22/46(a)

The University of Sydney

CHEM1902 - CHEMISTRY 1B (ADVANCED)

and

CHEM1904 - CHEMISTRY 1B (SPECIAL STUDIES PROGRAM)

CONFIDENTIAL | **TIME ALLOWED: THREE HOURS**

NOVEMBER 2009 | **SECOND SEMESTER EXAMINATION**

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

FAMILY NAME		SID NUMBER	
OTHER NAMES		TABLE NUMBER	

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 •.
- Electronic calculators, including programmable calculators, may be used. Students are warned, however, 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 sheet.
- Pages 19 & 24 are for rough working only.

OFFICIAL USE ONLY

~~**Multiple choice section**~~

	Marks	
Page	Max	Gained
2-9	33	

Short answer section

Page	Marks: Max	Marks: Gained		Marker
10	6			
11	6			
12	6			
13	7			
14	5			
15	3			
16	6			
17	4			
18	3			
20	4			
21	4			
22	10			
23	3			
Total	67			

Marks
6

- All forms of life depend on iron and the concentration of iron in the oceans and elsewhere is one of the primary factors limiting the growth rates of the most basic life forms. One reason for the low availability of iron(III) is the insolubility of the hydroxide, $Fe(OH)_3$, which has a K_{sp} of only 2×10^{-39}.

  Calculate the maximum possible concentration of Fe^{3+}(aq) in the pre-industrial era ocean which had a pH of about 8.2.

[Fe^{3+}(aq)] =

How many Fe^{3+}(aq) ions are present in a litre of seawater at this pH?

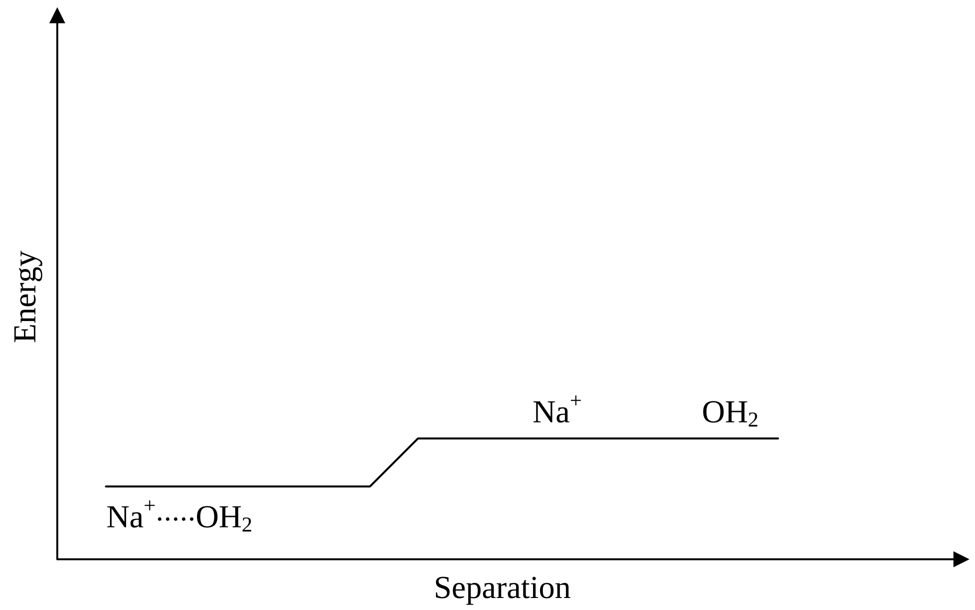
Answer:

The pH of the ocean is predicted to drop to 7.8 by the end of this century as the concentration of CO_2 in the atmosphere increases. What percentage change in the concentration of Fe^{3+}(aq) will result from this fall in pH?

Answer:

Marks
6

- Shown below is the energy profile for the separation of Na^+ from H_2O. Draw energy profiles for the separation of Mg^{2+} from Cl^- and for the breaking of the C–C bond in ethane to the same scales (approximately).



Name the inter- or intra-molecular forces involved in each of these three interactions.

Na^+ OH_2	
Mg^{2+} Cl^-	
C C	

Explain why bonds such as C–C are generally considered to be stronger than interactions such as that between Mg^{2+} and Cl^-.

Marks
6

- When cobalt(II) chloride is reacted with ethane-1,2-diamine (en) and the product is oxidised in the air, a purple compound with the empirical formula $CoCl_3{\cdot}2en$ is obtained. When reacted with silver nitrate only one chloride ion is released. The compound can be resolved into its enantiomeric forms.

  Give the structural formula of the compound.

  Give the name of the compound.

  Draw the structure of the metal complex component of the compound.

  What is the *d* electron configuration of the Co in this complex?

  What types of isomers can be formed by a compound with this empirical formula?

  Which of the possible isomers has formed? Explain the logic you have used in determining this.

Marks
7

- Nitrogen monoxide, a noxious pollutant, reacts with oxygen to produce nitrogen dioxide, another toxic gas:

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

The following rate data were collected at 225 °C.

Experiment	$[NO]_0$ (M)	$[O_2]_0$ (M)	Initial rate, $-d[O_2]/dt$, ($M\ s^{-1}$)
1	1.3×10^{-2}	1.1×10^{-2}	1.6×10^{-3}
2	1.3×10^{-2}	2.2×10^{-2}	3.2×10^{-3}
3	2.6×10^{-2}	1.1×10^{-2}	6.4×10^{-3}

Determine the rate law for the reaction.

Calculate the value of the rate constant at 225 °C.

Answer:

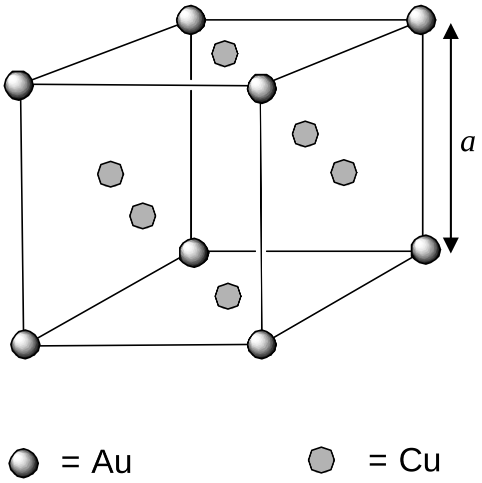
Calculate the rate of appearance of NO_2 when $[NO] = [O_2] = 6.5 \times 10^{-3}$ M.

Answer:

Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your answer.

Marks
5

- The diagram below shows the structure of an alloy of copper and gold with a gold atom at each of the corners and a copper atom in the centre of each of the faces. The unit cell dimension (edge length, *a*) for this alloy is 0.36 nm.



What is the chemical formula of the alloy?

Answer:

Given that pure gold is 24 carat and gold alloyed with 25% by weight of another metal is termed 18 carat gold, what carat gold is this alloy?

Answer:

What is the volume of the unit cell?

Answer:

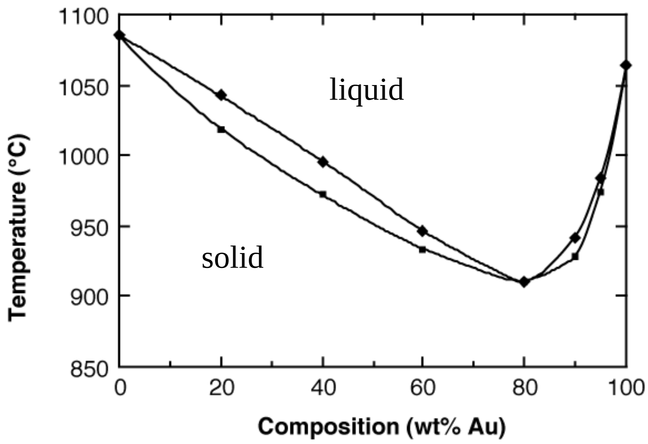
What is the density of the alloy?

Answer:

THIS QUESTION CONTINUES ON THE NEXT PAGE

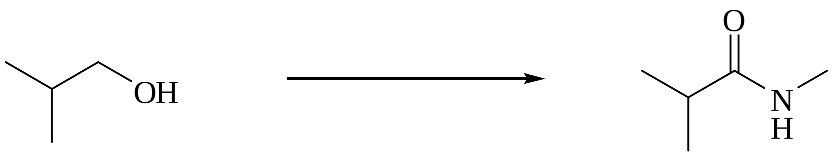
Marks
3

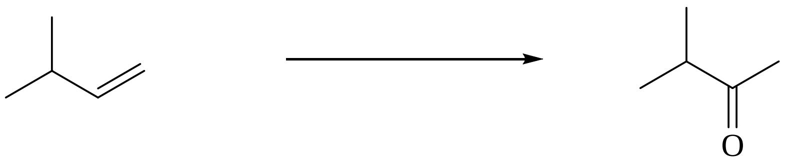
Shown below is the phase diagram for the Cu/Au system. Describe what would be seen as a sample of the alloy is heated from 900 to 1100 ^{o}C.

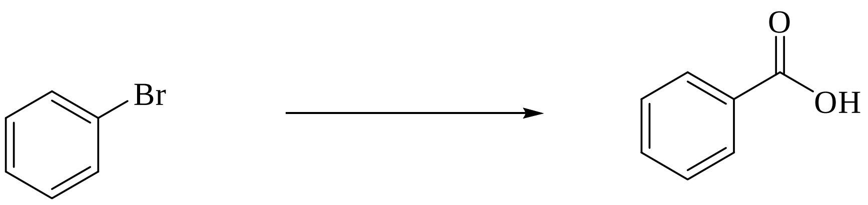


Marks
6

- Suggest reagents to accomplish the following transformations. More than one step is required in all cases.

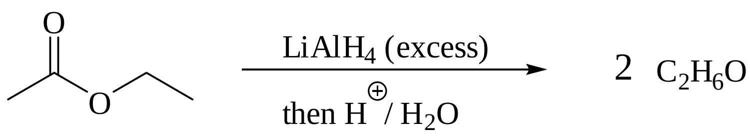






Marks
4

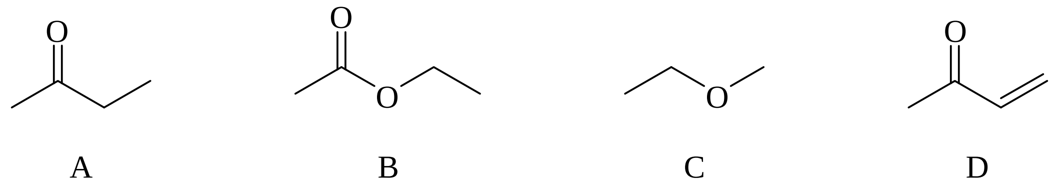
- Propose a structure for the product of the following reaction. Outline a mechanism for its formation. Show all curly arrows and any intermediates.

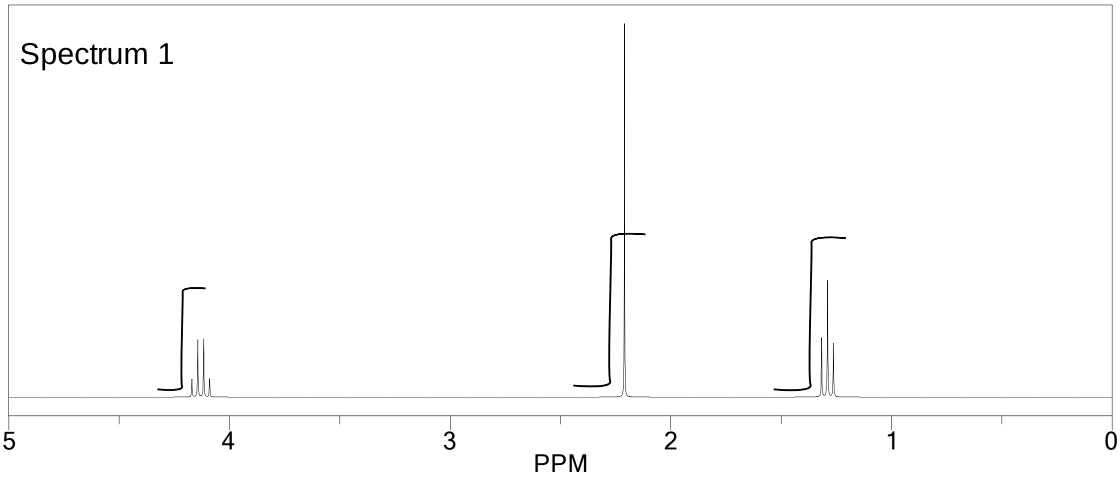


THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
4

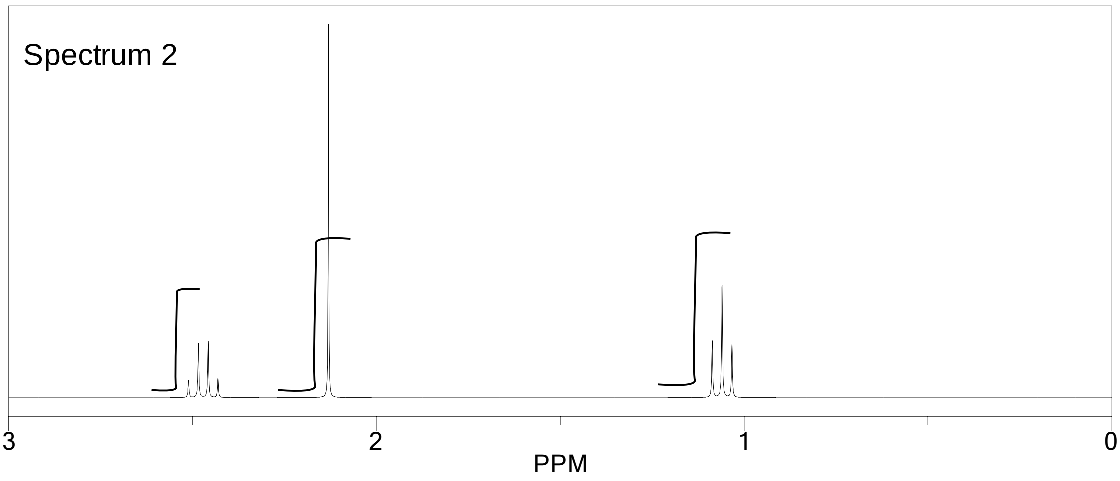
- The ^{1}H NMR spectra of these four compounds are shown below. Match each compound to its spectrum, and assign each spectrum as fully as you can.





Spectrum of: A B C D (Circle the correct answer.)

Assignment:

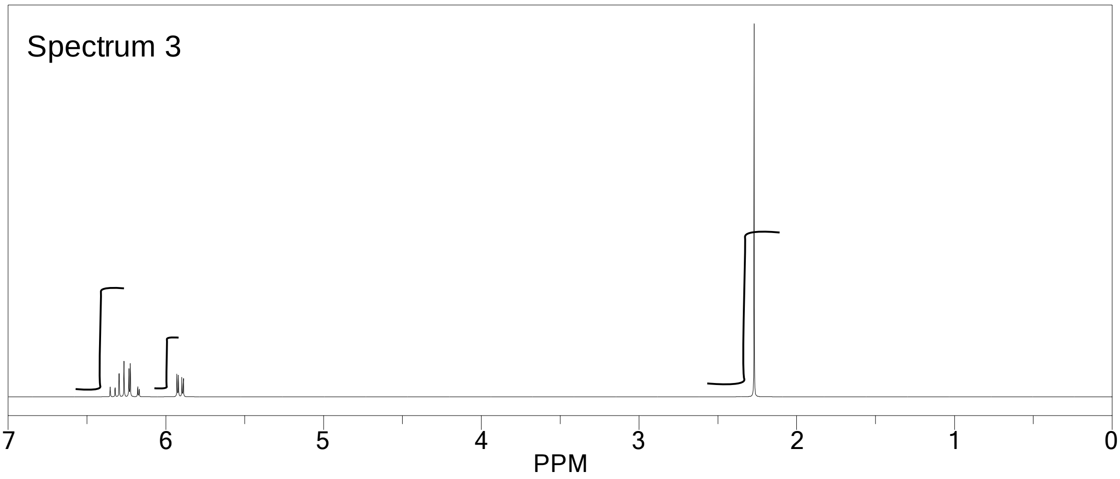


Spectrum of: A B C D (Circle the correct answer.)

Assignment:

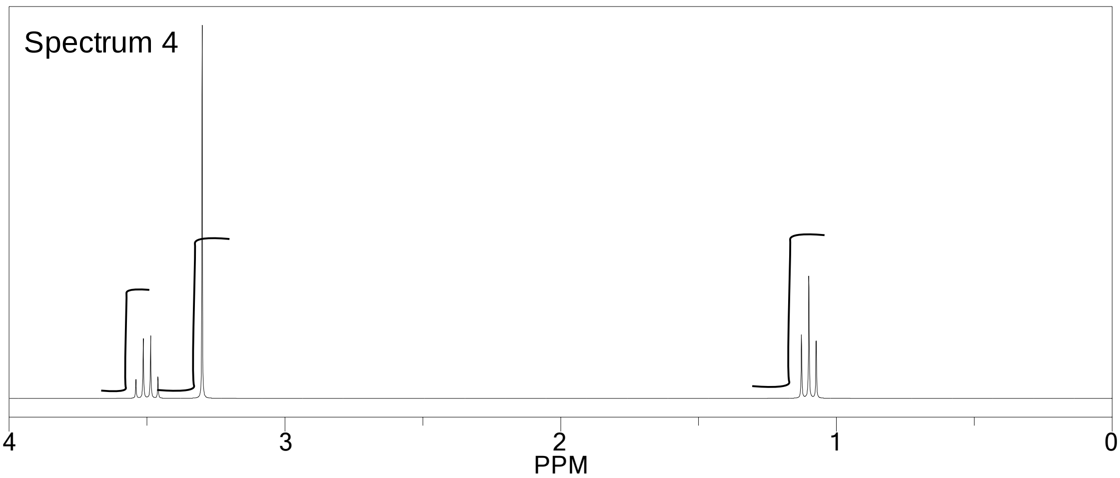
THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
4



Spectrum of: A B C D (Circle the correct answer.)

Assignment:

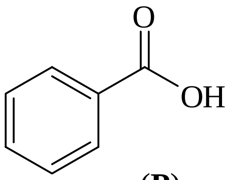


Spectrum of: A B C D (Circle the correct answer.)

Assignment:

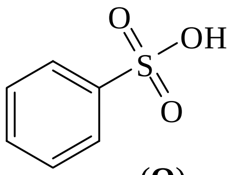
Marks
3

- For each of the following pairs of compounds, identify which is the stronger acid and give reasons for your choice.

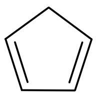


(**P**)

and

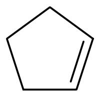


(**Q**)



(**R**)

and



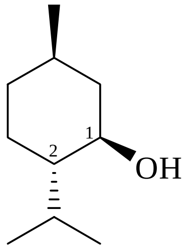
(**S**)

CF_3CO_2H (**T**) and CH_3CO_2H (**U**)

Marks
10

- The following questions pertain to the terpene natural product menthol (**J**), whose structure is shown. Carbons 1 and 2 are numbered to help you construct your answer.

J



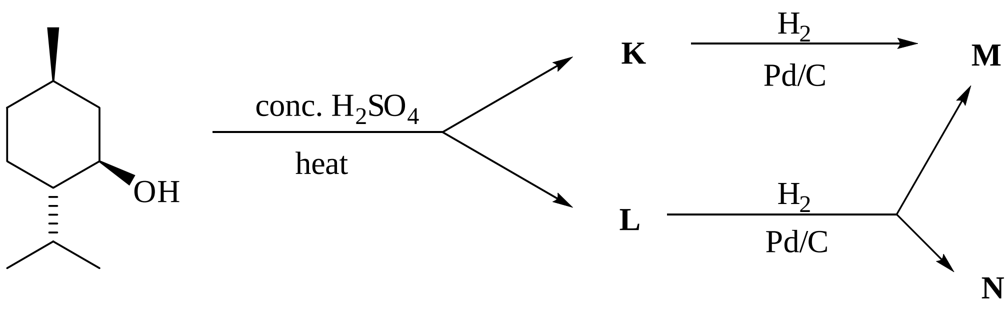
Ignoring the stereochemistry, what is the systematic name for menthol?

Assign the absolute configuration at C1 and at C2. Explain your reasoning.

C1	C2

When menthol (**J**) is heated with concentrated sulfuric acid, two isomeric products **K** and **L** are formed. When **K** and **L** are treated with excess H_2 in the presence of a Pd/C catalyst, two products **M** and **N** are observed: **K** gives only **M**, while **L** gives a mixture of **M** and **N**. Propose structures for **K**, **L**, **M** and **N**.

J



K	**L**	**M**	**N**

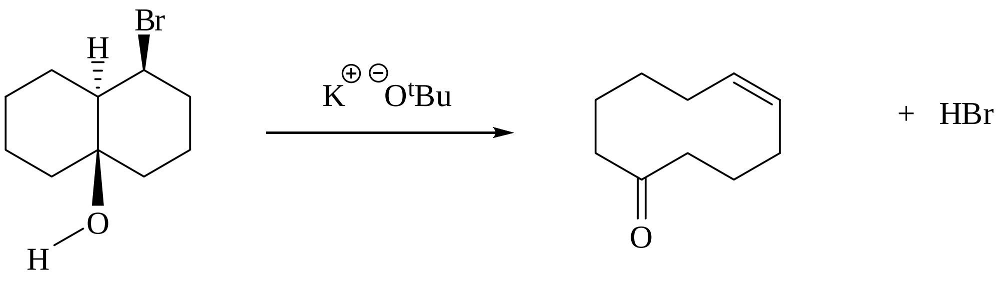
What is the isomeric relationship between **K** and **L**?

What is the isomeric relationship between **M** and **N**?

Which (if any) of the compounds **J**, **K**, **L**, **M** and **N** are optically active?

Marks
3

- Add curly arrows to complete the mechanism of the unusual E2 reaction shown below, the Grob Fragmentation. (Note that KO^{t}Bu is potassium *tert*-butoxide, a strong base.)



Explain briefly why the relative stereochemistry of the OH and Br groups in the starting material is important in this reaction.

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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	1 Pa = 1 N m^{-2} = 1 kg m^{-1} s^{-2}
0 °C = 273 K	1 Ci = 3.70×10^{10} Bq
1 L = 10^{-3} m^3	1 Hz = 1 s^{-1}
1 Å = 10^{-10} m	1 tonne = 10^3 kg
1 eV = 1.602×10^{-19} J	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
10^{12}	tera	T

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

Standard Reduction Potentials, *E*°

Reaction	*E*° / V
$S_2O_8^{2-}$ + $2e^-$ → $2SO_4^{2-}$	+2.01
$Co^{3+}(aq)$ + e^- → $Co^{2+}(aq)$	+1.82
$Ce^{4+}(aq)$ + e^- → $Ce^{3+}(aq)$	+1.72
$MnO_4^-(aq)$ + $8H^+(aq)$ + $5e^-$ → $Mn^{2+}(aq)$ + $4H_2O$	+1.51
$Au^{3+}(aq)$ + $3e^-$ → $Au(s)$	+1.50
$Cl_2(g)$ + $2e^-$ → $2Cl^-(aq)$	+1.36
$O_2(g)$ + $4H^+(aq)$ + $4e^-$ → $2H_2O$	+1.23
Br_2 + $2e^-$ → $2Br^-(aq)$	+1.10
$MnO_2(s)$ + $4H^+(aq)$ + e^- → $Mn^{3+}(aq)$ + $2H_2O$	+0.96
$NO_3^-(aq)$ + $4H^+(aq)$ + $3e^-$ → $NO(g)$ + $2H_2O$	+0.96
$Pd^{2+}(aq)$ + $2e^-$ → $Pd(s)$	+0.92
$Ag^+(aq)$ + e^- → $Ag(s)$	+0.80
$Fe^{3+}(aq)$ + e^- → $Fe^{2+}(aq)$	+0.77
$I_2(aq)$ + $2e^-$ → $2I^-(aq)$	+0.62
$Cu^+(aq)$ + e^- → $Cu(s)$	+0.53
$Cu^{2+}(aq)$ + $2e^-$ → $Cu(s)$	+0.34
$Sn^{4+}(aq)$ + $2e^-$ → $Sn^{2+}(aq)$	+0.15
$2H^+(aq)$ + $2e^-$ → $H_2(g)$	0 (by definition)
$Fe^{3+}(aq)$ + $3e^-$ → $Fe(s)$	–0.04
$Pb^{2+}(aq)$ + $2e^-$ → $Pb(s)$	–0.13
$Sn^{2+}(aq)$ + $2e^-$ → $Sn(s)$	–0.14
$Ni^{2+}(aq)$ + $2e^-$ → $Ni(s)$	–0.24
$Co^{2+}(aq)$ + $2e^-$ → $Co(s)$	–0.28
$Fe^{2+}(aq)$ + $2e^-$ → $Fe(s)$	–0.44
$Cr^{3+}(aq)$ + $3e^-$ → $Cr(s)$	–0.74
$Zn^{2+}(aq)$ + $2e^-$ → $Zn(s)$	–0.76
$2H_2O$ + $2e^-$ → $H_2(g)$ + $2OH^-(aq)$	–0.83
$Cr^{2+}(aq)$ + $2e^-$ → $Cr(s)$	–0.89
$Al^{3+}(aq)$ + $3e^-$ → $Al(s)$	–1.68
$Mg^{2+}(aq)$ + $2e^-$ → $Mg(s)$	–2.36
$Na^+(aq)$ + e^- → $Na(s)$	–2.71
$Ca^{2+}(aq)$ + $2e^-$ → $Ca(s)$	–2.87
$Li^+(aq)$ + e^- → $Li(s)$	–3.04

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

Useful formulas

Quantum Chemistry $E = h\nu = hc/\lambda$ $\lambda = h/mv$ $E = -Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$ $T\lambda = 2.898 \times 10^6$ 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** $PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$ $E_k = ½mv^2$
Radioactivity $t_{½} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age = 8033 $\ln(A_0/A_t)$ years	**Kinetics** $t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Colligative Properties and 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 and Equilibrium** $\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $\Delta_{univ}S° = R \ln K$ $K_p = K_c (RT)^{\Delta n}$
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]							

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]