Topics in the November 2013 Exam Paper for CHEM1904

Click on the links for resources on each topic.

2013-N-2:

- Crystal Structures
- Metal Complexes

2013-N-3:

- Metal Complexes
- Coordination Chemistry

2013-N-4:

- Weak Acids and Bases
- Calculations Involving pK_a

2013-N-5:

- Solubility Equilibrium
- Metal Complexes

2013-N-6:

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

2013-N-7:

- Alkenes
- Stereochemistry

2013-N-8:

- Amines

2013-N-9:

- Alkenes
- Alcohols

2013-N-10:

- Alkenes
- Alcohols

2013-N-11:

- Organic Halogen Compounds
- Carboxylic Acids and Derivatives

2013-N-12:

- Aldehydes and Ketones

2223(a)

THE UNIVERSITY OF SYDNEY

CHEM1902 - CHEMISTRY 1B (ADVANCED)

and

CHEM1904 - CHEMISTRY 1B (SPECIAL STUDIES PROGRAM)

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2013 **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 19 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 13, 20, 22 and 24 are for rough working only.

Multiple choice section

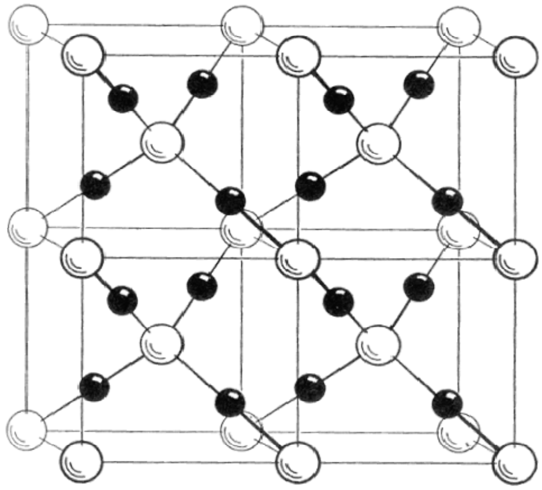
	Marks	
Pages	Max	Gained
2-9	29	

Short answer section

Page	Marks			Marker
	Max	Gained		
10	7			
11	8			
12	9			
14	6			
15	6			
16	8			
17	3			
18	6			
19	6			
21	7			
23	5			
Total	71			
Check Total				

Marks
7

- Copper oxide is used as a photovoltaic material in solar cells and it crystallizes with the structure shown below. The large white spheres represent the oxygen atoms and the smaller black spheres represent copper atoms.



How many unit cells are represented in the above diagram? Explain your answer.

From the solid-state structure shown above, determine the empirical formula for copper oxide.

What is the oxidation state of copper in this compound?

Use the box notation to predict whether the copper ions are paramagnetic.

Silver oxide is another Group 11 metal oxide and its solid-state structure is identical to that of copper oxide even though the ionic radius for the copper ion (118 pm) is smaller than that of the silver ion (139 pm). Account for this observation.

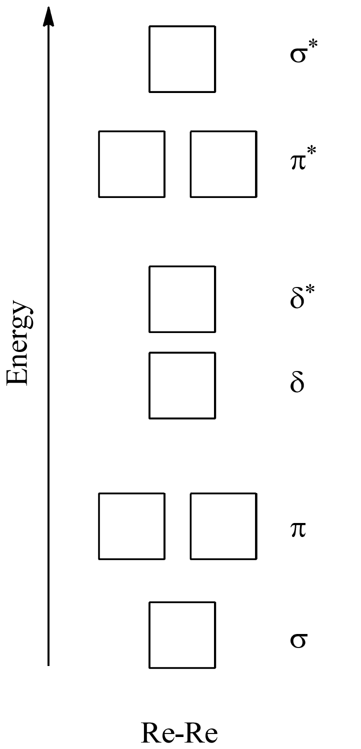
Marks
8

- $K_2[Re_2Cl_8]\cdot 2H_2O$ is an historically important example of a metal-metal bonded complex. Name the complex by using standard IUPAC nomenclature.

What is the oxidation state of Re in this complex?

How many *d*-electrons are on each Re atom in this complex?

$K_2[Re_2Cl_8]\cdot 2H_2O$ possesses an extremely short Re–Re bond (224 pm), much shorter than the bonding distance between Re atoms in Re metal (274 pm)! Propose a reasonable explanation for the very short Re–Re bond length in the complex by adding *d*-electrons into the (*partial*) MO scheme shown below. Determine the bond order for the metal-metal bond and draw a structure for the complex.



Reduction of the Re complex by **one** electron gives rise to a paramagnetic species in which the Re–Re distance increases significantly. Propose a reasonable hypothesis for the bond-lengthening phenomenon.

Marks
9

- Boric acid, $B(OH)_3$, is a weak acid (pK_a = 9.24) that is used as a mild antiseptic and eye wash. Unusually, the Lewis acidity of the compound accounts for its Brønsted acidity. By using an appropriate chemical equation, show how this compound acts as a Brønsted acid in aqueous solution.

Solution A consists of a 0.40 M aqueous solution of boric acid at 25 °C. Calculate the pH of Solution A.

pH =

At 25 °C, 1.00 L of Solution B consists of 101.8 g of $NaB(OH)_4$ dissolved in water. Calculate the pH of Solution B.

pH =

Using both Solutions A and B, calculate the volumes (mL) required to prepare a 1.0 L solution with a pH = 8.00.

Page Total:

Marks
6

- What is the solubility of $Cu(OH)_2$ in mol L^{-1}? K_{sp} ($Cu(OH)_2$) is 1.6×10^{-19} at 25 °C.

Answer:

The overall formation constant for $[Cu(NH_3)_4]^{2+}$ is 1.0×10^{13}. Write the equation for the reaction of Cu^{2+} ions with excess ammonia solution.

Calculate the value of the equilibrium constant for the following reaction.

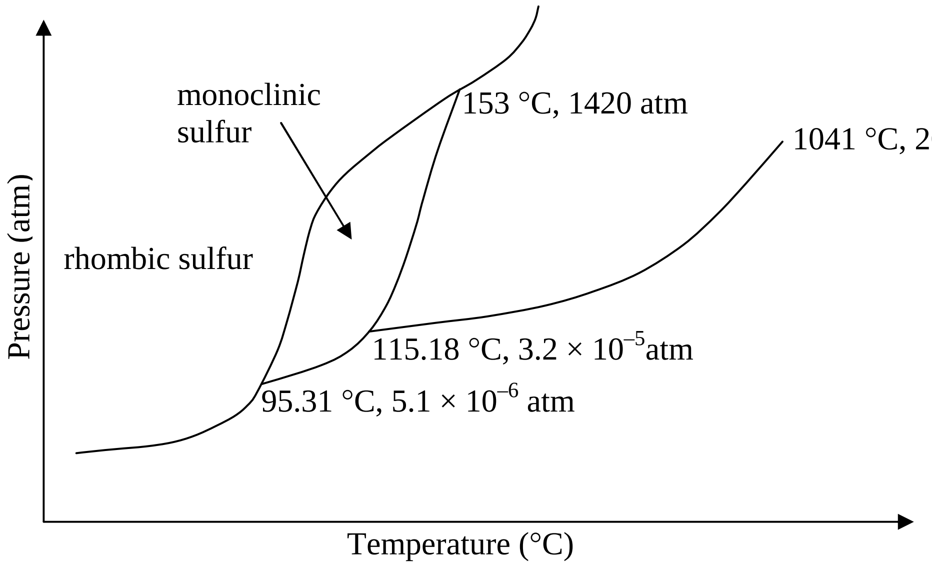
$$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$$

Answer:

Would you expect $Cu(OH)_2(s)$ to dissolve in 1 M NH_3 solution? Briefly explain your answer.

Marks
6

- The diagram below shows the phase diagram of sulfur. Note that 'rhombic' and 'monoclinic' refer to two different crystalline forms of the element.



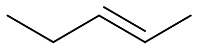
Determine the number of triple points for sulfur and indicate which species are present at each of the triple points.

Which crystalline form of sulfur is predicted to be more dense? Briefly explain your answer.

"Plastic" sulfur is a tough elastic substance that is formed when molten sulfur (m.p. = 115.2 °C) is poured into cold water. On standing, it slowly crystallizes. Predict which crystalline form is formed at room temperature and pressure. Also, explain why "plastic" sulfur is not shown on the above phase diagram.

Marks
8

- Addition of HBr to the isomer of 2-pentene shown below gives 3 isomeric products, **A**, **B** and **C**, in an approximate ratio of 50:25:25 respectively.

 $\xrightarrow{\text{HBr}}$ **A** + **B** + **C**

Draw the three products **A**, **B** and **C**.

A	**B**	**C**

Explain the ratio of products observed.

What is the isomeric relationship between **A** and **B**?

What is the isomeric relationship between **B** and **C**?

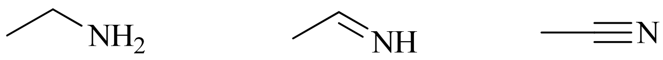
Assign the stereochemistry of the starting material isomer. Show your working.

Draw the other configurational isomer of 2-pentene and assign its stereochemistry.

What product(s) would you expect from the addition of HBr to this stereoisomer, and in what ratio?

Marks
3

- Consider the amine **D**, imine **E** and nitrile **F** shown below. Draw any lone pairs of electrons that are required to complete the structures.



D **E** **F**

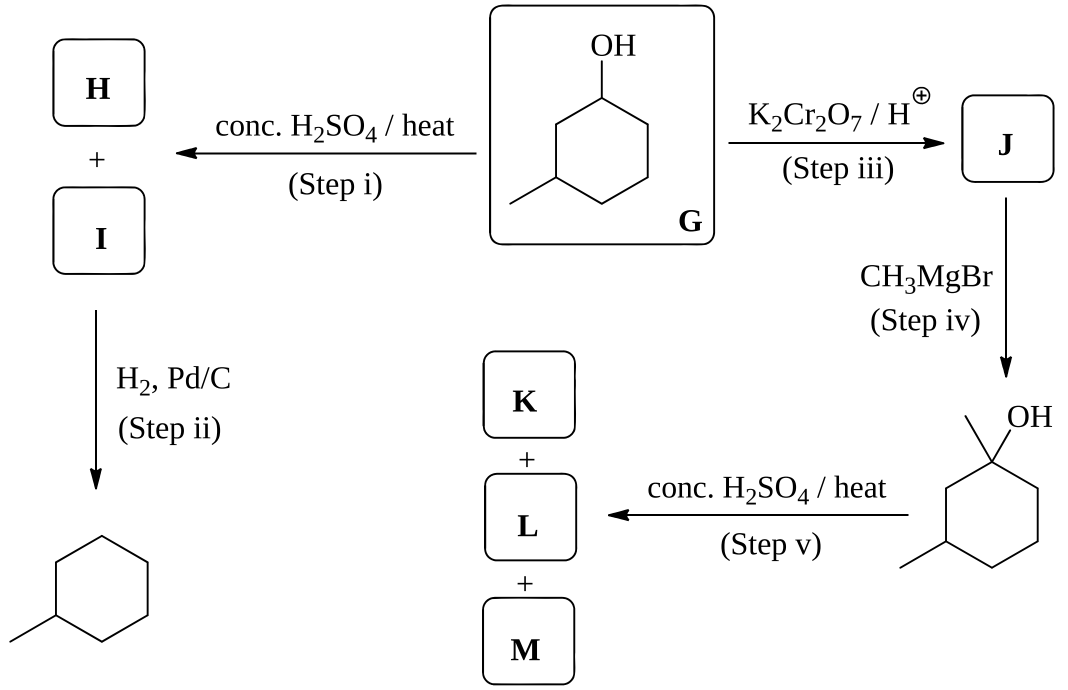
What is the hybridisation at *N* in compound **D**?	
What is the hybridisation at *N* in compound **E**?	
What is the hybridisation at *N* in compound **F**?	

Which of these compounds is the most basic? Why?

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
6

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



Suggest structures for compounds **H** – **M** in the reaction sequences above.

H	**I**	**J**
K	**L**	**M**

What approximate ratio **H** : **I** do you expect? Why?

What type of reaction is occurring in Step i?	
What type of reaction is occurring in Step ii?	
What type of reaction is occurring in Step iii?	
What type of reaction is occurring in Step iv?	

THIS QUESTION CONTINUES ON THE NEXT PAGE.

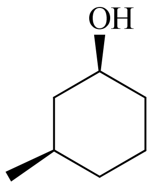
Page Total:

Marks
6

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

How many configurational stereoisomers of **G** are there?

Assign the absolute configuration of stereoisomer **G_1** below. Show your working.



G_1

Draw **G_2** (the enantiomer of **G_1**) and **G_3** (a diastereomer of **G_1**)

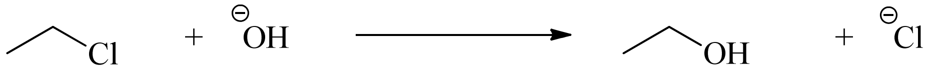
G_2 (enantiomer of **G_1**)	**G_3** (diastereomer of **G_1**)

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Page Total:

Marks
7

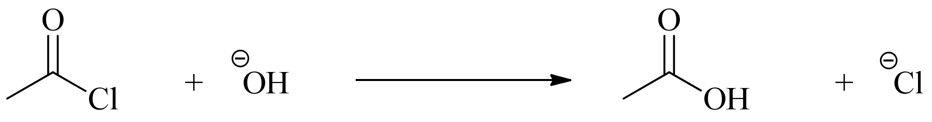
- The hydroxide anion can react with chloroethane via a mechanism that is abbreviated S_N2, as shown below. Add curly arrows to the reaction scheme to complete a mechanism for this reaction.



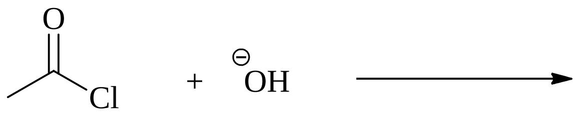
Explain what each part of the abbreviation S_N2 means.

S =	
N =	
2 =	

The hydroxide anion undergoes an apparently similar reaction with ethanoyl chloride:



Draw a mechanism (using curly arrows) for this reaction, thereby demonstrating how it is fundamentally different to the reaction of chloroethane above.

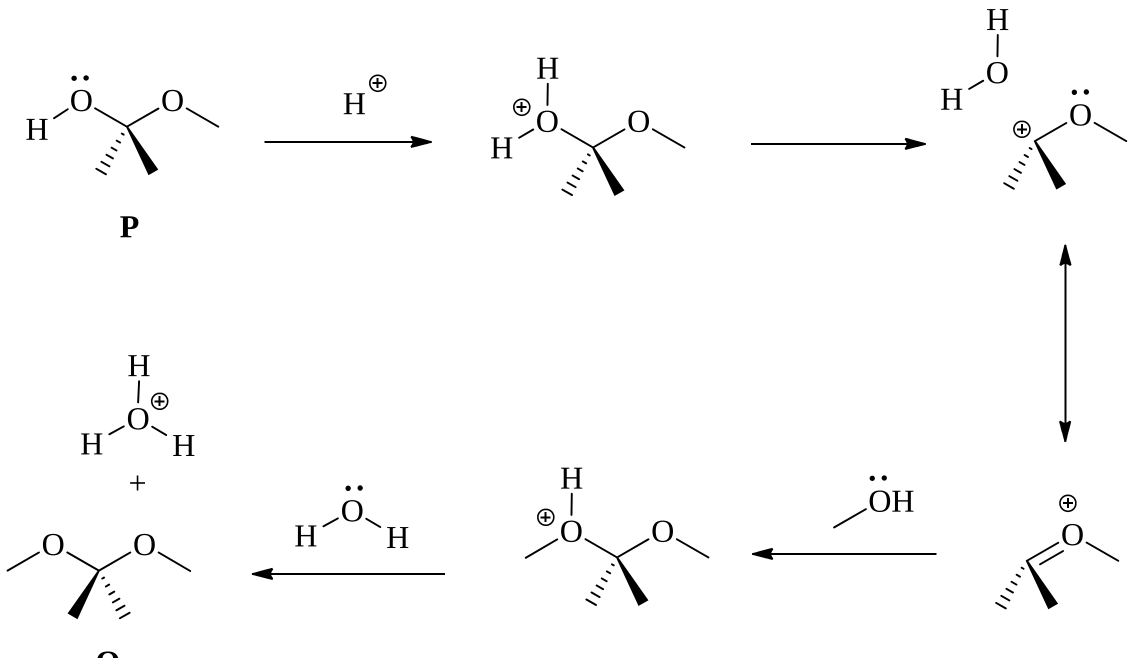


In each of these reactions, a full molecular orbital of the hydroxide anion (the HOMO) interacts with an empty molecular orbital of the organic halogen compound (the LUMO).

Which orbital is the LUMO in chloroethane?	
Which orbital is the LUMO in ethanoyl chloride?	

Marks
5

- A step-by-step mechanism for the formation of an acetal from a hemiacetal is outlined below. Demonstrate your understanding of reaction mechanisms by adding curly arrows to complete this mechanism.
  Note: you don't need to have seen this mechanism before to answer this question.



Overall, what type of reaction (**P** → **Q**) is shown here?

Identify one nucleophile and one electrophile in the scheme above.

nucleophile	electrophile

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
10^{12}	tera	T

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 $E = h\nu = hc/\lambda$ $\lambda = h/mv$ $E = -Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$ $T\lambda = 2.898 \times 10^6$ 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** $t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
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 = $4\pi r^2$ Volume of sphere = $^4/_3\ \pi r^3$	**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 $A = -\log\frac{I}{I_0}$ $A = \varepsilon cl$ $E = -A\frac{e^2}{4\pi\varepsilon_0 r}N_A$	**Colligative Properties & Solutions** $\Pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $c = kp$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$

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]		114 FLEROVIUM **Fl** [289]		116 LIVERMORIUM **Lv** [293]		

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]