Topics in the November 2012 Exam Paper for CHEM1904

Click on the links for resources on each topic.

2012-N-2:

- Crystal Structures

2012-N-3:

- Weak Acids and Bases
- Calculations Involving pK_a

2012-N-4:

- Metal Complexes
- Coordination Chemistry

2012-N-5:

- Kinetics

2012-N-6:

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

2012-N-7:

- Alkenes
- Alcohols
- Organic Halogen Compounds
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2012-N-8:

- Amines
- Carboxylic Acids and Derivatives

2012-N-9:

- Alkenes
- Stereochemistry

2012-N-10:

- Alcohols
- Organic Mechanisms and Molecular Orbitals

2012-N-11:

- Aromatic Compounds
- Organic Mechanisms and Molecular Orbitals

2012-N-12:

- Alcohols
- Organic Halogen Compounds

2012-N-13:

- Alcohols
- Carboxylic Acids and Derivatives
- Aromatic Compounds

2223(a)

THE UNIVERSITY OF SYDNEY

CHEM1902 - CHEMISTRY 1B (ADVANCED)

and

CHEM1904 - CHEMISTRY 1B (SPECIAL STUDIES PROGRAM)

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2012 **TIME ALLOWED: THREE HOURS**

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

FAMILY NAME		SID NUMBER	
OTHER NAMES		TABLE NUMBER	

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-8	29	

Short answer section

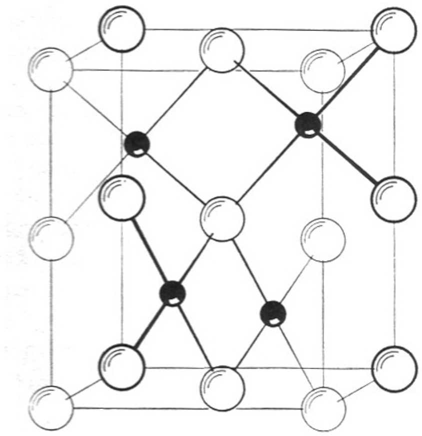
Page	Marks			Marker
	Max	Gained		
9	8			
11	9			
12	6			
13	7			
14	6			
15	6			
16	5			
19	7			
20	3			
21	4			
22	4			
23	6			
Total	71			
Check Total				

INSTRUCTIONS TO CANDIDATES

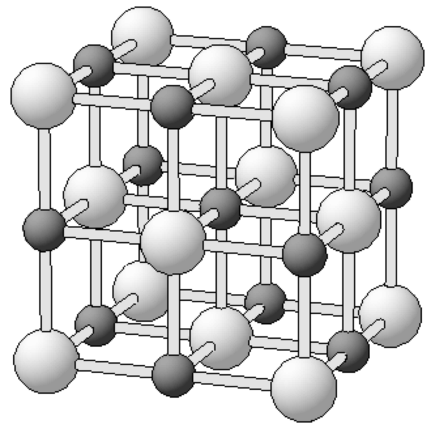
- All questions are to be attempted. There are 19 pages of examinable material.
- Complete the written section of the examination paper in **INK**.
- Read each question carefully. Report the appropriate answer and show all relevant working in the space provided.
- The total score for this paper is 100. 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 10, 17, 18 and 24 are for rough working only.

Marks
8

- PdO is used as a hydrogenation catalyst and it crystallizes with the tetragonal structure shown below. NiO has a variety of uses and crystallizes with the rocksalt structure. The large spheres represent the oxygen atoms and the smaller spheres represent palladium or nickel atoms.



palladium(II) oxide, PdO



nickel(II) oxide, NiO

Show the structure on the left is consistent with the formula PdO.

What is the coordination number about each metal atom?

Pd:	Ni:

The radius of the Pd^{2+} ion is 86 pm, that of the Ni^{2+} ion is 69 pm. Give a reason why the larger ion has a smaller coordination number.

Does either structure contain a close-packed arrangement of O^{2-} ions?

PdO: YES / NO	NiO: YES / NO

If YES, indicate the layers on the unit cell(s) above.

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 0.050 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 10.18 g of $NaB(OH)_4$ dissolved in water. Calculate the pH of Solution B.

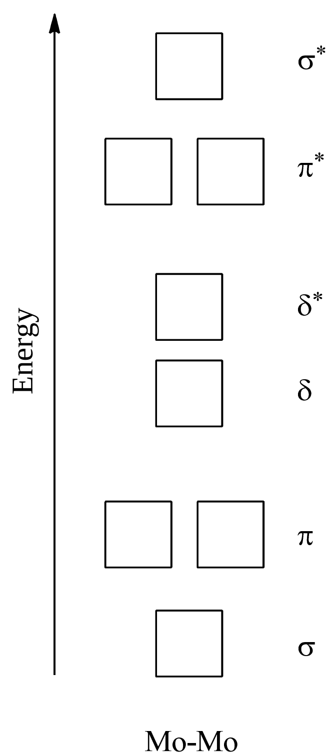
pH =

Using both Solutions A and B, calculate the volumes (mL) required to prepare a 1.0 L solution with a pH = 8.50.

Marks
6

- The red species $K_4[Mo_2Cl_8]$ is an historically important example of a metal-metal bonded complex. Use standard nomenclature to name the complex salt.

$K_4[Mo_2Cl_8]$ possesses an extremely short Mo–Mo bond (214 pm), much shorter than the bonding distance between Mo atoms in Mo metal (273 pm)! Propose a reasonable explanation for the very short Mo–Mo bond length in the complex by adding *d*-electrons into the (partial) MO scheme shown below. Draw a structure for the complex that is consistent with the completed MO scheme and your explanation.



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

Marks
7

- Four experiments were conducted to discover how the initial rate of consumption of BrO_3^- ions in the reaction below varied as the concentrations of the reactants were changed.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

Experiment	Initial concentration (mol L^{-1})			Initial rate
	BrO_3^-	Br^-	H^+	(mol L^{-1} s^{-1})
1	0.10	0.10	0.10	1.2×10^{-3}
2	0.20	0.10	0.10	2.4×10^{-3}
3	0.10	0.30	0.10	3.5×10^{-3}
4	0.20	0.10	0.15	5.4×10^{-3}

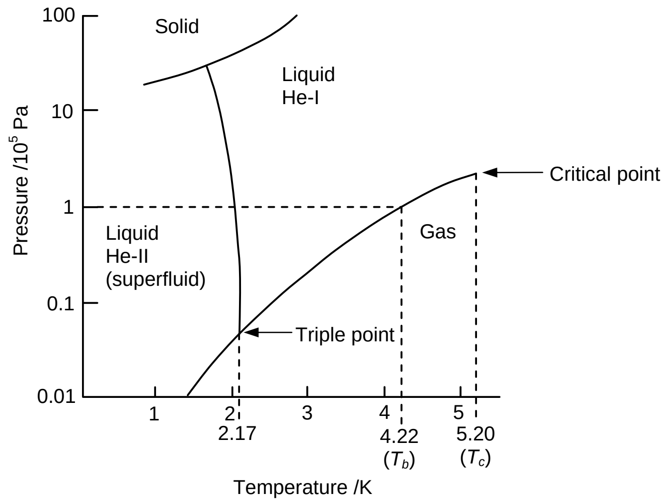
Use the experimental data in the table above to determine the order of the reaction with respect to *each* reactant.

What is the rate of formation of Br_2 when $[BrO_3^-] = [Br^-] = [H^+] = 0.10$ M?

Write the rate law for the reaction and determine the value of the rate constant, *k*.

Marks
6

- The diagram below shows a simplified phase diagram of helium.



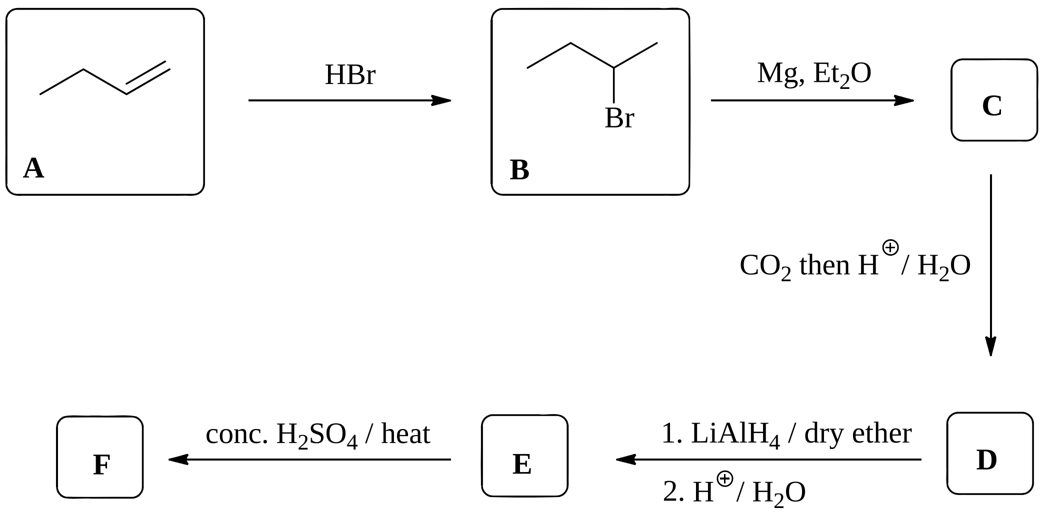
Describe two unusual properties of helium (other than the "superfluid" He-II phase) that are *not* shared by most substances.

Is it possible to liquefy helium above 5.20 K? Explain your answer.

Why is the liquefaction of He very difficult, even at low temperatures?

Marks
6

- Consider the following reaction sequence beginning with the alkene **A**.



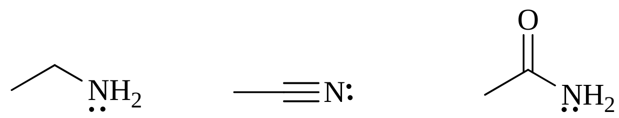
Suggest structures for compounds **C** – **F** in the reaction sequence above.

C	**D**
E	**F**

Describe the selectivity observed, and briefly explain the reasons for it, in the conversion of alkene **A** to compound **B**.

Marks
5

- Consider the three nitrogen-containing compounds **P**, **Q** and **R**.



P **Q** **R**

What is the hybridisation at *N* in compound **P**?

What is the hybridisation at *N* in compound **Q**?

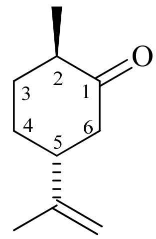
Use this information to decide which of **P** or **Q** is more basic. Explain your reasoning.

Show curly arrows and another structure to show how compound **R** is stabilised by resonance.

Which is more basic, compound **P** or compound **R**? Why?

Marks
7

- Consider the structure of dihydrocarvone shown below.

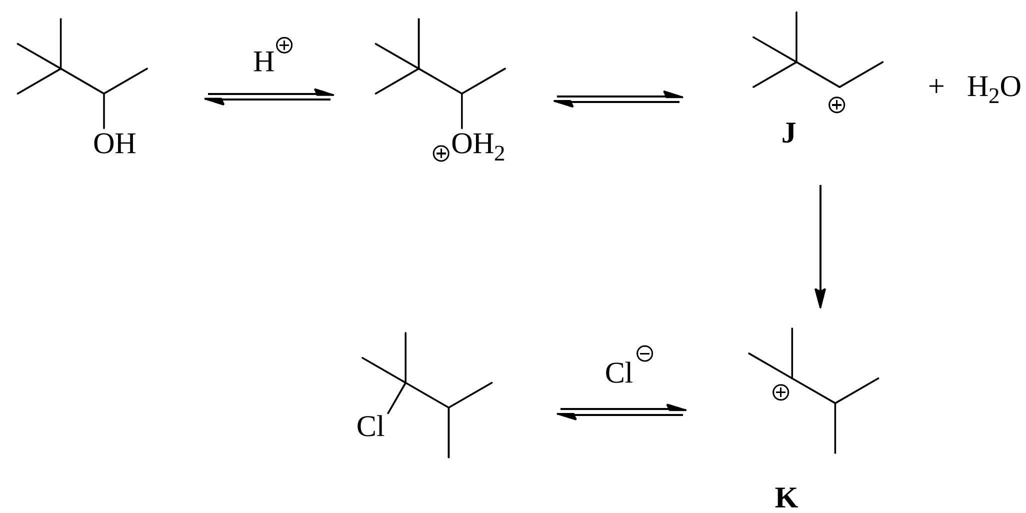


Assign the absolute configuration of dihydrocarvone. Explain your reasoning.

Draw all of the products that can result from the electrophilic addition of HBr to dihydrocarvone and explain the isomeric relationship between each pair.

Marks
3

- Apply your understanding of curly arrows to complete a mechanism for the following S_N reaction:

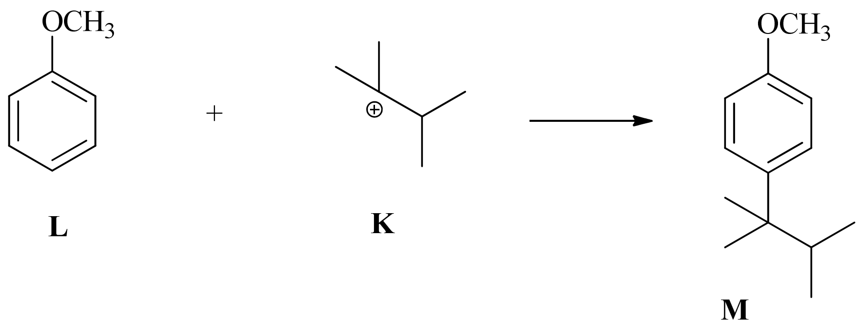


Why does the rearrangement step (**J** → **K**) occur?

THIS QUESTION CONTINUES ON THE NEXT PAGE.
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
4

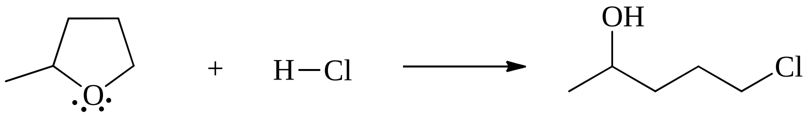
Reaction of **K** with anisole (methoxybenzene, **L**) gives **M** as the major product. Propose a mechanism for this transformation.



Briefly explain why the 4-substituted product **M** is formed preferentially.

Marks
4

- Propose a mechanism for the following reaction.



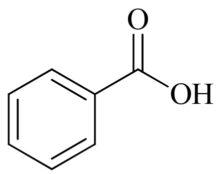
T

What isomeric product might also form in this reaction?

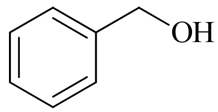
Why is **T** the major product?

Marks
6

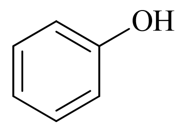
- Benzoic acid **H**, benzyl alcohol **I** and phenol **J** are shown below. The pK_a values of these three compounds are 15.2, 9.9 and 4.2, but not in that order.



H



I



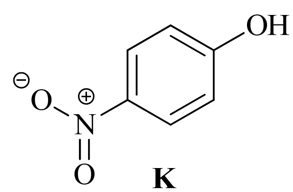
J

Assign the correct pK_a to each of these three compounds.

pK_a values:	**H** =	**I** =	**J** =

Draw resonance structures to explain your answer.

Would you expect 4-nitrophenol, **K**, to be more or less acidic than phenol, **J**? Explain your answer.



K

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

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

$\lambda = h/mv$

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

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

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

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

Electrochemistry

$\Delta G° = -nFE°$

$\text{Moles of } e^- = It/F$

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

$\quad = E° - (RT/nF) \times \ln Q$

$E° = (RT/nF) \times 2.303 \log K$

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

$E = E° - \frac{0.0592}{n} \log Q$ (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

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

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

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

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

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]						

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]