Topics in the November 2014 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2014-N-2:

- Crystal Structures

2014-N-3:

- Physical States and Phase Diagrams
- Crystal Structures

2014-N-4:

- Weak Acids and Bases
- Calculations Involving pK_a

2014-N-5:

- Weak Acids and Bases
- Calculations Involving pK_a

2014-N-6:

- Solubility Equilibrium

2014-N-7:

- Hydrolysis of Metal Ions
- Metals in Biology
- Coordination Chemistry

2014-N-8:

- Aldehydes and Ketones
- Alcohols
- Alkenes
- Alkynes
- Carboxylic Acids and Derivatives

2014-N-9:

- Stereochemistry
- Carboxylic Acids and Derivatives
- Amines

2014-N-10:

- Alcohols
- Stereochemistry

2014-N-11:

- Alkenes
- Alcohols
- Stereochemistry

2014-N-12:

- Synthetic Strategies

Confidential

THE UNIVERSITY OF SYDNEY

SEAT NUMBER: ………………………………………

STUDENT ID: …………………………………………

SURNAME: ……………………………………………

GIVEN NAMES: ……………………………………..

CHEM1102
Chemistry 1B

Final Examination
Semester 2, 2014

Time Allowed: Three hours + 10 minutes reading time

This examination paper consists of 24 pages

INSTRUCTIONS TO CANDIDATES

1. This is a closed book exam.
2. A simple calculator (programmable versions and PDA's not allowed) may be taken into the exam room.

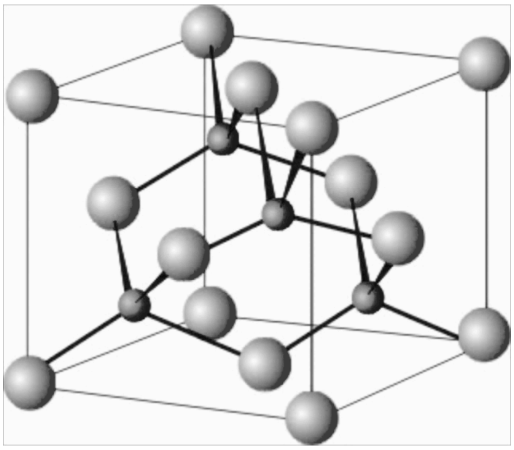
Make	Model

3. The total score for this paper is 100. The possible score per page is shown in the adjacent table.
4. The paper comprises 30 multiple choice questions and 11 pages of short answer questions. ANSWER ALL QUESTIONS.
5. Follow the instructions on page 2 to record your answers to the multiple choice questions. Use a dark lead pencil so that you can erase errors made on the computer sheet.
6. Answer all short answer questions in the spaces provided on this question paper. Credit may not be given where there is insufficient evidence of the working required to obtain the solution.
7. Take care to write legibly. Write your final answers in ink, not pencil.
8. 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.

	Marks			
Page(s)	Max	Gained		Marker
~~2-9~~	~~30~~			~~MCQ~~
10	5			
11	5			
12	6			
13	5			
15	9			
16	7			
17	8			
18	6			
20	7			
21	4			
23	8			
Total	100			
Check Total				

Marks
5

- The cubic form of boron nitride (borazon) is the second-hardest material after diamond and it crystallizes with the structure shown below. The large spheres represent the nitrogen atoms and the smaller spheres represent boron atoms.



From the unit-cell shown above, determine the empirical formula of boron nitride.

Answer:

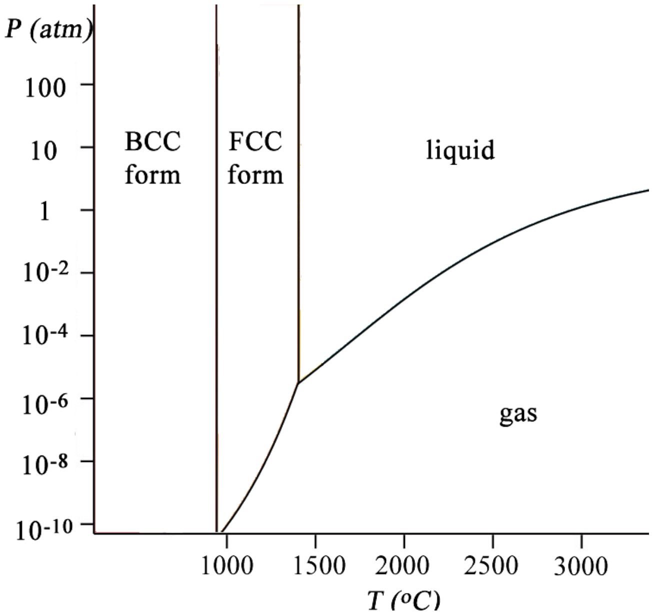
Determine the oxidation state of the boron atoms.

Answer:

The cubic form of boron nitride is more thermally stable in air than diamond. Provide a reasonable explanation for this observation.

Marks
5

- A simplified phase diagram for iron is shown below, with the solid part divided into the body-centred cubic (BCC) and face-centred cubic (FCC) phases.



Which form of iron is stable at room temperature and pressure?

If molten iron is cooled slowly to around 1200 °C and then cooled rapidly to room temperature, the FCC form is obtained. Draw arrows on the phase diagram to indicate this process and explain why it leads to the FCC form as a metastable phase.

The line dividing the BCC and FCC forms is almost, but not quite vertical. Predict which way this line slopes and explain your answer.

Marks
6

- Solution A consists of a 0.050 M aqueous solution of benzoic acid, C_6H_5COOH, at 25 °C. Calculate the pH of Solution A. The pK_a of benzoic acid is 4.20.

pH =

Other than water, what are the major species present in solution A?

Solution B consists of a 0.050 M aqueous solution of ammonia, NH_3, at 25 °C. Calculate the pH of Solution B. The pK_a of NH_4^+ is 9.24.

pH =

Other than water, what are the major species present in solution B?

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
5

Write the equation for the reaction that occurs when benzoic acid reacts with ammonia?

Write the expression for the equilibrium constant for the reaction of benzoic acid with ammonia?

What is the value of the equilibrium constant for the reaction of benzoic acid with ammonia?

Answer:

What are the major species in the solution that results from dissolving equimolar amounts of benzoic acid and ammonia in water?

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Page Total:

Marks
9

- The salt calcium oxalate, $CaC_2O_4{\cdot}H_2O$, is sparingly soluble. Write down the chemical equation for its dissolution in water and the expression for K_{sp}.

What is the molar solubility of calcium oxalate? $K_{sp} = 2.3 \times 10^{-9}$

Answer:

If additional calcium oxalate is added to a saturated solution, what is the effect on $[Ca^{2+}(aq)]$?

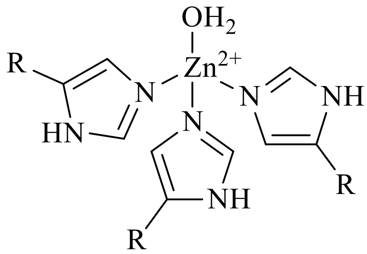
Following blood donation, a solution of sodium oxalate is added to remove $Ca^{2+}(aq)$ ions which cause the blood to clot. The concentration of $Ca^{2+}(aq)$ ions in blood is 9.7×10^{-5} g mL^{-1}. If 100.0 mL of 0.1550 M $Na_2C_2O_4$ is added to 100.0 mL of blood, what will be the concentration (in mol L^{-1}) of Ca^{2+} ions remaining in the blood?

Answer:

Page Total:

Marks
7

- The structure below represents the active site in carbonic anhydrase, which features a Zn^{2+} ion bonded to 3 histidine residues and a water molecule.



The pK_a of uncoordinated water is 15.7, but the pK_a of the water ligand in carbonic anhydrase is around 7. Suggest an explanation for this large change.

When studying zinc-containing metalloenzymes, chemists often replace Zn^{2+} with Co^{2+}. Using the box notation to represent atomic orbitals, work out how many unpaired electrons are present in the Zn^{2+} and Co^{2+} ions.

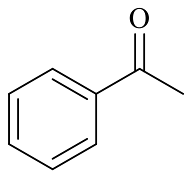
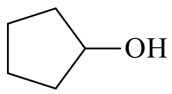
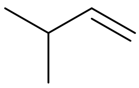
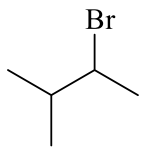
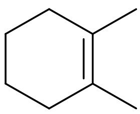
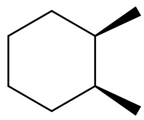
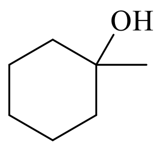
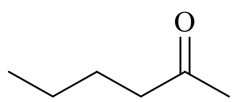
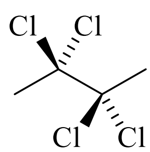
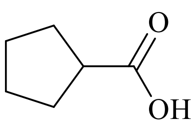
Suggest why it is useful to replace Zn^{2+} with Co^{2+} when studying the nature of the active site in carbonic anhydrase.

Suggest two differences in the chemistry of Zn^{2+} and Co^{2+} ions that may affect the reactivity of the cobalt-containing enzyme.

Page Total:

Marks
8

- Complete the following table.

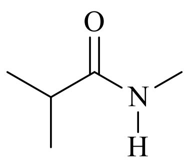
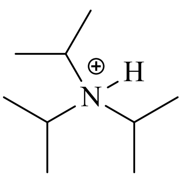
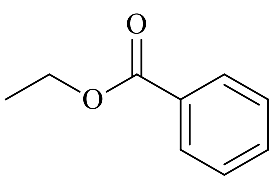
STARTING MATERIAL	REAGENTS/CONDITIONS	THE MAJOR ORGANIC PRODUCT(S)
	1. $NaBH_4$ 2. $H^{\oplus}$ / H_2O	
	hot concentrated H_2SO_4	
		
		
	dilute aqueous H_2SO_4	
	$Cr_2O_7^{2\ominus}$ / $H^{\oplus}$	
	2 equivalents of Cl_2	
	$SOCl_2$	

Marks

- Draw the structure of (*S*)-pent-4-en-2-ol. **3**

When (*S*)-pent-4-en-2-ol reacts with bromine, Br_2, two stereoisomers are formed. Draw the structure of both products.

- Draw the structure of the organic product(s) formed when each of the following compounds is treated with 4 M sodium hydroxide. The first reaction requires heating. **3**

Compound	Organic products
	
	
	

Page Total:

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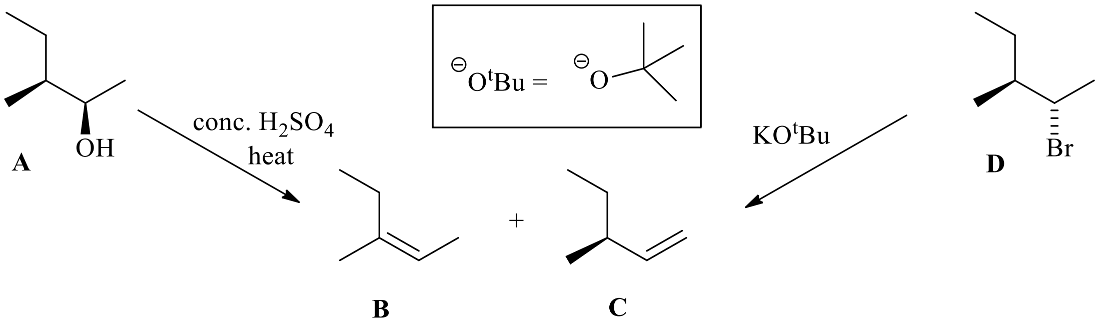
7

- The elimination of H_2O from alcohol **A** can form the isomeric alkenes **B** and **C**. Elimination of HBr from the alkyl halide **D** can generate the same two alkenes.



Assign the absolute configuration of alcohol **A**. Show your working.

Name compound **B** fully.

A diastereoisomer of **B** is also formed in these reactions. Draw the enantiomer of **A** and the diastereoisomer of **B**.

enantiomer of **A**	diastereoisomer of **B**

Propose a mechanism for the formation of **B** from **A** under the conditions shown. Use curly arrows and draw the structures of any intermediates.

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Page Total:

Marks
4

Explain why compound **C** is the minor product of this reaction.

Propose a mechanism for the formation of **C** from **D** under the conditions shown. Use curly arrows and draw the structures of any intermediates.

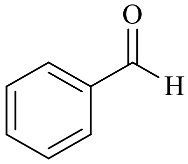
Compound **C** is the major product formed from **D** under these conditions. What would be the major product if the enantiomer of **D** were exposed to the same reaction conditions?

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
8

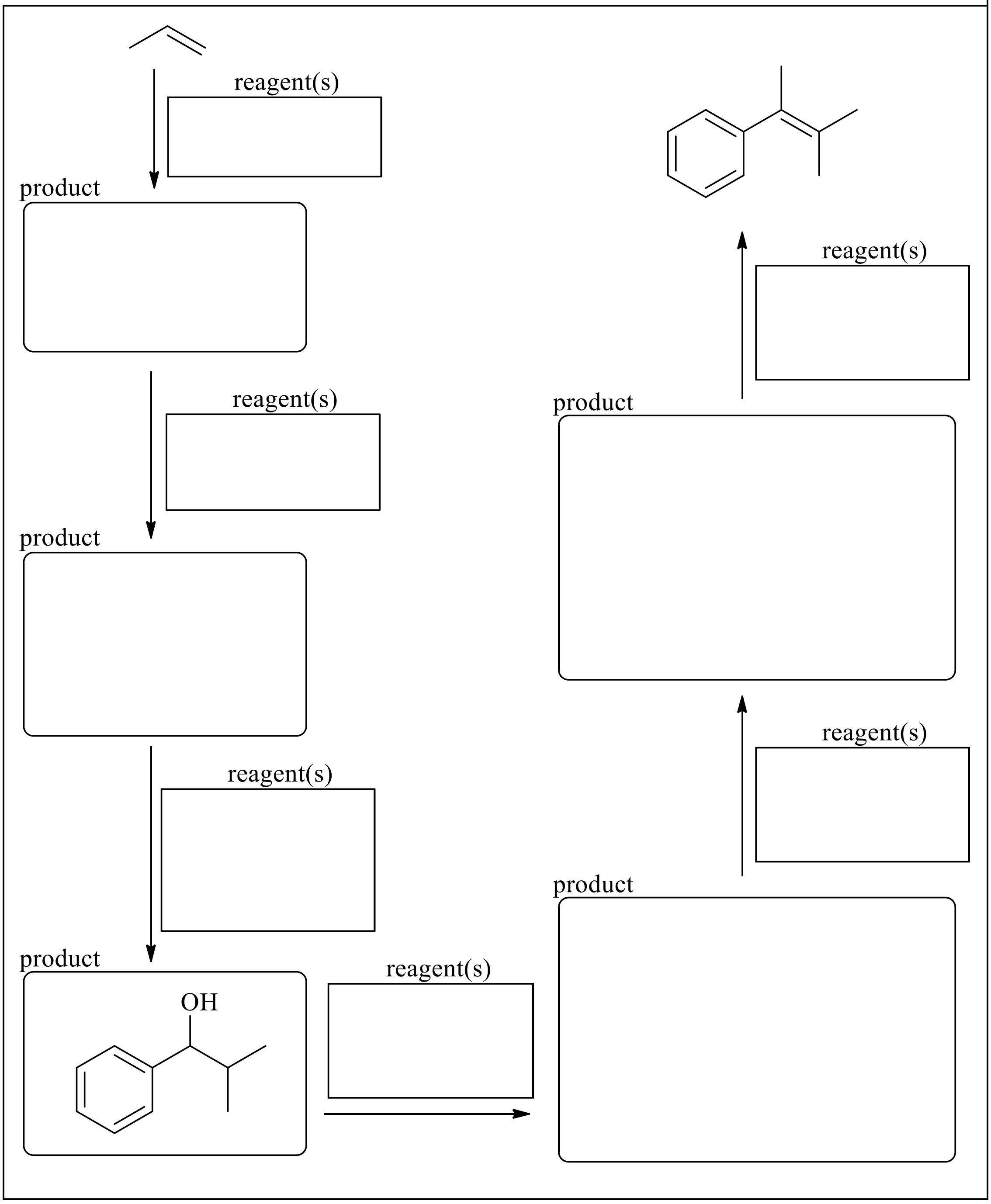
- Propene can be converted into 1,2-dimethyl-1-phenylpropene using a sequence of 6 reactions. Demonstrate your knowledge of Grignard reactions by suggesting a plausible sequence. Make sure you draw the correct structure for each intemediate product and clearly indicate the reagent(s) required for each reaction. The following list of suggested reagents is sufficient to accomplish all necessary reactions, but you may use other reagents if you wish. One of the intermediates is shown for you.

Suggested reagents:



HBr dilute HCl $K_2Cr_2O_7$ / $H^{\oplus}$

conc. HCl Mg CH_3MgBr



THIS PAGE IS FOR ROUGH WORKING ONLY.

Page Total:

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

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

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	
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36	
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23	(+0.82 at pH = 7)
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	+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	
$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$	+0.62	
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+0.53	
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34	
$BiO^+(aq) + 2H^+(aq) + 3e^- \rightarrow Bi(s) + H_2O$	+0.32	
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+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	(–0.41 at pH = 7)
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	–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	

Useful formulas

Thermodynamics & Equilibrium

$\Delta U = q + w = q - p\Delta V$

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

$\Delta_{univ}S° = R \ln K$

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

Electrochemistry

$\Delta G° = -nFE°$

Moles of $e^- = It/F$

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

$\quad = E° - (RT/nF) \times \ln Q$

$E° = (RT/nF) \times 2.303 \log K$

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

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

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 $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$\ln x = 2.303 \log x$

Area of circle = πr^2

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

Volume of sphere = $^4/_3\, \pi r^3$

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

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]