculate:
- the molarity of $\text{CH}_3\text{CH}_2\text{OH}$, and
 - the mole fraction of $\text{CH}_3\text{CH}_2\text{OH}$ in this solution.
6. (a) The volume of a gas is 45.0 L at 45°C and 750 mmHg. What volume will it occupy at 25°C and 1 atm pressure?
- (b) Calculate the density of gaseous CH_4 at 50°C and 1.20 atm.
- (c) Calculate the molar mass of a gas if 0.455 g occupies a volume of 250 mL at 27°C and 772 mmHg.
- (d) The number of CH_4 molecules in a gas mixture is four times the number of C_2H_4 molecules. The partial pressure of CH_4 is 100 mmHg. What is the partial pressure of C_2H_4 in the mixture?
7. Commercial "antacids" frequently contain oxides or carbonates which react with excess stomach acid, assumed to be HCl. Each tablet of a certain antacid contains aluminium hydroxide (200 mg) and magnesium hydroxide (200 mg). Assume the hyperacidity is due to HCl in the gastric juices, calculate the amount of acid neutralized by each tablet. Express your answer as mL of 0.100 M HCl.
8. (a) The volume of a gas is 45.0 L at 25°C and 750 mmHg. What volume will it occupy at the same temperature, but at 1.00 atm pressure?
- (b) 500 mL of a gas at 10°C , exerts a pressure of 1.0 atm. What will be the pressure if the temperature is increased to 50°C and the volume is kept constant?
- (c) Calculate the molar mass of a gas if the gas has a density of 3.64 g L^{-1} at 27°C and 772 mmHg.
9. Write balanced *ionic* equations for the following chemical reactions. Include the state of matter of each species but do not include spectator ions.
- Example: Solid calcium sulfite reacts with hydrochloric acid to give sulfur dioxide gas.
- Overall equation: $\text{CaSO}_3(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{CaCl}_2(\text{aq})$
- Net ionic equation: $\text{CaSO}_3(\text{s}) + 2 \text{H}^+(\text{aq}) \rightarrow \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{Ca}^{2+}(\text{aq})$
- Solid strontium carbonate reacts with hydrochloric acid to give gaseous carbon dioxide.
 - Lead nitrate solution, when mixed with sodium iodide solution, gives a yellow precipitate of lead iodide.
 - When excess dilute sulfuric acid was added with stirring, to solid barium carbonate, carbon dioxide gas was liberated, and solid barium sulfate was formed.
 - $\text{Fe}^{3+}(\text{aq}) + \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Fe}(\text{OH})_3(\text{s}) + \text{NH}_4^+(\text{aq})$
 - When potassium metal is added to water a violent reaction ensues. Hydrogen gas is liberated and the resultant solution is basic.

HARDER CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

10. A 3.92 g sample of a pure ammonium salt NH_4X (X^- is an unknown monatomic anion) was analysed by treatment with excess NaOH, liberating $\text{NH}_3(\text{g})$ which was absorbed in 250.0 mL of a 0.400 M solution of HCl. The excess HCl was titrated with 2.00 M NaOH and required 80.0 mL for neutralization. Identify X, and show all your calculations.
11. Air consists of 21 % oxygen, 78 % nitrogen and 1 % argon by volume. Calculate:
- the concentration in mol m^{-3} , of each gas at 273 K,
 - the average molar mass of air,
 - the number of oxygen molecules in 15 g air.
12. Ethane gas, C_2H_6 , burns in air as indicated by the equation:
- $$2 \text{C}_2\text{H}_6(\text{g}) + 7 \text{O}_2(\text{g}) \rightarrow 4 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$$
- For complete combustion of 25.0 litres of ethane, determine:
- the volume of oxygen required,
 - the volume of air required (assuming air consists of 21 % oxygen by volume),
 - the volume of carbon dioxide produced. (Assume all volumes are measured at the same temperature and pressure).
13. Saccharin (molar mass = $183.18 \text{ g mol}^{-1}$) and calcium cyclamate (molar mass = $396.55 \text{ g mol}^{-1}$) are substitutes for sugar.
- Calculate the percentage, by mass, of each element in $\text{Ca}(\text{C}_6\text{H}_{11}\text{NHSO}_3)_2$ (calcium cyclamate)
 - The composition of saccharin is 45.89 % carbon, 2.75 % hydrogen, 26.20 % oxygen, 7.65 % nitrogen and 17.51 % sulfur by mass. Determine the empirical formula and the molecular formula of saccharin.

NUMERICAL ANSWERS

- (b) (iii) 41.5 g; (iv) 68.2%
- 11.60 % Sn, 17.60 % Pb, 49.50 % Bi, 21.30 % In
- (a) 52.1 % C, 13.1 % H, 34.7 % O, (b) molecular formula: $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$
- (b) 917 g
- (a) (i) 40.8 g (ii) 59.2 % H_2O ; (iii) 481 g; (iv) 13.2 mol
(b) (i) 2.171 M; (ii) $X_{\text{ethanol}} = 0.042$;
- (a) 41.6 L (b) 0.73 g L^{-1} (c) 44.1 g mol^{-1} (d) 25 mm Hg
- 146 mL
- (a) 44.4 L, (b) 1.14 atm, (c) 88.3 g mol^{-1}
- Br
- (a) $\text{O}_2 \text{ conc.} = 9.4 \text{ mol m}^{-3}$; (b) 29; (c) 6.5×10^{22} ;
- (a) 87.5 L; (b) 417 L; (c) 50.0 L;
- (a) 10.11 % Ca, 36.34 % C, 6.10 % H, 7.07 % N, 16.17 % S, 24.21 % O; (b) $\text{C}_7\text{H}_5\text{O}_3\text{NS}$

PROBLEM SET 2: ELECTRONIC STRUCTURE OF ATOMS

References: Blackman, *et al.* 'Chemistry': 4.1 – 4.5

CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

1. Consider the following questions and write down a few dot points for each.
 - (a) What is visible light made of (and other forms of electromagnetic radiation)?
 - (b) How is the wavelength of a photon related to its wavenumber, energy and frequency?
 - (c) What are 'energy levels' in an atom and why do we call them 'discrete'?
 - (d) What is the 'ground state' and what meant by the term 'energy transition' in the context of electrons and atoms?
 - (e) How does an electron's transition from a higher energy level to a lower energy level relate to the energy of the emitted photon? Is this an example of absorption or emission?
 - (f) An atom can have an infinite number of allowed energies. What are all the allowed energies above the ground state referred to as?
2. Below is a black-and-white image of a spectra. When printed in full-colour*, the grey sections show a rainbow of colours from violet (left) to red (right), and the darker regions black.
 - (a) In the **emission** spectrum what do the coloured lines represent?
 - (b) Why are the lines coloured (in the visible region) on an emission spectrum, but dark on an absorption spectrum?
 - (c) Why do lines in the emission and absorption spectra of the same atom appear at the same wavelength?
 - (d) Describe how energy levels in a hydrogen atom relate to spectral lines observed below.

Hydrogen absorption spectrum



Hydrogen emission spectrum



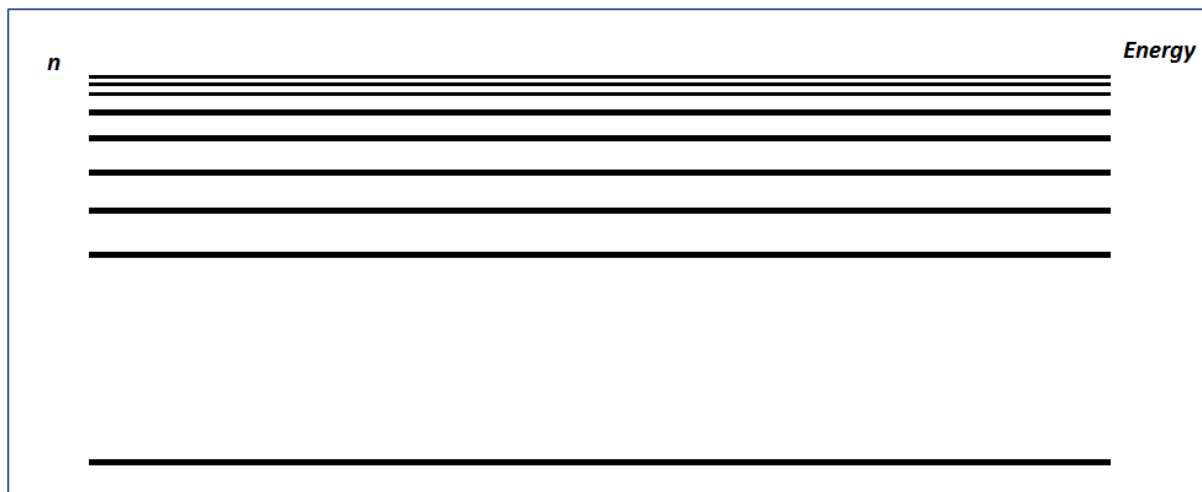
400 nm

700 nm

*Follow this QR code to see what this spectrum looks like in colour:



3. (a) Label the following points on the blank energy level diagram below:
- Energy levels (n) 1-6 and ∞ (infinity)
 - Match the potential energy for each level: $-21.56 \times 10^{-19} \text{ J}$, $-5.45 \times 10^{-19} \text{ J}$, $-2.42 \times 10^{-19} \text{ J}$, $-1.36 \times 10^{-19} \text{ J}$, $-0.87 \times 10^{-19} \text{ J}$, $-0.61 \times 10^{-19} \text{ J}$, and 0 J .
 - Ground state



- Draw **all** the allowable **absorption** transitions for a single electron in the first 6 energy levels of a hydrogen atom.
 - $21.56 \times 10^{-19} \text{ J}$ of energy is required to remove one electron from a single ground state H atom. Between what energy level is this transition occurring and what is this commonly referred to as?
 - On a new sheet of paper, sketch an energy level diagram showing the Lyman, Balmer, and Paschen series of transitions that occur when energy is lost by a hydrogen atom.
 - Consider the energy transition for an electron from energy level $n=4$ to $n=2$.
 - Would this result in an emission or absorption of a photon?
 - Use the values on the energy diagram to determine the wavelength of the photon.
 - From which region of electromagnetic spectrum is the photon (if in the visible region then what colour does this correspond to)?
4. The Rydberg equation can be used in place of an energy diagram to predict the nature of the photons involved in emission and absorption energy transitions, where n_1 and n_2 are integers (whole numbers) representing discrete energy levels (principle quantum numbers) with $n_2 > n_1$.

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

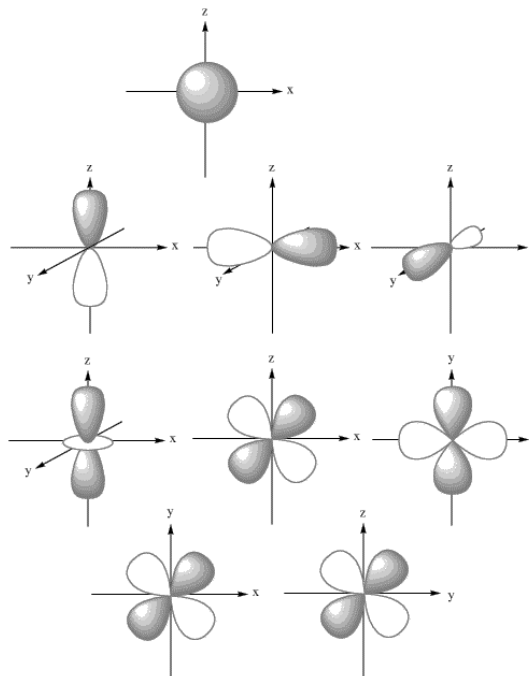
- Consider a sample of hydrogen atoms all in the ground state.
 - What wavenumber ($\frac{1}{\lambda}$) would a beam of photons need to have to excite the hydrogen atoms to the third energy level? What wavelength (in nm) is this?
 - Calculate the photon's energy and frequency from your answers to part (i).
 - What region of the electromagnetic spectrum would the beam of photons (from answer above) belong to?

- (iv) As the sample of hydrogen atoms returns to the ground state how many emission lines would you expect to observe? (assuming you can detect photons in UV, Visible and Infra-red).
- (b) If the electron of the hydrogen atom is raised from the lowest energy level ($n = 1$) to the energy level $n = \infty$, the electron becomes free of the atom and the $H^+(g)$ ion is produced. Calculate the energy of the photon required for this process (in $J \text{ atom}^{-1}$ and in $kJ \text{ mol}^{-1}$).

5. (a) Describe what an atomic orbital is in terms of probability and electron density.

(b) Consider the images to the right. Circle all the orbitals that are the same 'type' and label them s, p or d. How many of each orbital type are there?

(c) Match the orbital type (e.g. s orbital) with the value of the azimuthal quantum number (l) for $l = 0-3$



6. (a) Give a valid set of four quantum numbers for each of the electrons in a ground state nitrogen atom.

(b) Show how the Pauli principle and Hund's rule are involved in your answer to part (a).

7. Which of the following are not permissible sets of quantum numbers for an electron in an atom?

	n	l	m_l	m_s
(a)	3	2	-1	$+\frac{1}{2}$
(b)	2	3	-1	$-\frac{1}{2}$
(c)	3	2	-3	$+\frac{1}{2}$
(d)	4	1	1	$+\frac{3}{2}$

For any value which is not permitted, substitute an allowed value.

8. (a) Using the Aufbau principle and arrows-in-labelled-boxes notation, write the ground state electronic configurations for the following isolated atoms or ions:

(i) N; Be; K; C

(ii) Cu; Fe; Ti; Ni

(iii) Ti^{2+} ; Na^+ ; Fe^{2+} ; Cr^{3+}

(iv) F^- ; H^- ; N^{3-} ; Se^{2-}

(b) Write the ground state configurations of each of the above species using $1s^1$ notation.

(c) Write the formulae for two cations and two anions which are isoelectronic with argon. Which of these ions has the largest ionic radius?

(d) Which of the ions in (a) (iii) are paramagnetic?

EXTRA PRACTICE QUESTIONS

Attempt these in your own time. The tutor will NOT cover these questions unless the class finished early and there is extra time. You may need to look up the values for some of these questions in the SI Chemical Data book. For help with these questions, see the Duty Tutor.

9. The wavelengths of light emitted by atomic hydrogen are given by the equation:

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

where R_H is the Rydberg constant for hydrogen with the value $R_H = 1.096776 \times 10^7 \text{ m}^{-1}$.

- (a) The Lyman series in the spectrum of the hydrogen atom originate from transitions for which the lower energy level has $n = 1$. Calculate the wavenumber (either in m^{-1} or cm^{-1}), wavelength (either in nm or m) and the frequency (s^{-1} or Hz) of the two longest wavelength lines in the Lyman series (speed of light is $c = 2.99792458 \times 10^8 \text{ ms}^{-1}$). Indicate the region of the spectrum corresponding to these transitions.
- (b) If the electron of the hydrogen atom is raised from the lowest energy level ($n = 1$) to the energy level $n = \infty$, the electron becomes free of the atom and the $\text{H}^+(\text{g})$ ion is produced. Calculate the energy required for this process (in J atom^{-1} and in kJ mol^{-1}).

10. (a) Complete the following table of quantum numbers.

Symbol	Name	Permitted values	Physical interpretation
n			
l			
m_l			
m_s			

- (b) What is the maximum number of electrons that can be accommodated in:

- (i) all orbitals with $n = 6$, $l = 1$?
- (ii) all sublevels with $n = 4$?

11. (a) The yellow spectral line of sodium occurs at 589 nm. Calculate the frequency and energy of one photon of this light.
- (b) A potassium atom loses $4.28 \times 10^{-19} \text{ J}$ of energy by emitting a single photon. Calculate the wavelength of the emitted photon.
12. (a) Using the Aufbau principle and arrows-in-labelled-boxes notation, write the ground state electronic configurations for the following isolated atoms or ions:
- (i) O; B; Si; Ca
- (ii) Sc; Cr; Ni; Zn
- (iii) Ti^+ ; Ca^+ ; Zn^{2+} ; Cr^{3+}
- (iv) O^{2-} ; Na^{2+} ; P^- ; Br^-
- (b) Write the ground state configurations of each of the above species using $1s^1$ notation.
- (c) Which of the ions in (a) (iii) are paramagnetic?
- (d) Which, if any, of the ions in (a) (iv) are isoelectronic with a noble gas?

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13. This question will require you to do some research using whatever resources you choose.
- (a) What is a Rydberg atom?
 - (b) What are typical quantum numbers for an electron in a Rydberg atom?
 - (c) How large is a regular atom compared to the wavelength of visible light? How large is a Rydberg atom?
 - (d) Why are Rydberg atoms very fragile?

NUMERICAL ANSWERS

3. (e)(ii) 486 nm
4. (a) (i) $9.751 \times 10^6 \text{ m}^{-1}$; 102.5 nm; (ii) $1.93 \times 10^{-18} \text{ J}$; $2.92 \times 10^{15} \text{ Hz}$ (iv) 3,
(b) $2.18 \times 10^{-18} \text{ J atom}^{-1}$; 1,312 kJ mol⁻¹
9. (a) $8.225820 \times 10^6 \text{ m}^{-1}$; 121.5584 nm; $2.466039 \times 10^{15} \text{ Hz}$ and $9.749120 \times 10^6 \text{ m}^{-1}$; 102.5734 nm;
 $2.922713 \times 10^{15} \text{ Hz}$. (b) $2.178688 \times 10^{-18} \text{ J atom}^{-1}$; 1312 kJ mol⁻¹.
10. (b) (i) 6 (ii) 32.
11. (a) $5.09 \times 10^{14} \text{ Hz}$, $3.37 \times 10^{-19} \text{ J}$; (b) 464 nm

PROBLEM SET 3: PERIODICITY OF ATOMIC PROPERTIES AND INTRODUCTION TO BONDING

References: Blackman, *et al.* 'Chemistry': 4.6 – 4.9

CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

- On the periodic table below, colour in the blocks of elements which have s, p and d valence orbitals (use a different colour for each orbital type). The electron configurations of the noble gases and orbital filling diagram below may help you to do this.

Element	Symbol	Atomic Number	Electron Configuration
Helium	He	2	$1s^2$
Neon	Ne	10	$[He] 2s^2 2p^6$
Argon	Ar	18	$[Ne] 3s^2 3p^6$
Krypton	Kr	36	$[Ar] 3d^{10} 4s^2 4p^6$
Xenon	Xe	54	$[Kr] 4d^{10} 5s^2 5p^6$
Radon	Ra	86	$[Xe] 4f^{14} 5d^{10} 6s^2 6p^6$

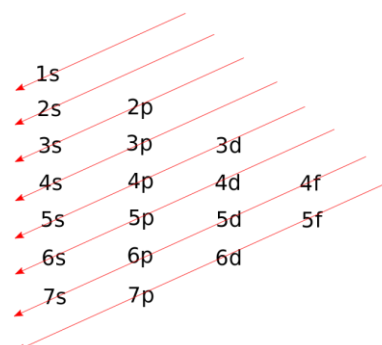


Figure 1: Orbital filling diagram (Source: Adrignoloa)

- Why is there a gap between Be and B and between Mg and Al in the periodic table?
- Add labels to your periodic table in question 1, showing the surplus or deficit of electrons of each group compared to the nearest noble gas electron configuration.
- Think about the following chemical terms. How would you define these in one or two sentences?
 - Atomic radius
 - Ionic radius
 - Valence electron
 - Dipole moment
 - Electronegativity
 - Electron affinity
 - Ionisation energy
- Consider the answer to question 2 to help you predict the trends in electronegativity, atomic radius and ionisation energy in the periodic table and draw arrows on the table from question 1 to show these trends.

- (b) Which of these trends could we use to predict the type of bonds (ionic or covalent) that might exist between two or more atoms?

5. Which element am I?

- (a) I have a high electron affinity. The element on my left in the Periodic Table has a lower electron affinity. The element on my right in the Periodic Table has a higher ionization energy and basically no electron affinity. I am toxic in my elemental state, but I am very commonly found in my non-toxic ionic state. Within my group, I have the second highest ionization energy.
- (b) I am a metal. My atomic radius is smaller than the atomic radius of the element with one fewer protons, but my +1 ionic radius is larger than the +1 ionic radius of the element with one fewer protons. Of the two elements in my group that have biological importance, I am the one with higher electronegativity.

HARDER CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

6. a) Describe the trends in the effective charge (Z) of elements in the periodic table;
- i) down a group,
 - ii) across a period.
- b) How do these trends relate to trends in atomic radius and first ionisation energy discussed in question 4?
7. In each of the following pairs, which would be the larger ion? Give a reason for your answer.
- (a) K^+ and Cl^- (b) Cl^- and Br^- (c) Cu^+ and Cu^{2+}

EXTRA PRACTICE QUESTIONS

Attempt these in your own time. The tutor will NOT cover these questions unless the class finished early and there is extra time. You may need to look up the values for some of these questions in the SI Chemical Data book. For help with these questions, see the Duty Tutor.

8. (a) Explain what is meant by: (i) atomic radius (ii) ionic radius.
- (b) Is a cation smaller or larger than its parent atom?
- (c) Circle the species in each part that best fits the description given:
- (i) the largest atomic radius:
K, Na, Mg, Al, S, Cl, Br
 - (ii) the largest ionic radius:
 O^{2-} , F^- , N^{3-} , Na^+ , Mg^{2+} , Al^{3+}
 - (iii) a isolated paramagnetic ion:
 K^+ , Ni^{2+} , Cu^+ , Zn^{2+} , Sc^{3+}
 - (iv) the smaller ionic radius:
 Fe^{2+} , Fe^{3+}
 - (v) the most electronegative element:
Na, Cs, P, Al, Cl, I

9. Circle the species that best fits the description given:
- (a) the smallest atomic radius:
K, Na, Mg, Al, S, Cl, Br
- (b) the smallest ionic radius:
 O^{2-} , F^- , N^{3-} , Na^+ , Mg^{2+} , Al^{3+}
- (c) an isolated paramagnetic ion:
 Ca^{2+} , Cr^{3+} , Sc^{3+} , Br^- , Te^{2-}
- (d) the most polar molecule:
HCl, HF, HBr, HI
10. For each part below make a rough sketch of the shape of the periodic table and shade in the region described.
- (a) elements with the lowest first ionization energy
- (b) elements with the most exothermic electron affinity
- (c) elements with the highest electronegativity
- (d) elements which have the largest atomic radius in their group
- (e) elements which have the largest atomic radius in their period
11. In each of the following pairs, which would be the larger ion? Give a reason for your answer.
- (a) O^{2-} and F^- (b) S^{2-} and Se^{2-} (c) Tl^+ and Tl^{3+}
- (d) Cu^+ and Zn^{2+} (e) Na^+ and K^+ (f) K^+ and Sc^{3+}
12. (a) What happens when a bond is formed between two atoms?
- (b) Why do bonds form (for example) why do two hydrogen atoms form a molecule of H_2 ?
- (c) The classification of bonding types is better represented as a continuum than as discrete categories. Consider what this means in terms of electronegativity and the types of bonding you are familiar with.

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13. (a) Define the terms: (i) first ionization enthalpy and (ii) second ionization enthalpy
- (b) (i) Without using actual values, summarize the trend of first ionization enthalpy (I.E.) for the elements with atomic numbers 10 to 18 by plotting 1st I.E. versus atomic number
State briefly the general periodic changes in first ionization enthalpy, and any irregularities which occur. Suggest reasons.
- (ii) On the same axes plot the variation of second ionization enthalpy for the same elements. Give reason(s) for the features in the plot and compare with (i).
14. Another method to predict bond types (besides using electronegativity differences) is to compare the atomic volumes (based on the ionic radii) of the cations and anions. Starting from the assumption that a bond is totally ionic this approach looks at the polarizability of the anion and polarizing ability of the cation to assess how much electron density is pulled into the region between the ions. Discuss this using the series of halides as examples: NaF, NaCl, NaBr, NaI; and BeF_2 , $BeCl_2$, $BeBr_2$, BeI_2 . (Googling for 'Fajans rules' will get you more information on this approach to describing bonds.)

PROBLEM SET 4: MOLECULAR STRUCTURE – LEWIS DIAGRAMS

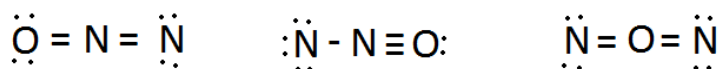
References: Blackman, *et al.* 'Chemistry': 5.3 – 5.5

CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

- For the following species (i)-(vi):
 - Determine the central atom in the species (where relevant)
 - Determine the total number of valence electron
 - What is the octet rule?
 - Use the information from (a) and (b) to draw the Lewis structure for the species
 - HCl
 - CF₄
 - H₂O
 - NH₄⁺
 - ClO₂[−]
 - CO

- Calculate the formal charge for each atom in the Lewis diagrams of N₂O



- Based on formal charge, which is the most accurate representation of bonding in the molecule and why?
- Consider the electron configurations in the periodic table for elements in the 3rd period and beyond: why do you think these elements (as a central atom) can form molecules where they have more than an octet of electrons?
 - Consider the electron configuration of Be. Why do you think it can form molecules where it has less than the octet of electrons? What other elements on the Periodic Table does this also apply to?
 - Draw a Lewis diagram for BeCl₂ and PCl₅. Use formal charge to show why they are the most suitable Lewis structures
 - Draw a Lewis structure of the sulfate anion (SO₄^{2−}) in which all the S–O bonds are single bonds. Label each atom with its formal charge.
 - Draw a Lewis structure for sulfate where two of the S–O bonds are double bonds and two are single bonds. Label each atom with its formal charge. How many of these resonance structures are there?
 - Based on your answers from (a) and (b), determine which of these two Lewis structures is more likely to represent the electron distribution in the sulfate anion.

HARDER CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

- Based on your answers to questions 1-4, discuss whether you think considering 'formal charge' or 'the octet rule' provides the better approach for determining the correct Lewis structure. (*note: there is no universal right answer to this question*).
- Draw all possible canonical (resonance) forms for each of these species:
 - NO₂[−]
 - CO₃^{2−}
 - Draw a Lewis structure for methanol (CH₃OH).

- (c) Would you expect the C–O bond in carbonate to be longer or shorter than the C–O bond in CH_3OH ?
 (d) Would you expect the bond energy for the C–O bond in carbonate to be larger or smaller than for the C–O bond in CH_3OH ?

7. Draw a Lewis structure for the following species. Indicate those species where the octet rule is violated, and use formal charge to show why they are the most suitable Lewis structures.

- (a) HCl (b) Cl_2 (c) CHCl_3 (d) CO (e) ClO_2^- (f) XeF_4 (g) PCl_5

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8. Draw Lewis structures for the following organic molecules.

- (a) H_2CO (c) CH_3NHCH_3
 (b) H_2CNH (d) CH_3COOH (take care with the connectivity of the atoms)

EXTRA PRACTICE QUESTIONS

Attempt these in your own time. The tutor will NOT cover these questions unless the class finished early and there is extra time. You may need to look up the values for some of these questions in the SI Chemical Data book. For help with these questions, see the Duty Tutor.

9. What is the total number of valence electrons in each of these species?

- (a) SCl_2 (c) CO_3^{2-}
 (b) BF_3 (d) PCl_5

10. (a) Draw Lewis structures for CH_4 and NH_4^+ .

- (b) Why are the Lewis structures of these two species so similar?

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11. (a) Draw the Lewis structure for AlCl_3 . Is the octet rule obeyed in this structure?

- (b) In the gas phase, two units of AlCl_3 are joined together to form the Al_2Cl_6 dimer. Write the Lewis structure for this molecule. Is the octet rule obeyed in Al_2Cl_6 ?

(c) AlCl_3 is classified as a "Lewis acid". What is a Lewis acid? Explain what this term means using the formation of Al_2Cl_6 from AlCl_3 as an example.

12. Draw a Lewis structure for each of the following species.

- (i) S_8 (ii) P_4 (iii) C_8H_8 (hint: a Platonic solid) (iv) H_2CCCH_2

NUMERICAL ANSWERS

1. (b)(i) 8, (ii) 8, (iii) 32, (iv) 48, (v) 8, (vi) 20

9. (a) 20, (b) 24, (c) 24, (d) 40

PROBLEM SET 5: MOLECULAR STRUCTURE – VSEPR THEORY, POLARITY AND HYBRID ORBITALS

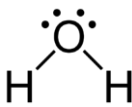
References: Blackman, *et al.* 'Chemistry': 5.5, 5.6. CHEM1031 and CHEM1051: 5.7

CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

- Describe the underlying theory of the VSEPR model.
 - What are the spatial arrangements (geometries) of 2, 3, 4, 5, and 6 groups of valence-shell electron domains about an atom, according to the VSEPR model?
 - How do you account for the π bonds in a species when counting the number of electron domains?

- Complete the table below:

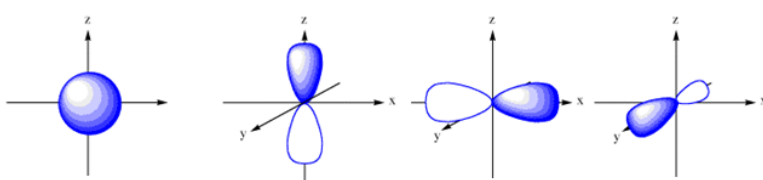
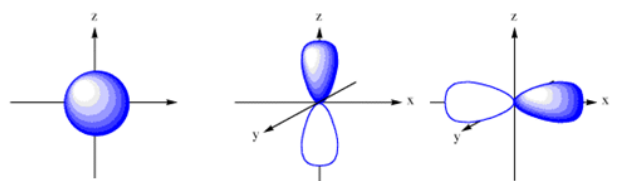
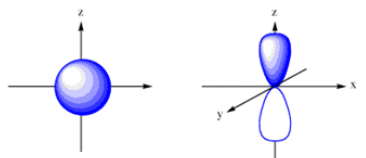
Molecule	Lewis diagram	Around central atom			VSEPR geometry (name)	Molecule Shape (name)
		# bonding domains	# non-bonding e ⁻ pairs	Total # e ⁻ domains		
H ₂ O		2	2	4	Tetrahedral	Bent
BH ₃						
CH ₄						
OCH ₂						
CO ₂						
PF ₅						

- Why is it possible for a molecule to have polar bonds yet have an overall zero dipole moment?
- For each of the following species, draw a sensible Lewis structure which also shows the shape of the species with approximate interbond angles marked. Show the orientation of electron pairs around the central atom and identify the VSEPR geometry and molecular shape of each species. Indicate which of the molecules are polar and which are non-polar (dipole moments are not defined for charged species).

(a) SF ₆	(b) BF ₃	(c) CO ₂	(d) NH ₄ ⁺
(e) OF ₂	(f) ICl ₃	(g) PCl ₅	(h) ClO ₂ ⁻
(i) XeF ₂	(j) PF ₃	(k) BrF ₅	(l) XeCl ₄

5. (a) Draw Lewis structures for CO_2 and SO_2 .
 (b) Use your Lewis structures and VSEPR theory to explain why CO_2 is non-polar, but SO_2 does have a permanent dipole moment.
6. (a) What is meant by (i) a sigma (σ) bond, and (ii) a pi (π) bond?
 (b) Make a sketch of: a σ bond with (i) $s-s$ overlap, (ii) $s-p$ overlap and (iii) end-to-end $p-p$ overlap.
 (c) Make a sketch of π bond consisting of sideways (lateral) $p-p$ overlap.
 (d) In your last tutorial (Problem Set 4 - Question 6) you demonstrated that the CO_3^{2-} ion exhibits delocalized electrons, and drew its resonance forms. Now, based on your understanding of the structure of π bond and $p-p$ overlap, sketch the valence orbitals on the atoms in the CO_3^{2-} ion and show how delocalized π bonding originates in this species.
7. Hybrid orbitals are the product of mixing and recasting different atomic orbitals from the same atom to form new orbitals of equal energy and maximum symmetry and orientation in space (i.e. all the same shape) for that atom. For example, if two atomic orbitals of different shape and energy are combined to make hybrid orbitals the result is two orbitals of same energy and shape that are 'mixes' of the two atomic orbitals.

Consider the above theory about hybridisation and complete the following table to show the different types of hybrid orbitals:

Unhybridized atomic orbitals	Hybridised orbitals shape	Hybrid orbital
		Name
		# of orbitals
		Name
		# of orbitals
		Name
		# of orbitals

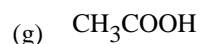
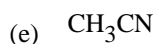
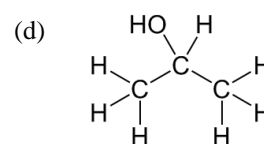
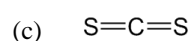
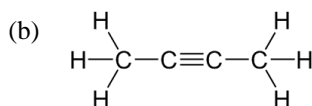
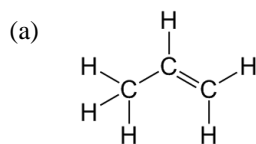
8. Consider hybridisation in molecules with VSEPR geometry and complete the table below:

	VSEPR geometry	Number of orbitals being hybridised = <i>total electron domains around central atom</i>	Hybridisation of the central atom	Approximate bond angles
(a) CO ₂				
(b) BF ₃				
(c) CCl ₄				

HARDER CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

9. What is the hybridization of each of the carbon atoms in the following compounds:



10. Draw a labelled sketch showing the atomic and hybrid orbitals on each atom in these molecules, and show how overlap of these orbitals gives rise to the bonds between the atoms in each molecule.
- (a) hydrazine (N₂H₄) (b) diazine (N₂H₂) (c) dinitrogen (N₂)
11. (a) Draw a sensible Lewis structure for methanal (formaldehyde).
 (b) Determine the shape of methanal.
 (c) Sketch the hybrid orbitals on the carbon and oxygen atoms which give rise to the bonding in methanal.

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12. In graphite, three of the four valence electrons from each carbon atom are involved in forming σ bonds from overlapping sp^2 orbitals. The fourth valence electron is involved in π bonding. A single crystal of graphite conducts electricity in the two dimensions which form the sheets, but not in the third dimension. Therefore electrical conduction occurs within a sheet but not between sheets.
- (a) Sketch the orbitals around a carbon atom in graphite and a neighboring atom, showing how orbital overlap gives rise to σ and π bonding.
 (b) Are the electrons involved in π bonding localized between pairs of carbons atoms?

- (c) Which of these statements best expresses a theoretical explanation (implied above, but not stated) for the conclusion that conduction occurs within a sheet but not between sheets?
- (i) Delocalization of π electrons in graphite takes place in two dimensions rather than three dimensions.
 - (ii) The distance between sheets in graphite is too large for electrons to move between the sheets.
 - (iii) π bonds must be present for the conduction of electricity
 - (iv) sp^2 hybridization gives rise to sheet structures.

(Adapted from Garratt *et al.* "A Question of Chemistry", Longman, 1999)

13. (a) How many electrons can occupy a single molecular orbital?
- (b) If we generate approximate molecular orbitals by combining atomic orbitals on the bonded atoms, how many molecular orbitals are formed from each pair of atomic orbitals?
- (c) How does an anti-bonding orbital compare with its related bonding orbital in terms of energy and nodal planes?
- (d) How many valence electrons and core electrons does a Be atom have?
- (e) Draw an arrows-in-boxes diagram to show the molecular orbitals occupied by valence electrons in Be_2 .
- (f) Calculate the bond order in Be_2 .
- (g) Regardless of its stability, would you expect Be_2 to be paramagnetic?
- (h) Calculate the bond order in Be_2^+ .
- (i) Which species of Be_2 and Be_2^+ would you expect to be stable?
14. Use arrows-in-boxes diagrams to rank the species C_2^- , C_2 , C_2^+ in order of
- (a) increasing bond order,
 - (b) increasing bond energy, and
 - (c) increasing bond length.

EXTRA PRACTICE QUESTIONS

Attempt these in your own time. The tutor will NOT cover these questions unless the class finished early and there is extra time. You may need to look up the values for some of these questions in the SI Chemical Data book. For help with these questions, see the Duty Tutor.

15. For each of the following species, draw a sensible Lewis structure, identify the shape of the molecule, and determine if it is polar.
- | | | |
|--------------------------|------------------------------|--------------------|
| (a) BF_3 | (d) H_3CCH_3 | (g) ClF_3 |
| (b) H_2S | (e) H_2CO | (h) SF_4 |
| (c) PCl_5 | (f) OF_2 | (i) XeF_2 |
16. What is the hybridization of each of the carbon atoms in the following compounds:
- | | |
|--------------------------------------|--|
| (a) $\text{CH}_3\text{CH}=\text{NH}$ | (d) $\text{CH}_3\text{C}\equiv\text{CCHO}$ |
| (b) $\text{CH}_3\text{COOCH}_3$ | (e) cyclobutane |
| (c) CH_3OCH_3 | (f) C_6H_6 (benzene) |
17. Which of the following would you expect to have sp^2 hybridization of the central atom?
- H_2CO ; NF_4^+ ; BF_4^- ; PBr_3 ; GaCl_3 ; NH_3 ; BeCl_2 ; SO_3^{2-}
- Justify your answers.

PROBLEM SET 6: INTERMOLECULAR FORCES, NON-IDEAL GASES, AND LIQUID-VAPOUR EQUILLIBRIA

References: Blackman, *et al.* 'Chemistry': 6.7, 6.8, 7.1, 7.2

CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

Intermolecular Forces

1.
 - (a) State clearly what is meant by hydrogen bonding; give two examples of substances where hydrogen bonding occurs.
 - (b) Draw the hydrogen-bonded structures, *if any*, for the hydrogen-bonding interaction which could occur between the following pairs of molecules:
 - (i) H_2O and NH_3
 - (ii) CH_3COOH and CH_3COOH
 - (iii) H_2O and CH_3OH
 - (iv) H_2O and CH_3CH_3
 - (v) H_2O and CH_3OCH_3
 - (vi) H_2O and CH_3NH_2
 - (c) How would you classify ionic bonding: as an '*intermolecular*' force, '*intramolecular*' force, or neither? Discuss in class.
2.
 - (a) Complete the following table by ticking the appropriate boxes to indicate the types of intermolecular forces acting between molecules in each of the compounds.

	Dispersion forces	Dipole/dipole forces	Hydrogen bonding
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$			
$\text{H}_2\text{NCH}_2\text{COOH}$			
$\text{CH}_3\text{CH}_2\text{OCH}_3$			
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$			

- (b) Consider the following series of substances.

	LiCl	BeCl_2	BCl_3
melting point / $^\circ\text{C}$	610	405	-107
boiling point / $^\circ\text{C}$	1350	520	12

What conclusions can you draw about the trend in the bonding in the compounds? Suggest reasons for this trend.

Non-ideal gases

3. What are the assumptions of the properties of an ideal gas? How might this change if gases are under high pressure (i.e. molecules are closer together)?

4. (a) The van der Waals equation includes corrections to the ideal gas equation, converting observed into ideal via the following relationship:

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT.$$

- (i) Consider these two equations and identify each pressure and volume term as either P_{ideal} , V_{ideal} , P_{observed} or V_{observed} below:

$$P_{\text{---}} V_{\text{---}} = nRT$$

$$\left(P_{\text{---}} + \frac{n^2a}{V_{\text{---}}^2}\right)(V_{\text{---}} - nb) = nRT$$

- (ii) Based on your answers for part (i), identify each pressure and volume term as either P_{ideal} , V_{ideal} , P_{observed} or V_{observed} for the following two relationships:

$$P_{\text{---}} = \left(P_{\text{---}} + \frac{n^2a}{V_{\text{---}}^2}\right)$$

$$V_{\text{---}} = (V_{\text{---}} - nb)$$

- (iii) Why is the pressure correction term $\left(\frac{n^2a}{V^2}\right)$ *added* to the measured pressure but the volume correction term (nb) is *subtracted* from the measured volume?
- (iii) 'a' and 'b' are the van der Waals constants. Write appropriate units for them.
Suggest reasons why these constants do not have the same magnitudes for all gases.
- (iv) Suggest a reason why the 'a' constant for NH_3 is greater than that for N_2 even though they both have similar 'b' constants.
- (v) Which of the two substances, N_2 or NH_3 , would have the higher normal boiling point? Why?
- (b) The molar volume of an ideal gas at 0°C and 1 atm is $22.415 \text{ L mol}^{-1}$, while H_2 is $22.432 \text{ L mol}^{-1}$, CO_2 is $22.263 \text{ L mol}^{-1}$ and NH_3 is $22.094 \text{ L mol}^{-1}$. Give two reasons for the differences, indicating the relative importance of each for the three gases.

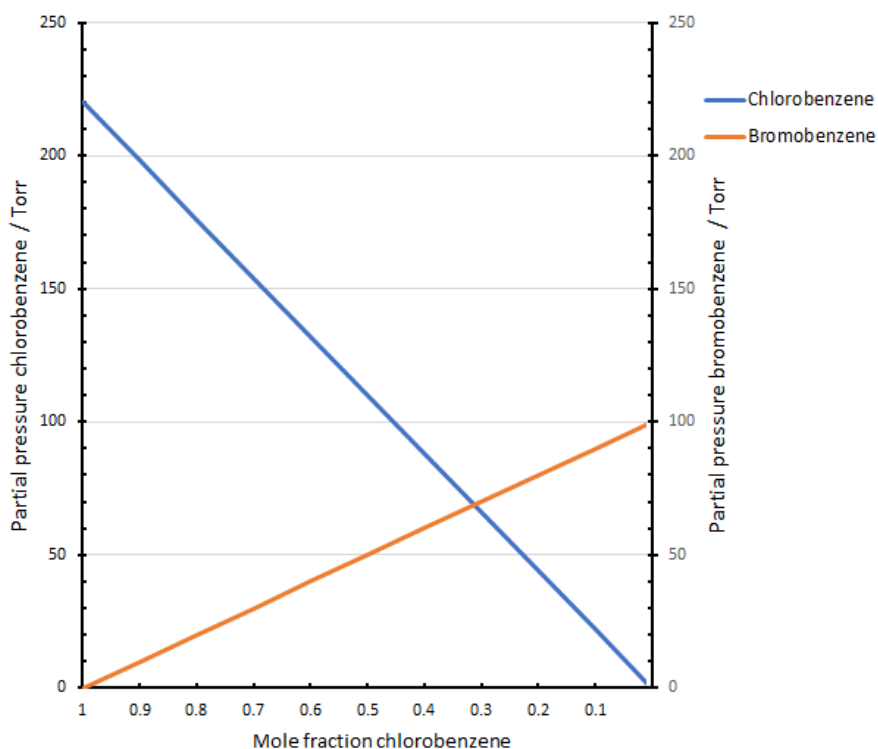
Ideal gas calculations in liquid-vapour equilibria

5. (a) What is the liquid-vapour equilibrium? Why are some liquids more volatile than other liquids?
- (b) What is meant by "the vapour pressure of a liquid"?
- (c) Circle the correct option / cross out the incorrect option:
- (i) The vapour pressure of a liquid is **dependent/independent** of the volume of liquid present.
- (ii) The vapour pressure of a liquid is **dependent/independent** of temperature.

NOTE: For the following set of questions, assume all systems described are closed.

6. The vapour pressure of water at 80°C is 355 mm Hg. A 100 cm^3 vessel contained water-saturated oxygen at 80°C , the total gas pressure being 760 mmHg. The contents of the vessel were transferred by pumping to a 50 cm^3 vessel at the same temperature. What were the partial pressures of oxygen and water vapour and what was the total pressure in the final equilibrated state? (Neglect the volume of any water which might condense.)

7. At 90 °C, pure chlorobenzene (molar mass, 112.6 g mol⁻¹) and pure bromobenzene (molar mass, 156.9 g mol⁻¹) are completely miscible and form an ideal solution.



Using the graph above:

- What is the equilibrium vapour pressure (P°) of pure chlorobenzene at 90°C
 - What is the equilibrium vapour pressure (P°) of pure bromobenzene at 90°C
 - What is the partial pressure of each component in the vapour when the mole fraction in the liquid is $X_{\text{chlorobenzene}} = 0.7$
 - What is the mole fraction in the vapour phase of each component for this mixture?
 - Draw a line on the diagram which gives the total vapour pressure of the system across the entire range of mole fractions.
 - What are the partial pressures of each compound and the total vapour pressure of the system when there are four times as many bromobenzene molecules as chlorobenzene molecules in the solution.
 - What is the composition of the solution (in terms of mole fraction) when there are equal numbers of molecules of each component in the vapour phase?
8. For a liquid mixture containing 33.8 g of acetone (CH₃OCH₃, equilibrium vapour pressure = 421.5 mmHg) and 172.6 g of ethyl acetate (CH₃COOC₂H₅, equilibrium vapour pressure = 186.3 mmHg) at 40 °C:
- Calculate the mole fraction of each component in the liquid mixture.
 - Calculate the partial pressure of each component in the vapour which is in equilibrium with the liquid mixture.
 - Calculate the mole fraction of each component in the vapour.

9. At 35 °C the vapour pressure of pure chloroform (CHCl_3) is 0.359 atm and that of acetone (CH_3COCH_3) is 0.453 atm. A solution containing 1.0 mole of chloroform and 4.0 moles of acetone is observed to have a vapour pressure of 0.400 atm at 35 °C.
- Using Raoult's Law, calculate the expected vapour pressure of the solution at 35°C, assuming ideal behaviour, and compare this value with the observed value.
 - Does this system show a positive or negative deviation from Raoult's Law?
 - Explain this deviation by comparing the forces between chloroform-acetone molecules compared to chloroform-chloroform and acetone-acetone molecules in the liquid.

HARDER CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

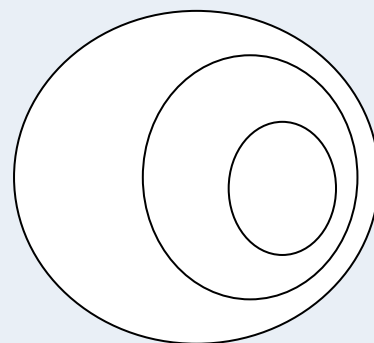
10. $\text{F}_2(\text{s})$, $\text{NF}_3(\text{s})$ and $\text{H}_2\text{O}(\text{s})$ are all molecular solids. Clearly explain what this means and indicate the type and relative strengths of all intermolecular and intramolecular forces of attraction. Comment briefly on the expected physical properties of molecular solids.
11. A drum of 200 L capacity fitted with a pressure gauge is partly filled with 80 L of an organic liquid and sealed. The pressure gauge then reads 740 mmHg at 25 °C. The drum is then accidentally dented and the capacity is reduced to 150 L. Given that the equilibrium vapour pressure of the organic liquid is 500 mmHg at 25 °C, calculate:
- the partial pressure of air in the drum after sealing, but before denting.
 - the total pressure inside the dented drum.
12. A sample of 2.0 cm^3 of liquid 1-bromobutane ($\text{C}_4\text{H}_9\text{Br}$) is placed in a 1.0 litre flask, which is then sealed. The temperature is kept constant at 25°C. Will any liquid remain in the flask once a point of observable change is reached at this temperature? (Density and vapour pressure of $\text{C}_4\text{H}_9\text{Br}(\text{l})$ at 25 °C are 1.275 g cm^{-3} and 41 mmHg).
13. At 55°C, acetone (CH_3COCH_3) has a vapour pressure of 738 mmHg and chloroform (CHCl_3) has a vapour pressure of 638 mmHg. Which of these liquids has the higher normal boiling point? Why? What are you assuming in making this prediction?

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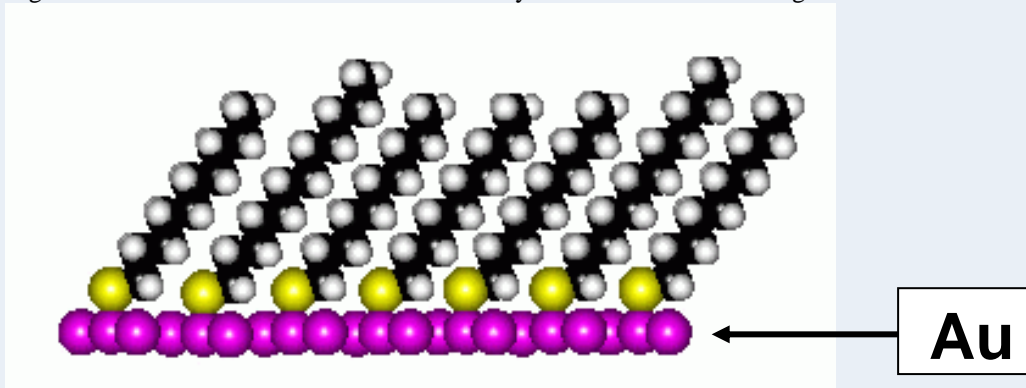
14. The adjacent diagram can be labelled to represent the relationship between substances having (i) hydrogen bonding (ii) dipole-dipole and (iii) dispersion forces between molecules. Label the three components of the diagram and populate it with the following substances:

hexane, water, iodine, ethanoic acid, diethyl ether, conc. sulfuric acid,
hydrogen sulfide, acetone.

(Adapted from B. Bucat and T. Shand, 1996)



15. The diagram below shows a self-assembled monolayer (SAM) of long-chain alkanethiol molecules deposited from aqueous solution onto a gold surface. The molecules shown here are of two different chain lengths, $\text{CH}_3(\text{CH}_2)_9\text{SH}$ and $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$. The thiol ($-\text{SH}$) group binds strongly to gold. Look at this SAM and identify as many different intramolecular and intermolecular interactions as you can. Propose an explanation for the fact that the molecules spontaneously organise in an ordered way on the gold surface. Can you think of another type of (commonly available) molecule which undergoes self assembly or self-organisation? Below: a self-assembled monolayer of thiols attached to a gold surface.



(Picture from P. Weiss, Penn. State U., <http://stm1.chem.psu.edu/Pictures.html> accessed February, 2009)

16. (a) What distinguishes a surfactant from other solutes when it is dissolved in water?
 (b) What features of a molecule cause it to act as a surfactant?
 (c) What is a micelle and under what circumstances do micelles form?
 (d) How does micelle formation improve the effectiveness of surfactants as dirt and oil removers?
 (e) Why does the fluid coating our lungs contain a very effective mix of surfactants?

EXTRA PRACTICE QUESTIONS

Attempt these in your own time. The tutor will NOT cover these questions unless the class finished early and there is extra time. You may need to look up the values for some of these questions in the SI Chemical Data book. For help with these questions, see the Duty Tutor.

17. Consider the following series of substances.

	F_2	Cl_2	Br_2	I_2
melting point / $^{\circ}\text{C}$	-220	-101	-7	114
boiling point / $^{\circ}\text{C}$	-188	35	58	183

What is the origin of the forces between molecules of F_2 , of Cl_2 , of Br_2 and of I_2 ? Suggest reasons for the observed trend in the boiling points of these compounds in terms of this force of attraction.

18. (a) What is meant by the 'normal boiling point of a liquid'?
 (b) For each of the following sets of substances predict the order of increasing normal boiling point, briefly state the reason for the order given:
 (i) CCl_4 ; CBr_4 ; CH_4 ; CH_2Cl_2 .
 (ii) HBr ; HI ; HCl ; HF .
 (iii) NaCl ; KCl ; RbCl ; CsCl .
 (iv) $\text{CH}_3\text{-O-CH}_2\text{-CH}_3$; $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$; $\text{HO-CH}_2\text{-CH}_2\text{-OH}$; $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}$.

19. (a) (i) Under conditions of constant temperature, 200 cm^3 of H_2 gas at a pressure of 800 mmHg, was forced into a cylinder of volume 600 cm^3 , which already contained O_2 gas (partial pressure of 400 mmHg) and Ne gas (partial pressure of 300 mmHg). What was the final pressure in the cylinder?
 (ii) Determine the mole fraction of each gas in the final mixture.
- (b) A 340 cm^3 flask contained helium at 123 kPa; a 570 cm^3 flask contained hydrogen also at 123 kPa. A stop cock connecting the two flasks was opened. Assuming the temperature remained constant what was the final total pressure and the mole percent of each gas in the resulting mixture? (Neglect the volume of the stop-cock).
20. Calculate the vapour pressure above a solution of 250.0 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) in 800.0 mL of water at 298K. The vapour pressure and density of pure water under these conditions are 23.76 mm Hg and 0.997 g mL^{-1} respectively.
21. (a) Glycerol is a viscous, non-volatile liquid at room temperature. Calculate the vapour pressure above a solution of 150.0 g of glycerol ($\text{C}_3\text{H}_8\text{O}_3$) in 700.0 mL of water at 298K. The vapour pressure and density of pure water under these conditions are 23.67 mm Hg and 0.997 g mL^{-1} respectively.
- (b) At 20.0°C the vapour pressure of pure methanol is 11.8 kPa and that of pure ethanol is 5.93 kPa. A gaseous mixture of methanol and ethanol is cooled and compressed until the first drops of liquid form at 20.0°C and a total pressure of 10.0 kPa. Assuming the liquid mixture behaves ideally, calculate the mole fractions of methanol in:
- (i) the liquid phase, and
 (ii) the gas phase

NUMERICAL ANSWERS

6. (b) $p_{\text{O}_2} = 810 \text{ mm Hg}$, $p_{\text{H}_2\text{O}} = 355 \text{ mm Hg}$, $p_{\text{total}} = 1165 \text{ mm Hg}$
7. (a) 220 torr (b) 100 torr (c) 154 torr (C), 30 torr (B); (d) 0.84 (C), 0.16 (B); (f) 44 torr (C), 80 torr (B); (g) 0.32 (C), 0.68 (B)
8. (a) acetone=0.23, ethyl acetate=0.77 (b) acetone=96.95 mmHg, ethyl acetate=143.45 mmHg (c) acetone=0.4, ethyl acetate=0.6
9. (a) 0.434 atm
11. (a) 240 mm Hg (b) 911 mm Hg
19. (a) (i) 967 mm Hg; (ii) $X_{\text{H}_2} = 0.276$ (b) 123 kPa; 37.4 % He
20. 23.37 mm Hg
21. (a) 22.7 mm Hg (b) (i) $X_{\text{methanol, liq}} = 0.694$ (ii) $X_{\text{methanol, gas}} = 0.818$

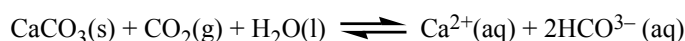
PROBLEM SET 7: CHEMICAL EQUILIBRIUM

References: Blackman, *et al.* 'Chemistry': 9.1, 9.2, 9.4, 9.5

CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

1. (a) Write expressions for the equilibrium constants K_p and K_c , in terms of the partial pressures and concentrations at equilibrium respectively, for each of the following reactions:
- (i) $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$
 - (ii) $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 - (iii) $2 \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightleftharpoons (\text{NH}_4)_2\text{S}(\text{s})$
 - (iv) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{HCl}(\text{g})$
- (b) For which, if any, of the reactions above, will the numerical values of K_p and K_c be equal?
2. (a) State Le Chatelier's Principle.
- (b) For each of the following equilibria, predict the effect that reducing the volume of the container (at constant temperature) would have on the number of mole of the product. State 'increase', decrease', no change' or 'unpredictable'.
- (i) $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{HBr}(\text{g})$
 - (ii) $2 \text{NO}(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{NOBr}(\text{g})$
 - (iii) $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{g})$
 - (iv) $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$
3. Complete this table to summarise how changes to the following **endothermic** reaction influence equilibrium (using Le Châtelier's principle):

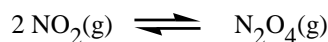


Change	Effect on equilibrium position (To the left/to the right/no change)	Effect on equilibrium constant (K) (Increase/ decrease/ no change)
(a) Increase concentration/partial pressure of a reactant		
(b) Increase concentration of a product		
(c) Decrease concentration /partial pressure of a reactant		
(d) Decrease concentration of a product		
(e) Decrease volume		
(f) Increase volume		
(g) Add or remove solid or liquid reactants from system		
(h) Increase temperature		
(i) Decrease temperature		
(j) Add a catalyst		

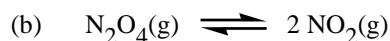
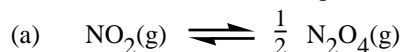
HARDER CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

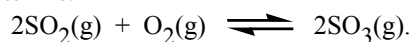
4. The equilibrium constant K_c for this reaction is 216 at 25 °C:



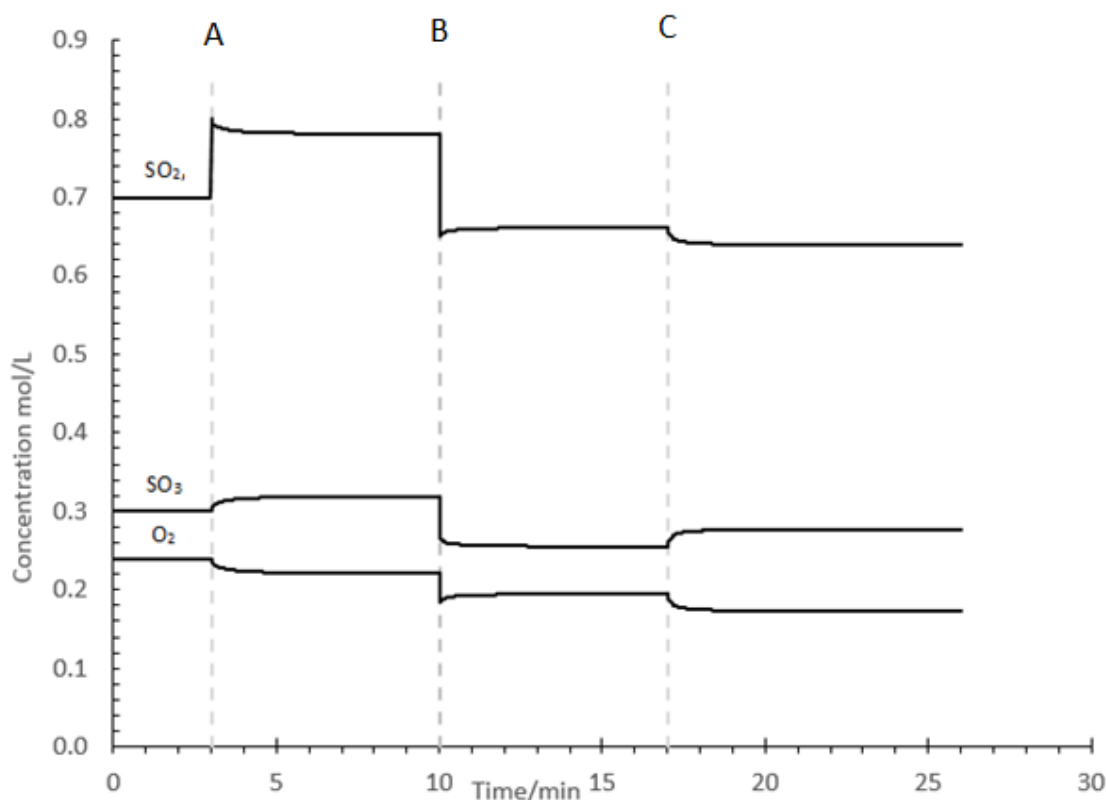
Determine the value of the equilibrium constant K_c for each of the following reactions at 25 °C:



5. The graph below tracks the concentrations SO_2 , SO_3 and O_2 in a system over time. The system is at equilibrium at $t=0$ and it is subsequently subjected to various disturbances at times A, B and C. The reversible reaction in this system is:



The formation of SO_3 is an endothermic process.

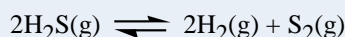


- (a) Calculate the value of the equilibrium constant K_c at $t = 0$.
- (b) Suggest changes which could have occurred to the equilibrium system at the time A, B, and C, providing justification for your answers.
- (c) Calculate the value of Q_c at time B and compare to the K_c you calculated in part (a). Use this to confirm that the direction of change observed in the graph after the change and that Le Châtelier's principle is adhered to. (*Extension: do the same for A*)
- (d) Calculate K_c :
- at 15 minutes
 - at 25 minutes

- (e) Would you expect either of the K_C values in part (d) to be the same as at 0 minutes? Why/why not?
- (f) Compare your answers from (a) and (d)(i). Has a new equilibrium position been established? Explain.
- (g) What is the difference between K_C and K_P ? Calculate K_P for the reaction at 0 minutes (assuming $T = 300\text{K}$).

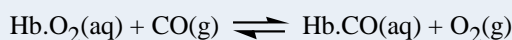
CHEM1031/1051 only

6. Hydrogen sulfide decomposes at high temperatures according to the following reaction:



For this reaction at 700°C $K_C = 9.30 \times 10^{-8}$. If 0.450 mol of H_2S is placed in a 3.00 L container, what is the equilibrium concentration of $\text{H}_2(\text{g})$ at 700°C ?

7. Haemoglobin carries O_2 from the lungs to tissues where the O_2 is released. Haemoglobin can be represented as Hb in its unoxygenated form and $\text{Hb} \cdot \text{O}_2$ in one of its oxygenated forms. One reason carbon monoxide is toxic is that it competes with oxygen in binding to haemoglobin:



- (a) If, for the above reaction, $\Delta G^\circ = -14.0\text{ kJ mol}^{-1}$ at 37.00°C , what is the ratio of $[\text{Hb} \cdot \text{CO}]$ to $[\text{Hb} \cdot \text{O}_2]$ when $[\text{O}_2] = [\text{CO}]$?
- (b) How does Le Chatelier's principle suggest a possible treatment for CO poisoning?

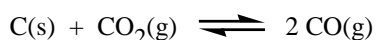
EXTRA PRACTICE QUESTIONS

Attempt these in your own time. The tutor will NOT cover these questions unless the class finished early and there is extra time. You may need to look up the values for some of these questions in the SI Chemical Data book. For help with these questions, see the Duty Tutor.

8. Give the equilibrium expression for the following reactions:

- (a) $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- (b) $\text{H}_2\text{O}(\text{g}) + \text{C}(\text{s}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}(\text{g})$
- (c) $\text{Ca}(\text{OH})_2(\text{s}) + 2\text{H}^+(\text{aq}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l}) + \text{Ca}^{2+}(\text{aq})$

9. When a mixture of carbon and carbon dioxide is heated, a reaction occurs to produce carbon monoxide:

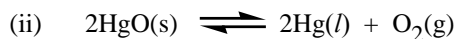
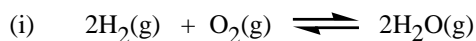


The reaction (which occurs in blast furnaces used to produce iron) is endothermic.

Equilibrium mixtures of carbon, carbon dioxide, and carbon monoxide were subjected to the changes shown in the following table. Complete the table by stating the effect each has on the amount of CO_2 present and on the value of K_P . Write 'increase', 'decrease', 'no change' or 'unpredictable'.

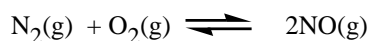
Change	Effect on	
	Amount of CO_2	K_P
Decreasing volume		
Adding $\text{CO}(\text{g})$		
Adding $\text{C}(\text{s})$		
Increasing temperature		

10. (a) Write expressions for the equilibrium constants K_p and K_c , in terms of the partial pressures and concentrations at equilibrium respectively, for each of the following reactions:

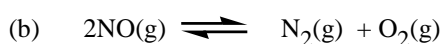
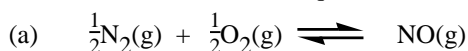


- (b) For each of the reactions above write an expression which relates the values of K_p and K_c .
(c) If the partial pressure of O_2 in equilibrium with a sample of $\text{HgO}(\text{s})$ at a particular temperature was 0.015 bar, what would be the value of K_p for reaction (ii) above at that temperature?

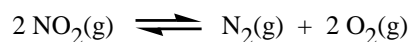
11. The equilibrium constant K_c for this reaction is 4.08×10^{-4} at 2000 K:



Determine the value of the equilibrium constant K_c for each of the following reactions at 2000 K:



12. The decomposition of nitrogen dioxide into oxygen and nitrogen:



is an exothermic reaction.

- (a) A mixture of nitrogen, oxygen and nitrogen dioxide at equilibrium is heated. Predict the effect that this increase in temperature would have on the concentration of NO_2 present and the value of the equilibrium constant (K_c) once equilibrium is re-established.
(b) If a mixture of nitrogen, oxygen and nitrogen dioxide is allowed to reach equilibrium, then additional O_2 is added, what effect will that have on the mole fractions of each of the gases?

NUMERICAL ANSWERS

4. (a) 14.7; (b) 4.63×10^{-3}

5. (a) $[\text{SO}_2] = \sim 0.70 \text{ M}$; $[\text{O}_2] = \sim 0.24 \text{ M}$; $[\text{SO}_3] = \sim 0.30 \text{ M}$; $K_c = \sim 0.77$

(c) Q at B = 0.91

(d) (i) $[\text{SO}_2] = \sim 0.68 \text{ M}$; $[\text{O}_2] = \sim 0.19 \text{ M}$; $[\text{SO}_3] = \sim 0.26 \text{ M}$; $K_c = \sim 0.77$

(ii) $[\text{SO}_2] = \sim 0.63 \text{ M}$; $[\text{O}_2] = \sim 0.17 \text{ M}$; $[\text{SO}_3] = \sim 0.31 \text{ M}$; $K_c = \sim 1.4$

(g) 0.031

6. $1.61 \times 10^{-3} \text{ M}$

7. (a) 228

10. (c) $K_p = 0.015$

11. (a) 2.02×10^{-2} ; (b) 2.45×10^3

PROBLEM SET 8: ACID, BASES, AND pH

References: Blackman, *et al.* 'Chemistry': 11.1 – 11.4, 11.6, 11.7

CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

1. (a) Consider the Brønsted–Lowry theory and define a conjugate acid/base pair.
- (b) Complete the following table, writing 'none' where appropriate:

Conjugate acid	Species	Conjugate base
	HCO_3^-	
	H_2O	
	HPO_4^{2-}	
	CN^-	
	HS^-	

2. Using the $\text{p}K_a$ values provided, arrange the following acids in order of decreasing acid strength:
- (a) HCO_3^- (HCO_3^- : $\text{p}K_{a,1} = 6.35$ $\text{p}K_{a,2} = 10.33$)
- (b) HF (HF: $\text{p}K_a = 3.17$)
- (c) H_2S (H_2S : $\text{p}K_{a,1} = 7.02$ $\text{p}K_{a,2} = 13.9$)
- (d) HPO_4^{2-} (H_3PO_4 : $\text{p}K_{a,1} = 2.15$ $\text{p}K_{a,2} = 7.20$ $\text{p}K_{a,3} = 12.38$)
3. (a) Based on your understanding of the dissociation of water and the value of $\text{p}K_w$, show how to determine the pOH for a solution of $\text{pH} = 4.4$
- (b) Calculate the pH of each of the following aqueous solutions:
- (i) Strong acid: 0.100 M H_2SO_4
- (ii) Strong base: 0.025 M $\text{Ba}(\text{OH})_2$
4. Consider the weak acid solution 0.5M HClO with $\text{p}K_a = 7.53$:
- (a) Calculate the K_a of HClO
- (b) Give the equilibrium expression for the addition of HClO to H_2O
- (c) Use the ICE table below to help you calculate concentrations of the species in solution
- | | HClO | H_3O^+ | ClO^- |
|---------------------------|---------------|------------------------|----------------|
| Initial concentration | | | |
| Change in concentration | | | |
| Equilibrium Concentration | | | |
- (d) Use the small x approximation method to solve for $[\text{H}^+]$ and pH

- (e) Repeat steps (a) – (d) for the following solutions:
- 2 M HNO_3 ($\text{p}K_a = 3.35$)
 - 0.8 M CH_3NH_2 (methylamine, $\text{p}K_b = 3.36$)
 - 1.5 M $\text{C}_5\text{H}_5\text{N}$ (pyridine, $\text{p}K_b = 8.77$)
5. Why is a solution of NaHSO_4 acidic while a solution of NaHCO_3 is basic? Would you expect Na_2HPO_4 to be acidic or basic?
6. Give equations for the reaction, if any, of each of the following substances with water. State whether the resulting solution is neutral, acidic, or basic:
- | | |
|--|----------------------|
| (a) sodium hydrogensulfate | (e) ammonium bromide |
| (b) iron(III) nitrate | (f) calcium hydride |
| (c) methylamine (CH_3NH_2) | (g) ammonium acetate |
| (d) potassium cyanide | (h) sodium chlorite |
7. (a) It is found that 0.20 M solutions of three potassium salts KX, KY and KZ have pH values of 7.0, 8.0 and 9.0 respectively. Arrange the acids HX, HY and HZ in order of increasing acid strength.
- (b) Lactic acid ($\text{CH}_3\text{CHOHCOOH}$) is present in sour milk. What is the pH of a 0.100 M solution of lactic acid? ($\text{p}K_a$ of lactic acid = 3.86)
8. (a) (i) If 25.00 mL of 0.224 M ammonia were mixed with 50.00 mL of 0.138 M ammonium chloride, what would be the pH of the final solution (K_a of $\text{NH}_4^+ = 5.8 \times 10^{-10}$) ?
- (ii) To what value would the pH change if 0.035 g of sodium hydroxide were added to this solution?
- (b) (i) Suppose a solution were prepared using ammonia and ammonium chloride as in part (a) (i) above, but after preparation of the solution, 75.00 mL of water were added to the resulting solution. What would be the pH of the final solution in this case?
- (ii) To what value would the pH of this solution change if 0.035 g of sodium hydroxide were added to 75.00 mL of solution?
- (c) Comment on any differences in behaviour of the solutions in parts (a) and (b).

HARDER CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

9. The first and second dissociation constants for H_2CO_3 are $K_1 = 4.5 \times 10^{-7}$ and $K_2 = 4.7 \times 10^{-11}$, calculate K for the equilibrium:
- $$\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons 2 \text{H}^+(\text{aq}) + \text{CO}_3^{2-}$$
10. The average pH of beer is 4.4. If the acidity is regarded as due only to the presence of dissolved CO_2 from the fermentation process, calculate the concentration of the carbonic acid in the beer. (Acidity arising from the second dissociation of carbonic acid may be neglected.)
11. What mass of potassium lactate should be added to 300.0 mL of 0.238 M lactic acid solution in order to produce a solution with a pH of 4.00? (Lactic acid is a monoprotic acid, with formula $\text{CH}_3\text{CHOHCOOH}$, and having a $\text{p}K_a$ value of 3.86.) (Assume no volume change on addition of solid.)

12. Calculate the pH of the following aqueous solutions prepared by adding:
- 20.0 cm³ 0.10 M NH₄Cl to 20.0 cm³ 0.18 M HCl (K_a of NH₄⁺ = 5.8 × 10⁻¹⁰).
 - 3.0 L HBr(g), measured at 27 °C, 757 mmHg pressure, to sufficient water to give 0.10 L of solution.
 - 20.0 cm³ 0.12 M HCl to 10.0 cm³ 0.16 M CH₃COOH + 20.0 cm³ 0.20 M KOH (K_a of CH₃COOH = 1.8 × 10⁻⁵).
 - 3.90 g barium hydroxide to H₂O to give total volume of 1.00 litre solution.
 - 0.60 L of 0.10 M NH₄Cl to 0.40 L of 0.10 M NaOH (K_a of NH₄⁺ = 5.8 × 10⁻¹⁰).
13. You have been asked to make a buffer solution with a pH of 5.2.
- Which of the conjugate acid/base pairs in the table below would be the most appropriate to use and why?

Conjugate Pair	K_a
CH ₃ COOH/CH ₃ COO ⁻	4.8 (Acetic Acid)
CH ₃ CHOHCOOH/CH ₃ CHOHCOO ⁻	3.9 (Lactic Acid)
HClO ₂ /ClO ₂ ⁻	1.96 (Chlorous Acid)
NH ₄ ⁺ /NH ₃	9.25 (Ammonium)

- Assume you have pre-prepared 0.1M solutions of the appropriate acid and base available. How much of each solution would you need to make 1 L of the requested buffer solution?

EXTRA PRACTICE QUESTIONS

Attempt these in your own time. The tutor will NOT cover these questions unless the class finished early and there is extra time. You may need to look up the values for some of these questions in the SI Chemical Data book. For help with these questions, see the Duty Tutor.

14. (a) How are acids and bases defined according to the:
- Arrhenius definition?
 - Brønsted definition?
 - Lewis definition?
- (b) Give different examples for each definition and write equations to illustrate the acid/base nature of the substances you have chosen.
15. Complete the following table by writing equations which illustrate the acid/base nature in aqueous solution of each substance:

Substance	Equation
HCl	
NH ₃	
Na ₂ CO ₃	
CH ₃ COOH	
Fe ³⁺ (aq)	

16. (a) Calculate the missing values in this table:

	$[\text{H}^+]/\text{mol L}^{-1}$	pH	$[\text{OH}^-]/\text{mol L}^{-1}$	pOH
(i)	2.0×10^{-2}			
(ii)		3.20		
(iii)			5.0×10^{-2}	
(iv)				4.60

- (b) Classify each of the solutions in (b) as acidic, neutral, or basic
- (c) Which of the solutions in (b) is the most acidic? Which is the most basic?
17. Determine the pH of the solution in each of the following cases:
- (a) A solution which is 0.089 M with respect to ammonia.
- (b) A solution which is 0.056 M with respect to ammonium chloride.
- (c) A solution which is 0.089 M with respect to ammonia and 0.056 M with respect to ammonium chloride.

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18. The value of the ion product for water (K_w) varies with temperature. At 25 °C $K_w = 1.0 \times 10^{-14}$ (standard state = 1 mol L⁻¹). Thus the pH of pure water at this temperature is 7.0. At higher temperatures K_w increases, so, for example, at 60 °C $K_w = 9.3 \times 10^{-14}$. Thus at 60 °C, the pH of pure water is 6.5 (verify this yourself). Does this mean pure water is acidic at 60 °C?
19. K_a for dichloroacetic acid (Cl_2CHCOOH) is 3.3×10^{-2} . Determine the pH of a 0.010 M solution of this acid by
- (a) using an approximation to simplify the calculation, and
- (b) without making any approximations. This will require solving a quadratic equation of the form $ax^2 + bx + c = 0$ using the general quadratic solution:
- $$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$
20. Determine the volume of 0.145 M hydrochloric acid which should be added to 250.0 mL of 0.096 M sodium monohydrogenphosphate in order to produce a solution of pH 6.60.
21. Calculate the pH of a solution made by adding 10.0 cm³ of 5.0×10^{-7} M HCl to 90.0 cm³ H₂O (hint: the trivial answer to this is not correct).

NUMERICAL ANSWERS

3. (a) 9.6 (b) (i) 0.700 (ii) 13.7
4. (a) 2.95×10^{-18} (d) 3.92
7. K_a for HY = 2×10^{-3} , for HZ 2×10^{-5} ; (b) 2.43
8. (a)(i) 9.15 (ii) 9.27 (b)(i) 9.15 (ii) 9.40
9. (c) 2.1×10^{-17}
10. $3.5 \times 10^{-3} M$
11. 12.6 g
12. (a) 1.05 (b) -0.08 (c) 8.63 (d) 12.66 (e) 9.54
13. (b) acetate = 715mL, acetic acid = 285mL
16. (a) (i) 1.70; 5.0×10^{-13} ; 12.30 (ii) 6.3×10^{-4} ; 1.6×10^{-11} ; 10.80 (iii) 2.0×10^{-13} ; 12.70; 1.30
(iv) 9.40; 4.0×10^{-10} ; 2.5×10^{-5}
17. (a) 11.09 (b) 5.25 (c) 9.44
19. (a) 1.7 (b) 2.1
20. 132 mL
21. 6.89

PROBLEM SET 9: THERMODYNAMICS

Reference: Blackman, *et al.* 'Chemistry': Chapter 8

CLASS QUESTIONS

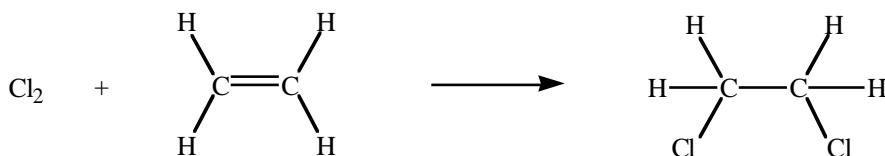
Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

- State the law of conservation of energy.
 - What is the difference between heat and work? Give an example of a process where heat and work is produced.
 - In many typical experiments heat is said to be "lost". Is this in keeping with the law of conservation of energy? (Hint: think about what constitutes a 'system' and its 'surroundings').
 - When does $\Delta H = \Delta U$?
 - Why are Chemists (and Biologists) more interested in ΔH than ΔU ?
 - Enthalpy is a state function. Use an example (such as climbing a mountain and the altitude gain) to explain what is meant by a state function
- If a kilogram of methane (natural gas) is burnt it would release 5.56×10^4 kJ of heat. The heat capacity of air is $29 \text{ J K}^{-1} \text{ g}^{-1}$, and the average mass of air in a room is 30 kg. If a room was initially at 10°C ,
 - calculate the temperature that the air would reach if 100 % of the heat is absorbed, and
 - discuss the discrepancy between the calculated value and that you would expect to observed in a "normal" room.
- A calorimeter, with calorimeter constant 7.31 J K^{-1} , was used to measure the heat of reaction for mixing 100.0 mL of 0.100 M Ag^+ with 100.0 mL of 0.100 M Cl^- . The temperature change was $+0.770 \text{ K}$ for the 200.0 g of solution (specific heat capacity = $4.35 \text{ J K}^{-1} \text{ g}^{-1}$, density = 1.00 g cm^{-3}) and the calorimeter.
 - What is the reaction occurring in the calorimeter?
 - How much heat was absorbed by the calorimeter?
 - How much heat was absorbed by the solution?
 - How much heat was released by the reaction?
 - What is the heat of reaction per mole of product formed?
- By using appropriate data from the table provided, calculate the standard enthalpy change and internal energy change associated with each of these reactions at 25°C :

Chemical species	$\Delta_f H^\circ / \text{kJ mol}^{-1}$ (298K)
$\text{CaCO}_3(\text{s})$	-1207
$\text{CaO}(\text{s})$	-635
$\text{CO}_2(\text{g})$	-394
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(\text{g})$	-255
$\text{O}_2(\text{g})$	0
$\text{H}_2\text{O}(\text{l})$	-286

- $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(\text{g}) + 9/2 \text{ O}_2(\text{g}) \rightarrow 3 \text{ CO}_2(\text{g}) + 4 \text{ H}_2\text{O}(\text{l})$ ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ is propan-1-ol)

5. For the addition of chlorine to ethene to produce 1,2-dichloroethane: $\text{C}_2\text{H}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{C}_2\text{H}_4\text{Cl}_2(\text{g})$



determine ΔH° at 298 K, in two ways:

- from average bond enthalpies, and
- from standard enthalpies of formation.

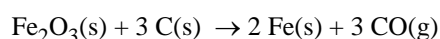
Average bond enthalpies (298K)	
Bond	$\Delta H / \text{kJ mol}^{-1}$
C–C	346
C=C	614
C–H	414
C–Cl	324
Cl–Cl	242

Standard enthalpies of formation (298K)	
Species	$\Delta_f H^\circ / \text{kJ mol}^{-1}$
$\text{Cl}_2(\text{g})$	0
$\text{C}_2\text{H}_4(\text{g})$	52
$\text{C}_2\text{H}_4\text{Cl}_2(\text{g})$	–127

6. With reference to appropriate data from the thermochemical equations below, use Hess's Law to calculate the standard enthalpy change for the following reaction: $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$



7. Consider the following reaction:



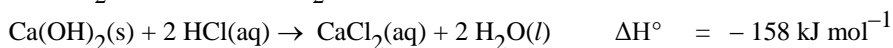
Chemical species	$\Delta_f H^\circ / \text{kJ mol}^{-1}$ (298K)	$S^\circ / \text{JK}^{-1} \text{mol}^{-1}$ (298K)
Fe_2O_3	–824	87
C	0	6
Fe	0	27
CO	–111	198

- Why is the enthalpy of formation ($\Delta_f H^\circ$) of Fe(s) and C(s) = 0 but entropy (S°) is not?
- Why are these entropy values positive?
- Using the values in the table above, calculate;
 - ΔH° and ΔS° at 298 K (*Hint: don't forget to consider the stoichiometry of each species in the reaction when summing values*)
 - ΔG° at 298 K and 1000 K, assuming ΔH° and ΔS° are independent of temperature over the range 298 K to 1000 K
 - Based on your answers from (ii), determine if the reaction is spontaneous or not at 298 K and 1000 K

HARDER CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

8. Using appropriate data from the thermochemical equations below, calculate the standard enthalpy change for the following reaction: $\text{CaCO}_3(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

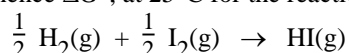


9. Pure acetylene, C_2H_2 , cannot be prepared directly from its constituent elements. However the following thermochemical data can all be determined experimentally:



Use Hess's Law to calculate the value of $\Delta_f H^\circ$ of $\text{C}_2\text{H}_2(\text{g})$.

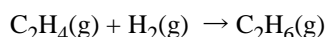
10. (a) Calculate ΔH° and ΔS° , and hence ΔG° , at 25°C for the reaction:



Chemical species	$\Delta_f H^\circ / \text{kJ mol}^{-1}$ (298K)	$S^\circ / \text{JK}^{-1} \text{mol}^{-1}$ (298K)
H_2	0	131
I_2	0	116
HI	26	207

- (b) Assuming that ΔH° and ΔS° are independent of temperature, calculate ΔG° and the equilibrium constant for the reaction in (a) under standard conditions at 1000°C .

11. Ethene reacts with hydrogen to form ethane according to the equation:



Chemical species	$\Delta_f H^\circ / \text{kJ mol}^{-1}$ (298K)	$S^\circ / \text{JK}^{-1} \text{mol}^{-1}$ (298K)
C_2H_4	52	220
H_2	0	131
C_2H_6	-84	230

- (a) Calculate the standard enthalpy change and the standard entropy change at 298 K for this reaction.
 (b) Calculate the standard Gibbs energy change at 200 K.
 (c) Would the value of K_p at this temperature be greater than or less than 1?
 (d) When will ΔG° and ΔG be equal to zero?

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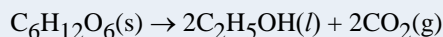
12. For the process $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$ $\Delta G_{298}^\circ = 8.6 \text{ kJ mol}^{-1}$. Calculate the vapour pressure of water under standard conditions at 25°C .

13. The equilibrium constant for the reaction:



is 2.10×10^{18} at 298K and 1.35×10^{11} at 500 K. Determine ΔH° for the reaction, assuming ΔH° and ΔS° are constant over this temperature range.

14. Microorganisms can bring about the fermentation of sugars into ethanol, for example, glucose:



Use data from SI Chemical Data to calculate the standard enthalpy change for this reaction. You will need to calculate the enthalpy of formation of liquid ethanol first.

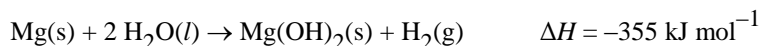
15. In biological applications of thermodynamics, it is often more useful to deal with energy changes per mass of reactant. In terms of heat produced (which can keep a living organism warm) per gram of carbohydrate, is the oxidation of glucose (to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$) more effective than the oxidation of sucrose?

EXTRA PRACTICE QUESTIONS

Attempt these in your own time. The tutor will NOT cover these questions unless the class finished early and there is extra time. You may need to look up the values for some of these questions in the SI Chemical Data book. For help with these questions, see the Duty Tutor.

16. (a) What is meant by a "standard enthalpy change"?
- (b) Write chemical equations including the states of matter for all reactants and products, to represent each of the following processes. Look up the value of the standard enthalpy change for each of the processes.
- (i) the standard enthalpy of formation of gaseous water.
 - (ii) the standard enthalpy of atomization of carbon.
 - (iii) the standard enthalpy of condensation of bromine.
 - (iv) the standard enthalpy of formation of $\text{Cr}^{3+}(\text{g})$.
 - (v) the standard enthalpy of formation of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}(\text{s})$
 - (vi) the molar enthalpy of sublimation of rubidium.
17. High quality coal (anthracite) is almost pure carbon. The combustion of carbon to carbon dioxide releases 393 kJ per mol of carbon burnt. If 1.000 kg of anthracite is burnt:
- | |
|---|
| $(\Delta_{\text{fus}}H = 6.0 \text{ kJmol}^{-1})$ |
| $(C_p^\circ = 75 \text{ JK}^{-1}\text{mol}^{-1})$ |
| $(\Delta_{\text{vap}}H = 46 \text{ kJmol}^{-1})$ |
- (a) How much heat is released?
 - (b) How much ice (in kg) at 273 K could be melted to give water at 273 K using the heat in (a)?
 - (c) How much ice (in kg) at 273 K could be melted to give water at 100 °C using the heat in (a)?
 - (d) How much ice (in kg) at 273 K could be melted to give steam at 373 K using the heat in (a)?

18. A pack has been developed so that small amounts of food can be heated without the need to light a fire or burn fuel. The researchers who designed the pack found that by mixing powdered magnesium metal with sodium chloride and iron particles the following exothermic reactions would occur rapidly when water was added:



Thus, when water is poured into a porous pad containing the powdered magnesium mixture, heat is released. This energy warms food contained in an adjacent sealed food pouch. Assume that the pack contains 0.10 g of powdered magnesium.

- Calculate the maximum amount of heat that can be released by adding water to the powdered magnesium.
 - Calculate the minimum mass of water that must be added to release this amount of heat.
 - The directions on the pack specify the addition of a certain volume of water. If 50 mL of water is added, calculate its maximum rise in temperature, assuming a heat capacity of $4.2 \text{ J K}^{-1} \text{ g}^{-1}$ and a density of 1.00 g mL^{-1} for all solutions.
19. By using appropriate data from SI Chemical Data, calculate the enthalpy change and internal energy change associated with this reaction at 25°C : $\text{CuO(s)} + \text{H}_2\text{(g)} \rightarrow \text{Cu(s)} + \text{H}_2\text{O(l)}$
20. When 2.50 g of ammonium chloride is dissolved in 100.0 g of water the temperature falls by 1.70 K. Calculate the enthalpy of solution of ammonium chloride, assuming a heat capacity of $4.2 \text{ J K}^{-1} \text{ g}^{-1}$ and a density of 1.00 g mL^{-1} for all solutions.
21. Without consulting a table of standard molar entropies predict whether ΔS° will be positive or negative for each of the following reactions:
- $2 \text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{CO}_2\text{(g)}$
 - $2 \text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{H}_2\text{O(l)}$
 - $2 \text{O}_3\text{(g)} \rightarrow 3 \text{O}_2\text{(g)}$
 - $2 \text{NH}_3\text{(g)} \rightarrow \text{N}_2\text{(g)} + 3 \text{H}_2\text{(g)}$
 - $2 \text{Na(s)} + \text{Cl}_2\text{(g)} \rightarrow 2 \text{NaCl(s)}$
 - $\text{H}_2\text{(g)} + \text{I}_2\text{(s)} \rightarrow 2 \text{HI(g)}$
22. (a) For this reaction: $\text{CH}_3\text{CH}_2\text{OH(g)} + 1/2\text{O}_2\text{(g)} \rightarrow \text{CH}_3\text{COOH(g)}$ calculate:
- the standard enthalpy change and the standard entropy change at 298 K.
 - the standard Gibbs energy change at 298 K.
 - the value of K_p at 298 K.
- (b) Calculate the standard enthalpy change for $\text{CH}_3\text{CH}_2\text{OH(g)} + 1/2\text{O}_2\text{(g)} \rightarrow \text{CH}_3\text{COOH(l)}$ at 298 K.

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23. For each of the following thermochemical processes, write the appropriate name(s) and insert the ΔH° value for the process.
- $\text{Ba(s)} \rightarrow \text{Ba(g)}$
 - $\text{Ba(g)} \rightarrow \text{Ba}^+\text{(g)} + \text{e}^-\text{(g)}$
 - $\text{Ba}^+\text{(g)} \rightarrow \text{Ba}^{2+}\text{(g)} + \text{e}^-\text{(g)}$
 - $\frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{O(g)}$
 - $\text{O(g)} + \text{e}^-\text{(g)} \rightarrow \text{O}^-\text{(g)}$
 - $\text{O}^-\text{(g)} + \text{e}^-\text{(g)} \rightarrow \text{O}^{2-}\text{(g)}$
 - $\text{Ba(s)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{BaO(s)}$
 - $\text{BaO(s)} \rightarrow \text{Ba}^{2+}\text{(g)} + \text{O}^{2-}\text{(g)}$

24. Experiments have been performed in which the force required to extend the length of a single DNA molecule has been measured (see for example the journal Science, 1996, vol 271, pp. 792–794). If the force required to extend the length of a DNA molecule is approximately 80 pN, calculate the mechanical work required to extend the molecule from 15 μm to 20 μm in length. Calculate the work required to extend one mole of DNA molecules from 15 μm to 20 μm in length.

NUMERICAL ANSWERS

2. (a) Air temp = 74°C
3. (b) heat absorbed_{calor} = 5.63 J, (c) heat absorbed_{solution} = 670 J;
(d) heat absorbed_{reaction} = 676 J; (e) $\Delta H_{\text{reaction}} = -67.6 \text{ kJ mol}^{-1}$;
4. (a) $\Delta H = 178 \text{ kJ mol}^{-1}$, $\Delta E = 176 \text{ kJ mol}^{-1}$; (b) $\Delta H = -2024 \text{ kJ mol}^{-1}$, $\Delta E = -2020 \text{ kJ mol}^{-1}$;
5. (a) -144 kJ mol^{-1} (b) -179 kJ mol^{-1}
8. -45 kJ mol^{-1} .
9. 228 kJ mol^{-1} ,
10. (a) -5 kJ mol^{-1} , $11 \text{ J K}^{-1} \text{ mol}^{-1}$, -8 kJ mol^{-1} ; (b) -19 kJ mol^{-1} , 6.0.
11. (a) -136 kJ mol^{-1} , $-121 \text{ J K}^{-1} \text{ mol}^{-1}$ (b) -112 kJ mol^{-1} .
12. 0.031 bar (0.031 atm or 23.6 mmHg or Torr);
13. -101 kJ mol^{-1} .
14. -71 kJ mol^{-1}
15. (glucose) 15.6 kJ g^{-1} ; (sucrose) 16.5 kJ g^{-1}
17. (a) $3.28 \times 10^4 \text{ kJ}$, (b) 98 kg, (c) 44 kg; (d) 10 kg.
18. (a) 1.5 kJ; (b) 0.15 g; (c) 7.0K
19. (b) $\Delta H = -129 \text{ kJ mol}^{-1}$, $\Delta E = -127 \text{ kJ mol}^{-1}$;
20. (b) 15.7 kJ mol^{-1}
22. (a) (i) -196 kJ mol^{-1} $-102.5 \text{ J K}^{-1} \text{ mol}^{-1}$ (ii) -165 kJ mol^{-1} (iii) 1×10^{29} (b) -248 kJ mol^{-1}
24. $4 \times 10^{-16} \text{ J}$, $2.4 \times 10^8 \text{ J} = 240 \text{ MJ}$

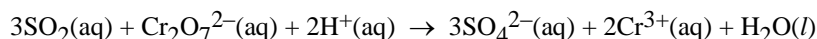
PROBLEM SET 10: REDOX REACTIONS AND ELECTROCHEMICAL CELLS

References: Blackman, *et al.* 'Chemistry': 12.1 – 12.8

CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

1. In the reaction:



- (a) Complete the table to determine the oxidation numbers for each target element (note some have been purposely left out):

Species	SO ₂	Cr ₂ O ₇ ²⁻	H ⁺	SO ₄ ²⁻	Cr ³⁺	H ₂ O
Element	S	Cr	H	S	Cr	H
Oxidation Number						

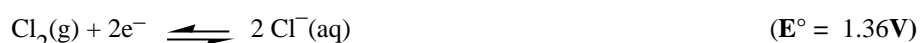
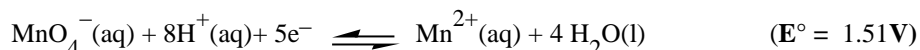
- (b) Which species contains the element that is *oxidised*?
(c) Which species contains the element that is *reduced*?
(d) Which is the oxidizing agent?

2. By means of ion electron half equations, write balanced overall ionic equations for each of the following reactions:

- (a) Copper metal reacted with dilute nitric acid solution to produce a solution of copper(II) nitrate and nitrogen dioxide gas.
(b) Ethanol was oxidized to ethanoic acid by acidified dichromate.
(c) Acidified solutions of iodide and iodate ions were mixed, producing iodine.

3. (a) What is meant by 'standard reduction potential'? Under what conditions is it measured?

- (b) Consider the following processes:



- (i) Which substance is the strongest reducing agent?
(ii) Which substance is the strongest oxidising agent?
(iii) Give an equation for the spontaneous reaction occurring in an electrochemical cell made from the standard Mg and Cl₂ couples.
(iv) Make a labelled drawing to represent this electrochemical cell. Mark on your drawing the following features: Anode, cathode, salt bridge, direction of electron flow, direction of movement of anions and cations in the salt bridge, identity and concentrations of all chemical species in the system.
(v) Write the conventional cell diagram for this cell.
(vi) What is E° , the standard cell potential for this cell?

4. Referring to the standard reduction table,
- Select the best oxidising agent from the following list:
 Al^{3+} , $\text{Br}_2(l)$, Sn^{2+} , Ag^+ , Cu^{2+} , Mg^{2+} .
 - Select the best reducing agent from the following list:
 $\text{Br}_2(l)$, Ag , Br^- , Cu^{2+} , Cl^- , Al .
 - Using the method of ion-electron half-equations write the balanced equation for the electrochemical cell formed between the half-cells of the oxidising and reducing agents you selected in parts (a) and (b).
 - Calculate E_{cell}° for this cell.
 - Make a fully labelled drawing of the electrochemical cell under standard conditions.
5. (a) Find the standard emf for each of the following galvanic cells (represented using conventional cell diagrams) and write the chemical equation for the reaction in the cell as written.
- $\text{Fe} | \text{Fe}^{2+} || \text{Cu}^{2+} | \text{Cu}$
 - $\text{Fe} | \text{Fe}^{2+} || \text{Ag}^+ | \text{Ag}$
 - $\text{Sn} | \text{Sn}^{2+} || \text{Br}^- | \text{Br}_2(l) | \text{Pt}$
 - $\text{Pt} | \text{Fe}^{2+}, \text{Fe}^{3+} || \text{Hg}^{2+} | \text{Hg}$
 - $\text{Zn} | \text{Zn}^{2+} || \text{Co}^{2+} | \text{Co}$
- (b) Calculate the emf of cell (ii) above, when $[\text{Ag}^+] = 10^{-3} \text{ mol L}^{-1}$; $[\text{Fe}^{2+}] = 2.0 \text{ mol L}^{-1}$ and temperature 25°C .

HARDER CLASS QUESTIONS

Attempt these questions before your tutorial class. Let your tutor know which questions you struggled with.

6. Using the half reaction method, give the overall balanced equation for the following reaction in acidic conditions:
- $$\text{Mn}^{2+}(\text{aq}) + \text{BiO}_3^-(\text{aq}) \rightleftharpoons \text{MnO}_3^-(\text{aq}) + \text{Bi}^{3+}(\text{aq})$$
7. Using the half reaction method, give the overall balanced equation for the following reaction in basic conditions:
- $$\text{Zn}(\text{s}) + \text{NO}_3^-(\text{aq}) \rightleftharpoons \text{Zn}(\text{OH})_4^{2-}(\text{aq}) + \text{NH}_3(\text{aq})$$
8. Give explanations for the following observations, including as many relevant chemical equations with appropriate E° values, as you can:
- Steel clips holding copper pipes against the brick wall of a house rust rapidly, but the copper pipes appear to be unaffected.
 - A piece of mild steel plate was de-greased and placed in a flask containing some de-aerated water; the flask was sealed and set aside for several days. No corrosion (rusting) was observed.
 - The standard electrode potentials of $\text{Zn}|\text{Zn}^{2+}$ and $\text{Fe}|\text{Fe}^{2+}$ are, respectively, -0.76 and -0.44 V, yet steel sheets are often protected by “galvanizing”, *i.e.* by being given a zinc coating.
 - A common sequence of events in the corrosion of chrome-plated steel is that a small scratch or pit occurs in the plating, then the surrounding coating appears to “blister” and can easily be peeled away.
 - Cracks develop in steel reinforced concrete structures when measures are not taken to prevent corrosion of the reinforcing rods.

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9. (a) For a cell in which the reaction $\text{Zn(s)} + \text{Ni}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Ni(s)}$ is occurring, use the Nernst equation: $E = E^\circ - \frac{RT}{nF} \ln Q$ to calculate:
- E_{cell} when $[\text{Ni}^{2+}] = 0.05 \text{ mol L}^{-1}$ and $[\text{Zn}^{2+}] = 0.85 \text{ mol L}^{-1}$.
 - the ratio $\frac{[\text{Ni}^{2+}]}{[\text{Zn}^{2+}]}$ when the cell is "flat".
- (b) A concentration cell is constructed from two half cells composed of the same materials but differing in ionic concentration. In the case of a cell constructed from two Zn electrodes having 1.0 M Zn^{2+} and 0.10 M Zn^{2+} respectively, determine which is the anode and which is the cathode, and calculate the E_{cell} at 298K.
10. (a) Calculate the Gibbs energy change for: $6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g})$.
- (b) Is the reaction in (a) spontaneous?
- (c) How is it that plants can carry out the reaction in (a)?
11. Assume a pH electrode responds to a change in $[\text{H}^+]$ exactly according to the Nernst equation (with $n = 1$). If the concentration of H^+ increases by a factor of 10, what will be the change in the potential of the pH electrode (at 298 K)? What change in pH does this correspond to?

EXTRA PRACTICE QUESTIONS

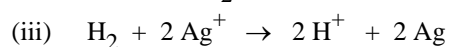
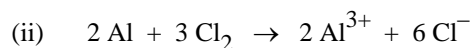
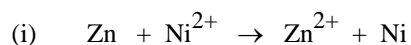
Attempt these in your own time. The tutor will NOT cover these questions unless the class finished early and there is extra time. You may need to look up the values for some of these questions in the SI Chemical Data book. For help with these questions, see the Duty Tutor.

12. (a) What is an oxidation number?
- (b) What is the oxidation number of the element indicated in each of the following species?

Species	H_2O_2	N_2O	Hg_2Cl_2	ClO^-	ClO_3^-	Cl_2O_7	SO_4^{2-}	SO_3^{2-}	$\text{Cr}_2\text{O}_7^{2-}$	MnO_4^-
Element	O	N	Hg	Cl	Cl	Cl	S	S	Cr	Mn
Oxid. No.										

13. By means of ion electron half equations, write balanced overall ionic equations for each of the following reactions:
- an acidified solution of oxalate ion was oxidized to carbon dioxide by permanganate ion,
 - adding acid to a solution of sodium thiosulfate produced elemental sulfur and sulfur dioxide.
14. (a) What is the difference between a galvanic (or voltaic) cell and an electrolytic cell?
- (b) Calculate the mass of cadmium that may be deposited from a solution of cadmium sulfate by the passage of a 1.02 ampere current for 2 hours 20 minutes.

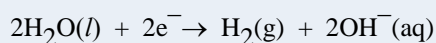
15. Represent the electrochemical cell based on each reaction shown below using the usual conventions for a cell diagram:



- (a) Calculate E° for each cell.
(b) Describe how a cell such as that in (i) could be recharged.
(c) Under what conditions does a cell go 'flat'? Does 'flat' mean necessarily that no reaction takes place?

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16. The amount of lactic acid produced in a sample of muscle tissue was analyzed by reaction with hydroxide ion. The hydroxide ion was produced in the sample by electrolysis, where the cathodic reaction is:



The hydroxide ions produced react immediately with the lactic acid. An acid/base indicator was used to detect the end-point. It required 115 s for a current of 1.56×10^{-2} A to reach the end-point. Calculate the mass of lactic acid that was present in the sample of muscle tissue.

NUMERICAL ANSWERS

3. (c) (vi) +3.72 V.
4. (d) 2.76 V.
5. (a) (i) +0.78 V, (ii) 1.24 V, (iii) +1.22 V, (iv) +0.08 V, (v) +0.48 V; (b) 1.05 V
9. (a) (i) 0.48 V; (ii) 2.6×10^{-18} ; (b) 0.0296 V
10. (a) +2875 kJ mol⁻¹
11. 0.059 V
14. (b) 4.99 g.
15. (a) (i) +0.52 V, (ii) +3.04 V, (iii) +0.80 V, (iv) +0.13 V, (v) +0.44 V.
16. 1.68×10^{-3} g

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