Topics in the November 2010 Exam Paper for CHEM1904

Click on the links for resources on each topic.

2010-N-2:

- Crystal Structures

2010-N-3:

- Coordination Chemistry

2010-N-4:

- Weak Acids and Bases
- Calculations Involving pK_a

2010-N-5:

- Intermolecular Forces and Phase Behaviour
- Physical States and Phase Diagrams

2010-N-6:

- Intermolecular Forces and Phase Behaviour
- Physical States and Phase Diagrams
- Weak Acids and Bases
- Calculations Involving pK_a

2010-N-7:

- Alkenes
- Alcohols
- Organic Halogen Compounds

2010-N-8:

- Structural Determination

2010-N-9:

- Organic Mechanisms and Molecular Orbitals
- Stereochemistry

2010-N-10:

- Aldehydes and Ketones
- Carboxylic Acids and Derivatives
- Synthetic Strategies
- Organic Mechanisms and Molecular Orbitals

2010-N-11:

- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2010-N-12:

- Aromatic Compounds

2223(a)

THE UNIVERSITY OF SYDNEY

CHEM1902 - CHEMISTRY 1B (ADVANCED)

and

CHEM1904 - CHEMISTRY 1B (SPECIAL STUDIES PROGRAM)

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2010 **TIME ALLOWED: THREE HOURS**

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

FAMILY NAME		**SID NUMBER**	
OTHER NAMES		**TABLE NUMBER**	

OFFICIAL USE ONLY

INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 21 pages of examinable material.
- Complete the written section of the examination paper in **INK.**
- Read each question carefully. Report the appropriate answer and show all relevant working in the space provided.
- The total score for this paper is 100. The possible score per page is shown in the adjacent tables.
- Each new question of the short answer section begins with a •.
- Only non-programmable, University-approved calculators may be used.
- Students are warned that credit may not be given, even for a correct answer, where there is insufficient evidence of the working required to obtain the solution.
- Numerical values required for any question, standard electrode reduction potentials, a Periodic Table and some useful formulas may be found on the separate data sheets.
- Pages 14 and 22 are for rough working only.

Multiple choice section

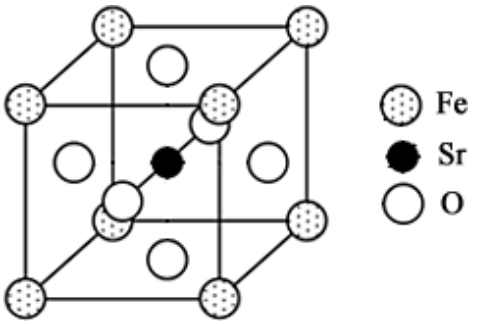
	Marks	
Pages	Max	Gained
2-10	30	

Short answer section

Page	Marks Max	Gained		Marker
11	9			
12	7			
13	8			
15	4			
16	6			
17	10			
18	8			
20	7			
21	6			
23	5			
Total	70			
Check Total				

Marks 9

- $SrFeO_3$ crystallises with the perovskite structure, shown below. The structure is cubic with iron atoms on each corner, oxygen atoms at the centre of each face and a strontium atom at the centre of the cube. Mixed metal oxides such as this are of current research interest because of their magnetic and possible superconducting properties.



Show the structure is consistent with the formula $SrFeO_3$ and give the coordination numbers of the Sr, Fe and O atoms.

Using the box notation to represent atomic orbitals, work out how many unpaired electrons are present on the iron cation in this compound.

It is possible to substitute the Sr^{2+} ions at the centre of the unit cell by La^{3+} ions to make a series of compounds with the formula $La_{1-x}Sr_xFeO_3$ with $0 \leq x \leq 1$. Suggest why this substitution is achieved without significant change to the unit cell dimensions and describe how charge balance is achieved in these compounds.

Page Total:

Marks 7

- The species $[Cr(en)_3][FeCl_4]_3$ is an example of a salt in which both the anion and cation are comprised of coordination complexes. Name the complex using standard IUPAC nomenclature (en = ethane-1,2-diamine).

Draw the structure of the cation. Is this complex chiral? Briefly explain your reasoning.

If the salt is dissolved in water and a saturated solution of KCl is added to the solution, different coloured complexes can be crystallised from the solution. Write the formulae for two of these complexes.

Marks 8

- Aqua ligands in coordination complexes are generally acidic. Briefly explain this phenomenon using $[Co(NH_3)_5(OH_2)]^{3+}$ as an example.

Solution A consists of a 0.10 M aqueous solution of $[Co(NH_3)_5(OH_2)](NO_3)_3$ at 25 °C. Calculate the pH of Solution A. The pK_a of $[Co(NH_3)_5(OH_2)]^{3+}$ = 5.69.

pH =

At 25 °C, 1.00 L of Solution B consists of 28.5 g of $[Co(NH_3)_5(OH)](NO_3)_2$ dissolved in water. Calculate the pH of Solution B.

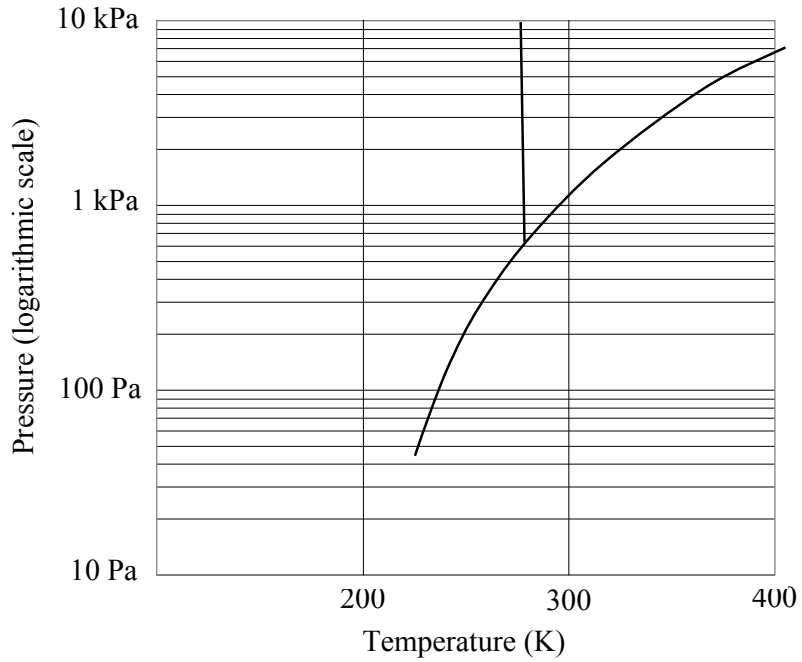
pH =

Using both Solutions A and B, calculate the volumes (in mL) required to prepare a 1.0 L solution with a pH = 7.00.

Page Total:

Marks
4

- The diagram below shows part of the phase diagram of water.



The average pressure on the surface of Mars is around 0.6 kPa. If the night time temperature is –60 °C and a summer day temperature is 20 °C, describe what happens to any water on the surface of Mars as the sun rises.

The highest surface pressure on Mars is thought to occur at the Hellas Basin, a low-lying area created by the impact of a large asteroid. If the pressure in this region is 1.2 kPa, use the phase diagram to estimate the temperature range in which liquid water will occur. Show your working on the phase diagram.

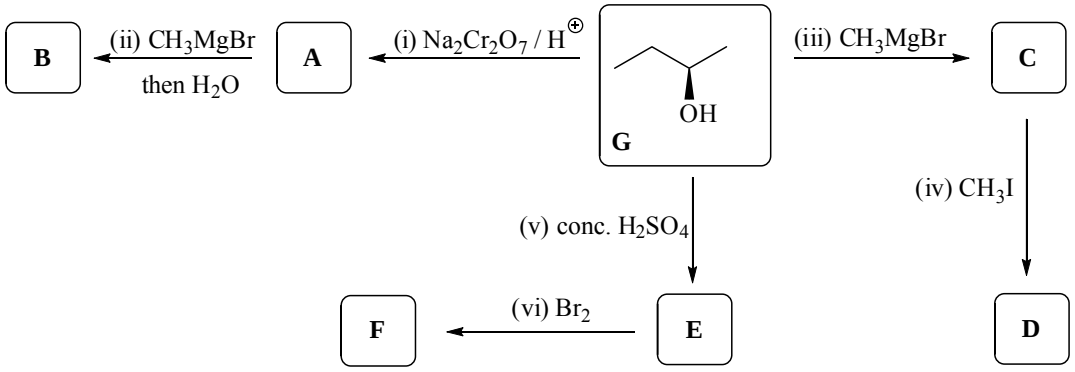
Page Total:

	Marks
• The critical point of H_2O is over 250 °C higher than for H_2S, H_2Se and H_2Te. Describe, at the molecular level, what needs to happen to the interactions between the water molecules to reach the critical point and why this requires a higher temperature in water than in the other group 16 hydrides.	**2**
• A dilute solution of ammonia has a pH of 10.54. Calculate what amount of HCl(g) must be added to 1.0 L of this solution to give a final pH of 8.46. The pK_a of NH_4^+ is 9.24.	**4**
Answer:	

Page Total:

Marks 10

- Consider the following reaction sequences beginning with the alcohol **G**.



What is the systematic name for **G**?

Suggest structures for compounds **A** – **F** in the reaction sequences above.

A	**B**	**C**
D	**E**	**F**

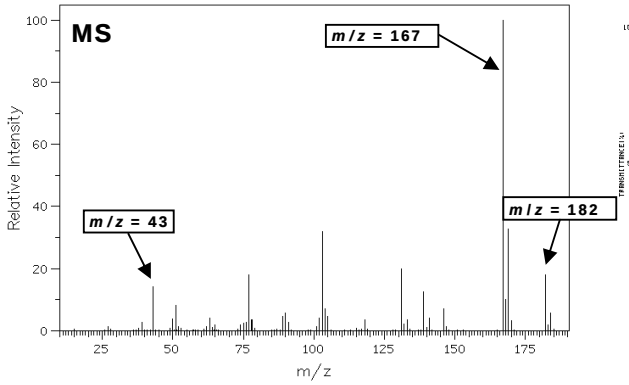
What type of reaction is occurring at each of the following steps?

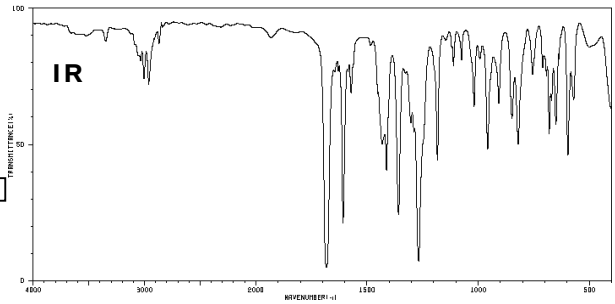
Step (iii)	
Step (iv)	
Step (v)	
Step (vi)	

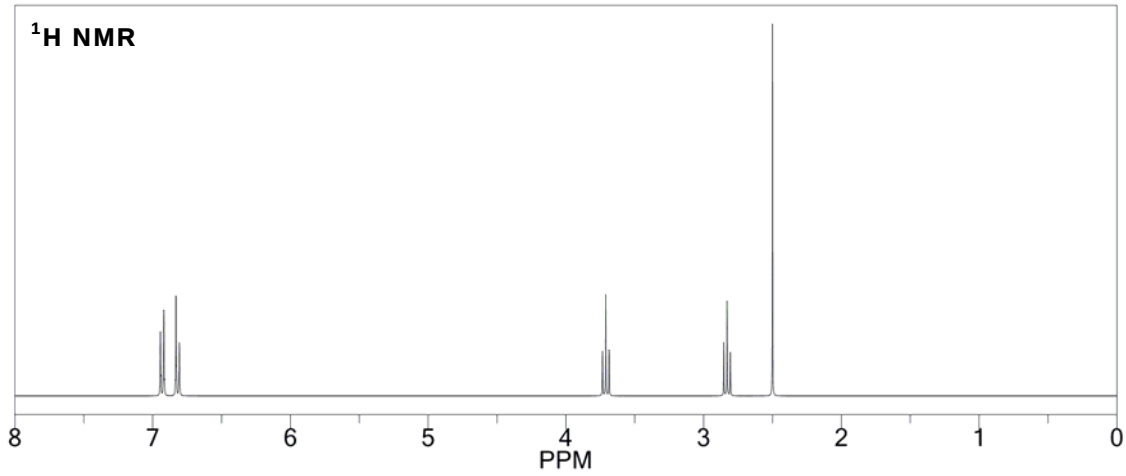
Page Total:

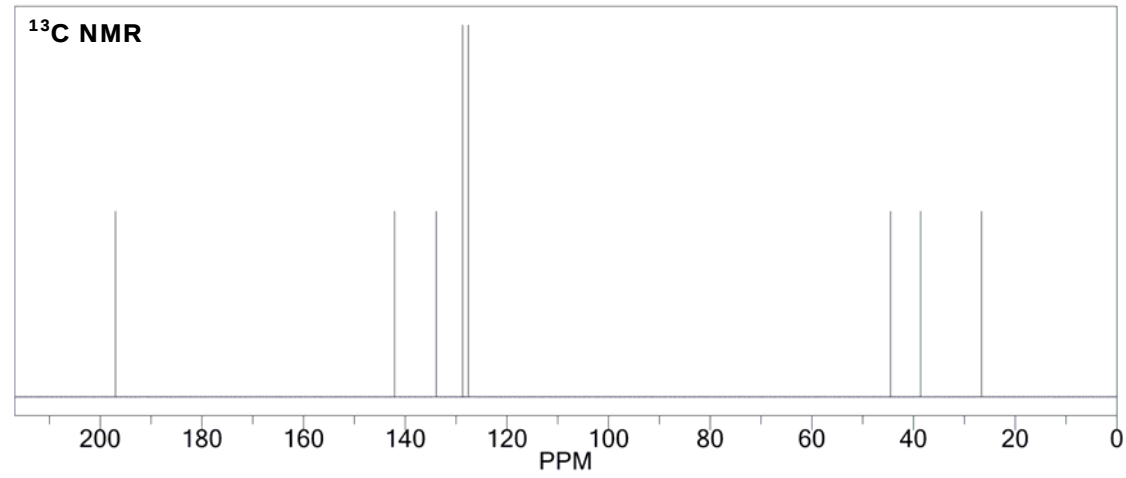
	Marks
• Shown on page 19 are the mass (MS), infrared (IR), ^{1}H and ^{13}C NMR spectra for a compound of empirical formula $C_{10}H_{11}ClO$. Use this information to deduce a structure for this compound. (NMR chemical shift ranges can be found on page 24.) Show your working below.	**8**
Working	
Structure	

Page Total:


MS
m/z = 167
m/z = 43
m/z = 182
Relative Intensity
m/z


IR

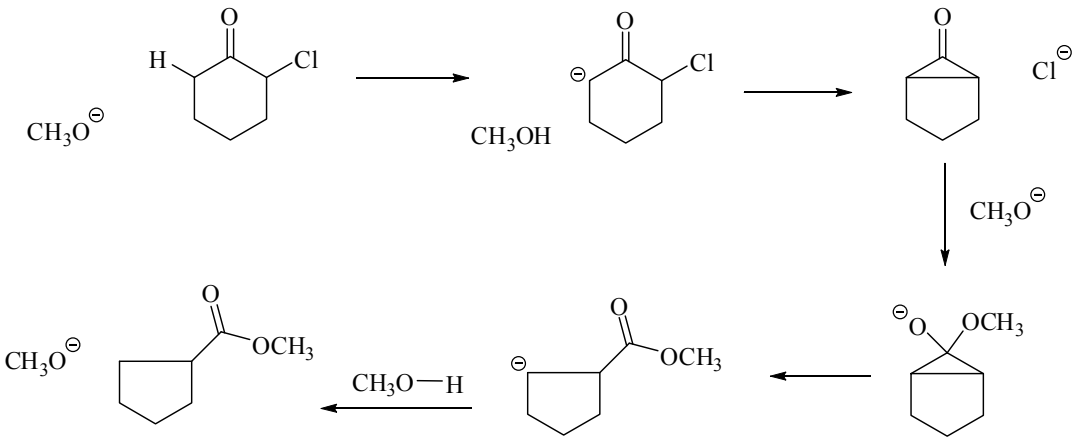

1H NMR
PPM


13C NMR
PPM

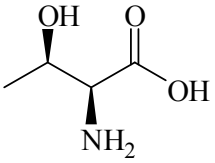
Page Total:

Marks

- Apply your understanding of 'curly arrows' to draw in the arrows required to complete a mechanism for the following reaction. **5**



- The systematic name of threonine is 2-amino-3-hydroxybutanoic acid. Assign the absolute configuration of L-threonine. Show your working. **2**

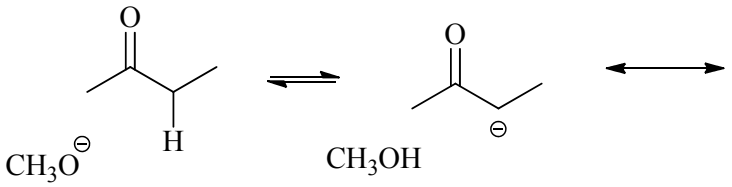


L-threonine

Page Total:

Marks 6

- Protons next to a carbonyl group can be removed by alkoxide bases as shown below.

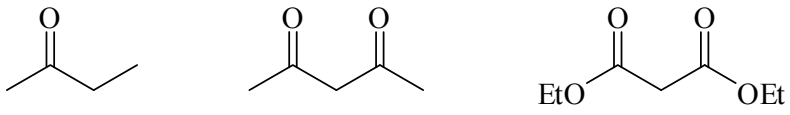


J **K** **L**

Apply your understanding of resonance to propose a structure **L** that explains how the carbonyl group increases the acidity of these hydrogens.

Add curly arrows to the reaction scheme above to complete a mechanism for the deprotonation of **J** to give **K**, and the stabilisation of **K** by resonance.

The pK_a values of compounds **J**, **M** and **N** are 9, 13 and 19, but not in that order. Match each compound with the correct pK_a, and explain your answer.



J **M** **N**

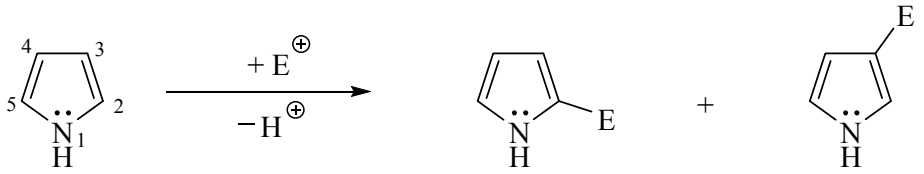
pK_a values:	**J** =	**M** =	**N** =

Reasoning for above assignments

Page Total:

Marks
5

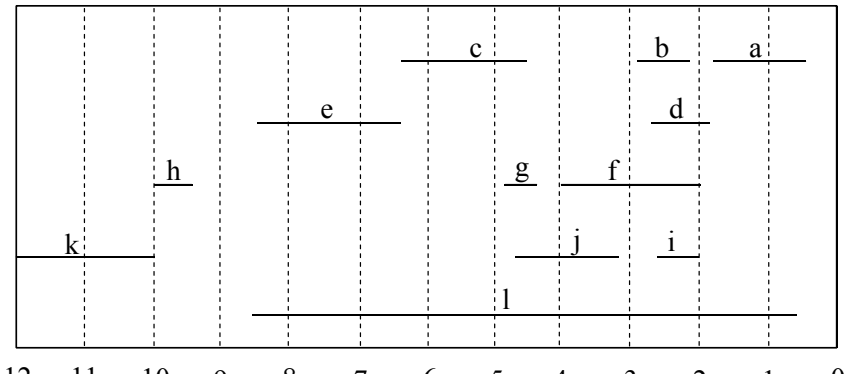
- In the electrophilic aromatic substitution (S_EAr) of pyrrole, the 2-substituted derivative is the major product.



Draw the cationic (Wheland-type) intermediate formed during reaction at the 2-position, and the equivalent intermediate formed during reaction at the 3-position. Using these structures, explain why reaction at the 2-position is faster, and leads to the major product.

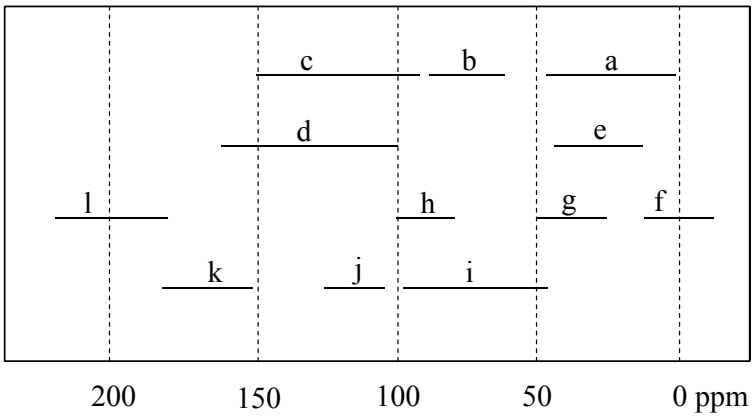
Page Total:

^{1}H NMR Chemical Shifts



a R—H
b Ph—C—H
c C=C—H
d C≡C—H
e Ph—H
f X—C—H (X = Cl, Br or I)
g F—C—H
h —C(=O)—H
i —C(=O)—C—H
j O—C—H
k —C(=O)—O—H
l ROH, PhOH, RNH

^{13}C NMR Chemical Shifts



a alkanes
b alkynes
c alkenes
d aromatics
e C-Br
f C-I
g C-Cl
h C-F
i C-O
j C≡N
k acids, esters, amides
l aldehydes, ketones

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Page Total:

CHEM1902 - CHEMISTRY 1B (ADVANCED)
CHEM1904 - CHEMISTRY 1B (SSP)

DATA SHEET

Physical constants

Avogadro constant, $N_A = 6.022 \times 10^{23}$ mol^{-1}

Faraday constant, $F = 96485$ C mol^{-1}

Planck constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light in vacuum, $c = 2.998 \times 10^{8}$ m s^{-1}

Rydberg constant, $E_R = 2.18 \times 10^{-18}$ J

Boltzmann constant, $k_B = 1.381 \times 10^{-23}$ J K^{-1}

Permittivity of a vacuum, $\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 J^{-1} m^{-1}

Gas constant, $R = 8.314$ J K^{-1} mol^{-1}

$= 0.08206$ L atm K^{-1} mol^{-1}

Charge of electron, $e = 1.602 \times 10^{-19}$ C

Mass of electron, $m_e = 9.1094 \times 10^{-31}$ kg

Mass of proton, $m_p = 1.6726 \times 10^{-27}$ kg

Mass of neutron, $m_n = 1.6749 \times 10^{-27}$ kg

Properties of matter

Volume of 1 mole of ideal gas at 1 atm and 25 °C = 24.5 L

Volume of 1 mole of ideal gas at 1 atm and 0 °C = 22.4 L

Density of water at 298 K = 0.997 g cm^{-3}

Conversion factors

1 atm = 760 mmHg = 101.3 kPa

0 °C = 273 K

1 L = 10^{-3} m^3

1 Å = 10^{-10} m

1 eV = 1.602×10^{-19} J

1 Ci = 3.70×10^{10} Bq

1 Hz = 1 s^{-1}

1 tonne = 10^3 kg

1 W = 1 J s^{-1}

Decimal fractions

Fraction	Prefix	Symbol
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

Decimal multiples

Multiple	Prefix	Symbol
10^3	kilo	k
10^6	mega	M
10^9	giga	G

CHEM1902 - CHEMISTRY 1B (ADVANCED)
CHEM1904 - CHEMISTRY 1B (SSP)

Standard Reduction Potentials, E°

Reaction	*E*° / V
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.72
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(g) + 7H_2O$	+1.36
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	+1.18
$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+} + 2H_2O$	+0.96
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O$	+0.96
$Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$	+0.92
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+0.53
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0 (by definition)
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	–0.04
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	–0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	–0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.24
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	–0.40
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	–0.83
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	–0.89
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	–1.68
$Sc^{3+}(aq) + 3e^- \rightarrow Sc(s)$	–2.09
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	–2.36
$Na^+(aq) + e^- \rightarrow Na(s)$	–2.71
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	–2.87
$Li^+(aq) + e^- \rightarrow Li(s)$	–3.04

CHEM1902 - CHEMISTRY 1B (ADVANCED)
CHEM1904 - CHEMISTRY 1B (SSP)

Useful formulas

Quantum Chemistry

$E = h\nu = hc/\lambda$

$\lambda = h/mv$

$E = -Z^2 E_R(1/n^2)$

$\Delta x \cdot \Delta(mv) \geq h/4\pi$

$q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$

$T\lambda = 2.898 \times 10^6$ K nm

Electrochemistry

$\Delta G° = -nFE°$

Moles of $e^- = It/F$

$E = E° - (RT/nF) \times 2.303 \log Q$

$= E° - (RT/nF) \times \ln Q$

$E° = (RT/nF) \times 2.303 \log K$

$= (RT/nF) \times \ln K$

$E = E° - \frac{0.0592}{n} \log Q$ (at 25 °C)

Acids and Bases

$pK_w = pH + pOH = 14.00$

$pK_w = pK_a + pK_b = 14.00$

$pH = pK_a + \log\{[A^-] / [HA]\}$

Gas Laws

$PV = nRT$

$(P + n^2a/V^2)(V - nb) = nRT$

$E_k = \frac{1}{2}mv^2$

Radioactivity

$t_{1/2} = \ln 2/\lambda$

$A = \lambda N$

$\ln(N_0/N_t) = \lambda t$

^{14}C age = 8033 $\ln(A_0/A_t)$ years

Kinetics

$t_{1/2} = \ln 2/k$

$k = Ae^{-Ea/RT}$

$\ln[A] = \ln[A]_o - kt$

$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

Colligative Properties & Solutions

$\Pi = cRT$

$P_{solution} = X_{solvent} \times P°_{solvent}$

$c = kp$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

$\Delta_{univ} S° = R \ln K$

$\ln \frac{K_2}{K_1} = \frac{-\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Miscellaneous

$A = -\log \frac{I}{I_0}$

$A = \varepsilon cl$

$E = -A \frac{e^2}{4\pi\varepsilon_0 r} N_A$

Mathematics

If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$\ln x = 2.303 \log x$

Area of circle = πr^2

Surface area of sphere = $4\pi r^2$

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 HYDROGEN **H** 1.008																	2 HELIUM **He** 4.003
3 LITHIUM **Li** 6.941	4 BERYLLIUM **Be** 9.012											5 BORON **B** 10.81	6 CARBON **C** 12.01	7 NITROGEN **N** 14.01	8 OXYGEN **O** 16.00	9 FLUORINE **F** 19.00	10 NEON **Ne** 20.18
11 SODIUM **Na** 22.99	12 MAGNESIUM **Mg** 24.31											13 ALUMINIUM **Al** 26.98	14 SILICON **Si** 28.09	15 PHOSPHORUS **P** 30.97	16 SULFUR **S** 32.07	17 CHLORINE **Cl** 35.45	18 ARGON **Ar** 39.95
19 POTASSIUM **K** 39.10	20 CALCIUM **Ca** 40.08	21 SCANDIUM **Sc** 44.96	22 TITANIUM **Ti** 47.88	23 VANADIUM **V** 50.94	24 CHROMIUM **Cr** 52.00	25 MANGANESE **Mn** 54.94	26 IRON **Fe** 55.85	27 COBALT **Co** 58.93	28 NICKEL **Ni** 58.69	29 COPPER **Cu** 63.55	30 ZINC **Zn** 65.39	31 GALLIUM **Ga** 69.72	32 GERMANIUM **Ge** 72.59	33 ARSENIC **As** 74.92	34 SELENIUM **Se** 78.96	35 BROMINE **Br** 79.90	36 KRYPTON **Kr** 83.80
37 RUBIDIUM **Rb** 85.47	38 STRONTIUM **Sr** 87.62	39 YTTRIUM **Y** 88.91	40 ZIRCONIUM **Zr** 91.22	41 NIOBIUM **Nb** 92.91	42 MOLYBDENUM **Mo** 95.94	43 TECHNETIUM **Tc** [98.91]	44 RUTHENIUM **Ru** 101.07	45 RHODIUM **Rh** 102.91	46 PALLADIUM **Pd** 106.4	47 SILVER **Ag** 107.87	48 CADMIUM **Cd** 112.40	49 INDIUM **In** 114.82	50 TIN **Sn** 118.69	51 ANTIMONY **Sb** 121.75	52 TELLURIUM **Te** 127.60	53 IODINE **I** 126.90	54 XENON **Xe** 131.30
55 CAESIUM **Cs** 132.91	56 BARIUM **Ba** 137.34	57-71	72 HAFNIUM **Hf** 178.49	73 TANTALUM **Ta** 180.95	74 TUNGSTEN **W** 183.85	75 RHENIUM **Re** 186.2	76 OSMIUM **Os** 190.2	77 IRIDIUM **Ir** 192.22	78 PLATINUM **Pt** 195.09	79 GOLD **Au** 196.97	80 MERCURY **Hg** 200.59	81 THALLIUM **Tl** 204.37	82 LEAD **Pb** 207.2	83 BISMUTH **Bi** 208.98	84 POLONIUM **Po** [210.0]	85 ASTATINE **At** [210.0]	86 RADON **Rn** [222.0]
87 FRANCIUM **Fr** [223.0]	88 RADIUM **Ra** [226.0]	89-103	104 RUTHERFORDIUM **Rf** [261]	105 DUBNIUM **Db** [262]	106 SEABORGIUM **Sg** [266]	107 BOHRIUM **Bh** [262]	108 HASSIUM **Hs** [265]	109 MEITNERIUM **Mt** [266]	110 DARMSTADTIUM **Ds** [271]	111 ROENTGENIUM **Rg** [272]	112 COPERNICIUM **Cn** [283]						

LANTHANOIDS	57 LANTHANUM **La** 138.91	58 CERIUM **Ce** 140.12	59 PRASEODYMIUM **Pr** 140.91	60 NEODYMIUM **Nd** 144.24	61 PROMETHIUM **Pm** [144.9]	62 SAMARIUM **Sm** 150.4	63 EUROPIUM **Eu** 151.96	64 GADOLINIUM **Gd** 157.25	65 TERBIUM **Tb** 158.93	66 DYSPROSIUM **Dy** 162.50	67 HOLMIUM **Ho** 164.93	68 ERBIUM **Er** 167.26	69 THULIUM **Tm** 168.93	70 YTTERBIUM **Yb** 173.04	71 LUTETIUM **Lu** 174.97
ACTINOIDS	89 ACTINIUM **Ac** [227.0]	90 THORIUM **Th** 232.04	91 PROTACTINIUM **Pa** [231.0]	92 URANIUM **U** 238.03	93 NEPTUNIUM **Np** [237.0]	94 PLUTONIUM **Pu** [239.1]	95 AMERICIUM **Am** [243.1]	96 CURIUM **Cm** [247.1]	97 BERKELLIUM **Bk** [247.1]	98 CALIFORNIUM **Cf** [252.1]	99 EINSTEINIUM **Es** [252.1]	100 FERMIUM **Fm** [257.1]	101 MENDELEVIUM **Md** [256.1]	102 NOBELIUM **No** [259.1]	103 LAWRENCIUM **Lr** [260.1]