THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

November 8th, 2006 Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** ON ***BOTH*** **YOUR ANSWER BOOKLET** AND **COMPUTER ANSWER SHEET**.

The examination consists of Parts 1 - 8, each of which should be attempted. Note that some parts provide you with a choice of questions, *i.e*. answer 4 out of 5. These will be graded in numerical order until the required number have been graded, regardless of whether they are right or wrong. Parts 1 - 5 will be computer graded, and only Parts 6, 7, and 8 are to be answered in the booklet provided. A periodic table with atomic numbers and atomic weights is located inside the front cover.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 40 which are to be answered on your computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a pencil only and ***not ink***. In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out ***both*** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***.

Absolutely no other electronic devices are allowed.

16% **PART 1 RELATIVE PROPERTIES**

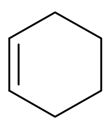
ANSWER ANY EIGHT (8) of questions 1-10 (2 marks per question)

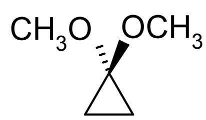
Arrange the items in **questions 1-10** in **DECREASING ORDER** (*i.e*. greatest, most etc. **first**) with respect to the indicated property.

Use the following code to indicate your answers.

A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

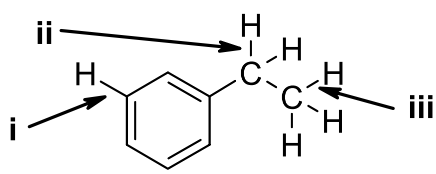
1. The number of types of hydrogen in each of the following molecules:


i

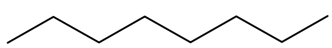

ii

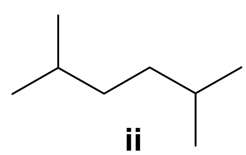
$CH_3CH_2CH_2CH_2CH_2I$
iii

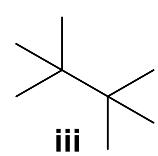
2. The relative strength of the CH bonds indicated in each of the following:



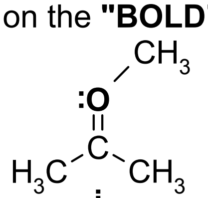
3. The relative heats of combustion, ΔH_C^o, of the following molecules (*least* exothermic to *most* exothermic)


i


ii


iii

4. The formal charge on the **"BOLD"** atoms in each of the following molecules:


i

CH_3**CH_2**Li
ii

:Ö: (with lone pairs above and below)
iii

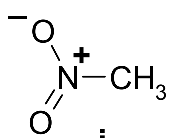
5. The relative energies of the following molecular orbitals in ethene **:**

C H σ	C C π	C C π^*
i	**ii**	**iii**

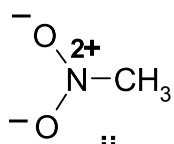
Use the following code to indicate your answers.

A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

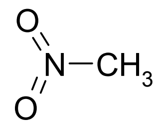
6. The relative importance of the following resonance contributors :



i



ii



iii

7. The relative energies of the most stable conformations of the following isomeric cyclohexanes:

i cis-1-t-butyl-4-methylcyclohexane

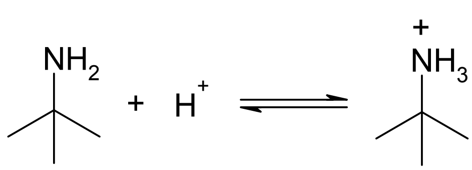
ii trans-1-t-butyl-4-methylcyclohexane

iii 1,1,2,3,3-pentamethylcyclohexane

8. The relative basicity of the following:

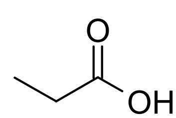
$CH_3CH_2O^-$	$^-NH_2$	$CH_3C{\equiv}CCH_2CH_2^-$
i	**ii**	**iii**

9. The relative amount of the conjugate acid of t-butyl amine formed by the reaction of t-butyl amine with1 mole equivalent of each of the following:



CH_3OH **i**

$HC{\equiv}CH$ **ii**

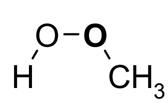


iii

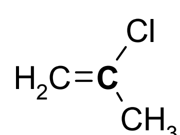
10. Oxidation state of the "**BOLD**" atoms in each of the following molecules:

$CH_3O\mathbf{C}H_2OCH_3$

i



ii



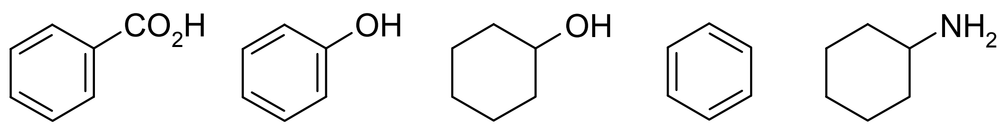
iii

9% **PART 2: LABORATORY**

ANSWER ALL of the questions 11-16 (1.5 marks per question).

For questions 11-16, select the answer from those provided. **If in some cases more than one answer may be correct, then all correct answers must be selected for full marks.**

11. Which of the following would dissolve in 5% NaOH ?



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

12. If the measured melting point of a pure sample here in Calgary is 200°C, then which of the following is closest to the value observed at sea level ?

A 190 °C **B** 195 °C **C** 200 °C **D** 205 °C **E** 210 °C

13. If reaction of 0.92 g of toluene (IUPAC = methylbenzene) with 1.00 g of bromine gave 1.02 g of (bromomethyl)benzene, then what is the % yield of (bromomethyl)benzene ?

A 95 % **B** 85 % **C** 76 % **D** 66 % **E** 59 %

14. How many types of hydrogen and carbon are there in 4-methylphenol ?

A 3H, 4C **B** 3H, 5C **C** 4H, 4C

D 4H, 5C **E** 5H, 4C **AB** 5H, 5C

15. Which of the following experimental methods would be **best** suited for the purification of a mixture of crystals from a solution ?

A thin layer chromatography **B** vacuum filtration **C** simple distillation

D fractional distillation **E** recrystallisation **AB** separatory funnel

16. Which of the following statements from the chromotography experiment is / are true ?

A R_f = distance traveled by sample / length of the plate

B More polar materials have smaller Rf values

C If two spots have the same Rf, then they *must* be identical samples

D If a sample shows up as two spots, Rf =0.75 and 0.33, then it's a pure sample

E Increasing the solvent polarity would increase the Rf values

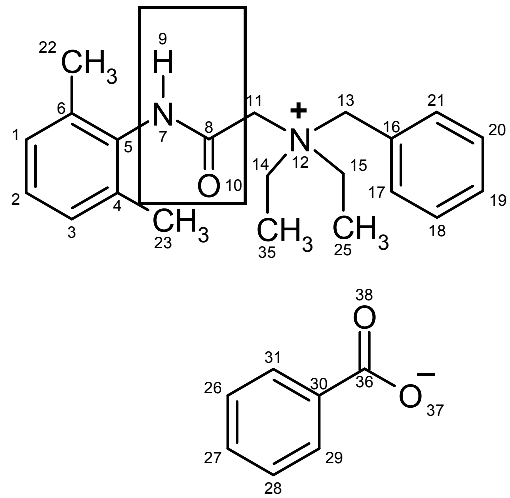
14% **PART 3: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 17-24 (2 marks per question)

BITREX (right) is a salt of two organic molecules that acts as a “bittering agent”: It is added to dangerous household chemicals to give them a nasty taste.

Questions 17-22 refer to the structure of BITREX - select the answer(s) from the options provided.

In some cases more than one answer may be correct and for full marks all correct answers must be selected.



17. What are the oxidation states of **N7** and **N12** ?

A. -3,-3 **B**. +3,+3 **C**. -1,-1 **D**. -3, +1 **E**. -3,-1

18. What is the name of the functional group in the rectangular box ?

A. amide **B**. amine **C**. aniline **D**. nitrile **E**. nitro

19. What type of amine is present in BITREX ?

A. primary **B**. secondary **C**. tertiary **D**. quaternary **E**. anionic

20. What is the total index of hydrogen deficiency (IHD) for the BITREX salt ?

A. 7 **B**. 9 **C**. 10 **D**. 13 **E**. 14

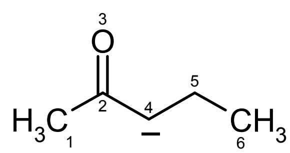
21. In BITREX, what are the hybridisations of **N7**, **N12** and **O10** respectively?

A. sp^3, sp^2, sp^2 **B.** sp^2, sp^3, sp^2 **C.** sp^3, sp^2, sp^3
D. sp^3, sp^3, sp^2 **E.** sp^2, sp^2, sp^3 **AB.** sp^2, sp^2, sp^2

22. In BITREX, which of the following atoms is the most basic ?

A. N7 **B. O10** **C. C11** **D. N12** **E. O37**

Questions 23-24 refer to the following CARBANION of 2-pentanone:



23. In the CARBANION of 2-pentanone, what are the hybridisations of **C1**, **C2** and **C4**, respectively ?

A. sp^3, sp^2, sp^2 **B.** sp^2, sp^3, sp^2 **C.** sp^3, sp^2, sp^3
D. sp^3, sp^3, sp^2 **E.** sp^2, sp^2, sp^3 **AB.** sp^2, sp^2, sp^2

24. In the CARBANION of 2-pentanone, what are the oxidation states of **C1**, **C2** and **C4**, respectively ?

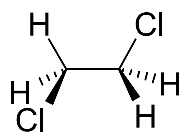
A. -3,+2, -2 **B**. +3, -2, -1 **C**. +3, -2, +1 **D**. -3, +2, -1 **E**. -3, +2, 0

12% PART 4: CONFORMATIONAL ANALYSIS

ANSWER ALL of the questions 25-32 (1.5 marks per question).

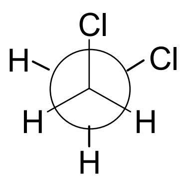
For each of the **questions 25-32** select the answer(s) from those provided. In some cases more than one answer may be correct in which case all correct answers should be selected for full marks.

25. What is the torsional angle between the two bonds involving chlorine atoms in molecule shown below?



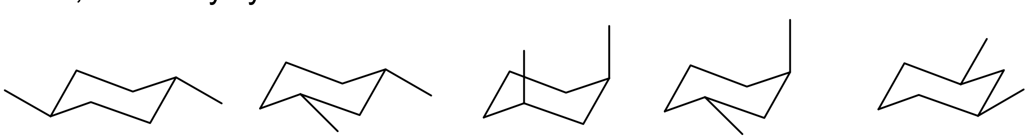
A 0^o
B 60^o
C 90^o
D 109.5^o
E 120^o
AB 180^o

26. What is the H-C-Cl bond angle in the molecule that is represented by the Newman projection shown below ?



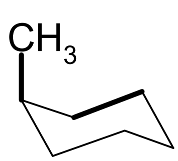
A 0^o
B 60^o
C 90^o
D 109.5^o
E 120^o
AB 180^o

27. Which of the following diagrams represents the most stable conformation of trans-1,3-dimethylcyclohexane?



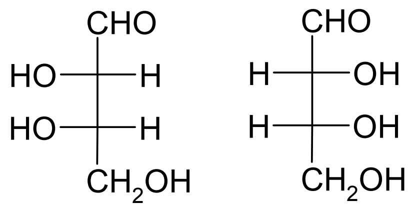
A **B** **C** **D** **E**

28. Which of the following terms **best** describes the relative postion of the two highlighted bonds in the conformation of methylcyclohexane shown below?



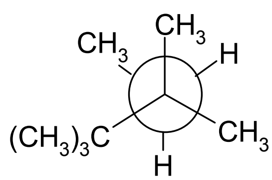
A eclipsed
B staggered
C anti
D gauche
E syn
AB trans

29. Which of the following terms **best** describes the relationship between the two molecules shown below ?

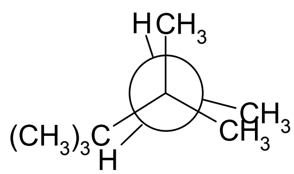


A constitutional isomers
B configurational isomers
C conformational isomers
D enantiomers
E diastereomers
AB they are the same molecule

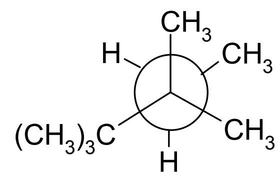
30. Which of the following conformations of 2,2,3,3-tetramethylpentane is the least stable?



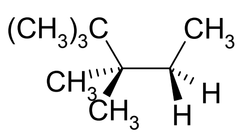
A



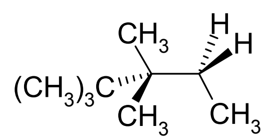
B



C

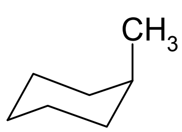


D

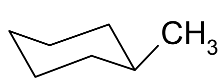


E

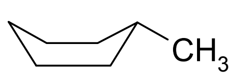
31. Which of the following conformations of methylcyclohexane is the **least** stable?



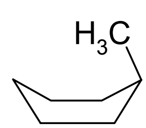
A



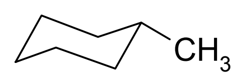
B



C

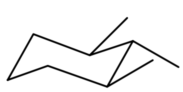


D

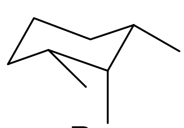


E

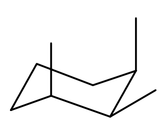
32. Which of the following structures is the most stable?



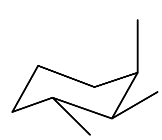
A



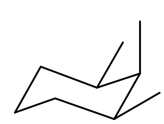
B



C



D



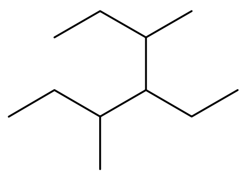
E

14% **PART 5: NOMENCLATURE**

ANSWER ANY SEVEN (7) of the questions 33-40 (2 marks per question).

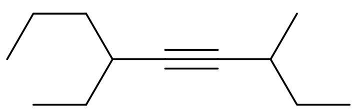
For each of questions 31 to 34, select the correct name for the compound shown:

33



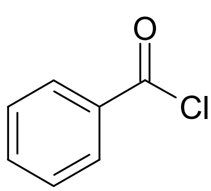
A. 2,3,4-triethylpentane
B. 3-(2-butyl)-4-methylhexane
C. 3-methyl-4-(2-butyl)hexane
D. 3,5-dimethyl-4-ethylheptane
E. 4-ethyl-3,5-dimethylheptane

34



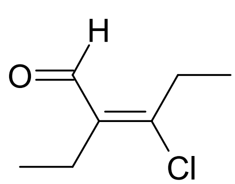
A. (E)-6-ethyl-3-methylnon-4-yne
B. 4-ethyl-7-methylnon-5-yne
C. 6-ethyl-3-methylnon-4-yne
D. (2-butyl)(3-hexyl)acetylene
E. 2,5-diethyloct-3-yne

35



A. Benzoyl chloride
B. Chloro phenyl ketone
C. Chloro benzaldehyde
D. Chloro phenyl ether
E. Chlorobenzaldehyde

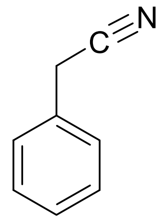
36



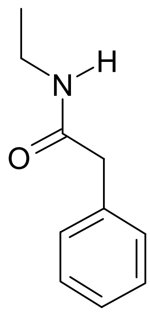
A. (E)-3-chloro-2-methylpent-2-enol
B. (Z)-3-chloro-4-ethylpent-3-enal
C. (E)-3-chloro-2-ethylpent-2-enone
D. (Z)-3-chloro-2-ethylpent-2-enal
E. (E)-3-chloro-2-ethylpent-2-enal

For each of questions 37 to 40, select the correct structure for the name provided:

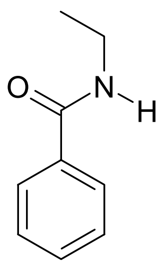
37. N-benzylethanamide



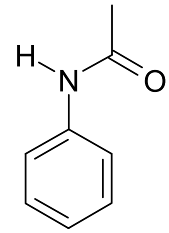
A



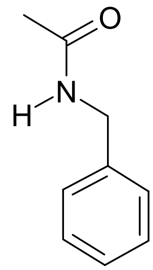
B



C

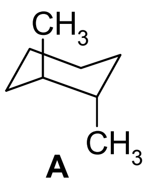


D

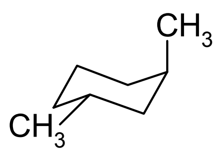


E

38. *cis* 1,2-dimethylcyclohexane :



A



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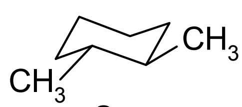

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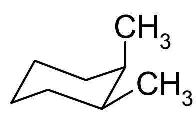
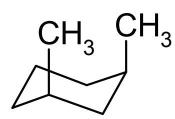
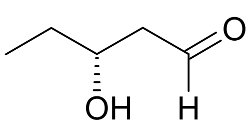


D

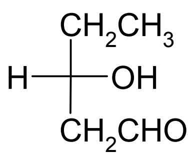


E

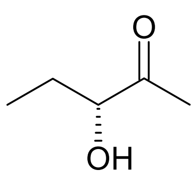
39. (S)-3-hydroxypentanal :



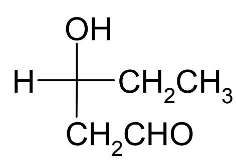
A.



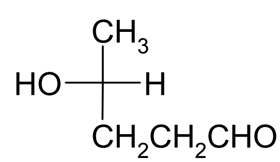
B.



C.

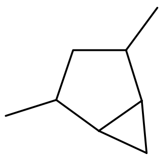


D.

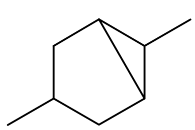


E.

40. 2,4-dimethylbicyclo[3.1.0]hexane:



A



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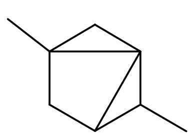
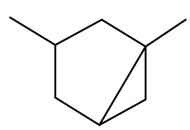
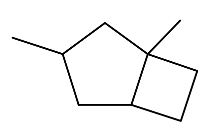


C



D



E

11% **PART 6: STRUCTURE DETERMINATION**:

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

***ALL* THE QUESTIONS IN THIS SECTION SHOULD BE ANSWERED BASED ON THE FOLLOWING DATA:**

Analysis was performed on a sample taken from an unlabelled drum found at a crash site involving a truck carrying the drum. The sample was determined to be a single compound by gas chromatography and elemental analysis indicated that the sample contained 66.61% C and 11.19% H by weight.

(a) Determine the molecular formula (which equals the empirical formula)

(b) What is the IHD of this molecular formula ? (IHD = index of hydrogen deficiency)

(c) Draw a structure of this molecular formula that contains only two types of carbon

(d) Draw a pair of enantiomers of this molecular formula – assign the configurations at the chirality centers.

(e) Draw a diastereomer of the enantiomers in part **(d)**

(f) Draw an aldehyde with this molecular formula containing three types of carbon

12% **PART 7: MECHANISM**

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

(a) Draw a mechanistic sequence using double headed (*i.e.* electron pair) curly arrows that represents the ***single reaction sequence*** described verbally by the following points in which butane-1-thiol is alkylated using 1-bromobutane in the presence of sodium hydroxide base, to yield dibutyl sulfide (a thioether).

Step 1. Deprotonation of butane-1-thiol by the hydroxide ion to create the conjugate base of butane-1-thiol.

Step 2. Attack on the electrophilic carbon of 1-bromobutane by the conjugate base of butane-1-thiol (a nucleophile) to yield dibutyl sulfide.

(b) NAME a different base (i.e. not hydroxide) that could be used to deprotonate butane-1-thiol.

(c) Based on the above sequence, what reagents could be used to synthesize phenyl methyl sulfide?

(d) In the synthesis of dibutyl ether (the oxygen analogue of dibutyl sulfide) using butan-1-ol and 1-bromobutane, explain why sodium hydroxide is a poor choice of base ?

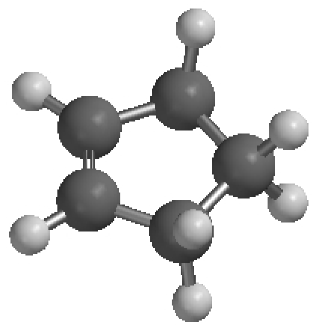
(e) Is a thiol more or less acidic than an alcohol ? Briefly explain why.

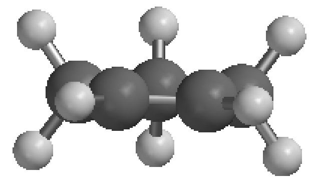
(f) What type of reaction is the overall process ?

12% **PART 8: THERMODYNAMICS**

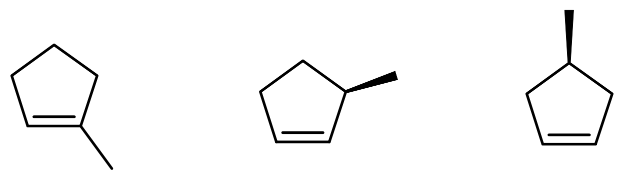
Write your answer in the booklet provided. Show your working as PARTIAL marks will be given.

3D representations of cyclopentene are shown below. The diagram on the right has the alkene unit directly towards you.





The structures of three methyl derivatives of cyclopentene are shown below:



i ii iii

(a) Name the molecules **i**, **ii**, **iii**

(b) What type of isomers are these three molecules ?

(c) Calculate ΔH_f^o, for isomer **i,** given that the following heats of combustion:

ΔH_C^o, C (graphite) = -93.9 kcal/mol
ΔH_C^o H_2 (gas) = -68.4 kcal/mol
ΔH_C^o for isomer **i** = -904.1 kcal/mol

(d) Given that the heats of formation, ΔH_f^o of the other two isomers are +2.1 kcal/mol and +3.5 kcal/mol:
(i) match all three isomers to their corresponding ΔH_f^o values
(ii) identify the most and least stable isomer

(e) Use the principles of conformational analysis to explain your choices in **(d) part ii**

(f) A fourth isomer of the methylcyclopentene structures above was found to have a ΔH_f^o of +2.1 kcal/mol, suggest a structure for this isomer.

** THE END **

IRH / AC / Nov 2006

PERIODIC TABLE

1 1A	2 2A	3	4	5	6	7	8	9	10	11	12	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57* **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)