2023 FALL Semester Mid-term Examination

For General Chemistry II

Date: October 16(Mon), Time Limit: 13:00 ~ 15:00

Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

Professor Name	Class	Student I.D. Number	Name

Problem	points	Problem	points	TOTAL pts
1	/10	**6**	/10	
2	/12	**7**	/6	
3	/12	**8**	/8	
4	/6	**9**	/12	**/100**
5	/14	**10**	/10	

** This paper consists of 20 sheets with 10 problems (***page 18 - 19***: Equation, constants & periodic table, ***page 20***: claim form). Please check all page numbers before taking the exam. Write down your work and answers in the Answer sheet. Please write down the unit of your answer when applicable. You will get 30% deduction for a missing unit.

NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.
(채점 답안지 분배 및 이의신청 일정)

1. Period, Location and Procedure

0 Return and Claim Period: **October 23 (Monday, 19:00 ~ 21:00, 2 hrs)**
The claim is permitted only on this period. Keep that in mind!
0 Location: Each designated room of Creative Learning Bldg. (E11)

Class	Room(E11)
A	401
B	402
C	403

0 Procedure

Rule 1: Students cannot bring their writing tools into the rooms (Use a pen only provided by TA)

Rule 2: With or without claim, you must submit the paper back to TA. (Do not go out of the room with it)

If you have any claims on it, write them on the claim form and attach it to the top of the exam paper with a stapler. Give them to your TA.

WARNING!!

If you deliberately alter any original answers or insert something on your marked paper to achieve a better grade, you will get a F grade for this course. Or if you don't keep the rules above, we will regard it as a kind of cheating and give you 0 point. So please don't cheat.

2. Final Confirmation

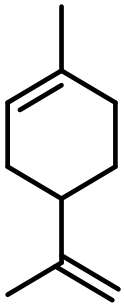
1) Period: ***October 26(Thu.) ~ 27(Fri.)***

2) Procedure: During this period, you can check the final score of the examination *on the website* again.
(No additional corrections. If there is no change in your score after reasoning, the claims were not accepted.)

***** For further information, please visit the General Chemistry website at www.gencheminkaist.pe.kr***

1. (total 10 pts)

Limonene is a colorless liquid aliphatic hydrocarbon classified as a cyclic monoterpene and is the major component in the oil of citrus fruit peels. Limonene has the molecular formula of $C_{10}H_{16}$ and the following chemical structure. The R-isomer, occurring more commonly in nature as the fragrance of oranges, is a flavoring agent in food manufacturing.

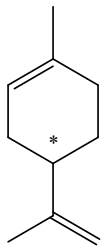


(a) Identify the chiral carbon center(s). (4 pts)

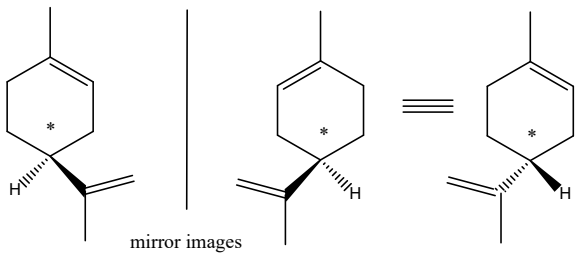
(b) Draw the optical isomers of limonene showing the 3D structure for chiral carbon center(s). (6 pts)

(Answer)

1)



2)



2. (total 12 pts)

Draw the structures of ethane, ethene, and acetylene with proper bond angles and explain their bonding by the valence bond (VB) model with orbital hybridization.

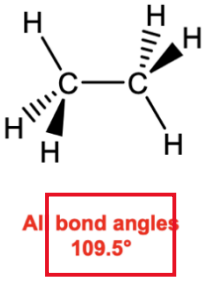
(a) Ethane (4 pts)

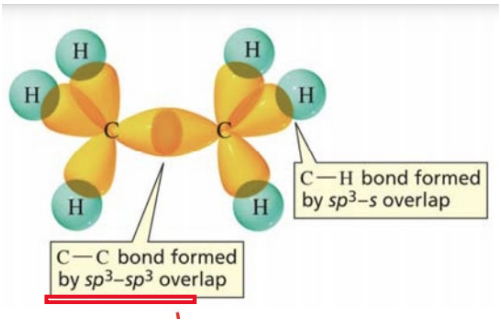
(b) Ethene (4 pts)

(c) Acetylene (4 pts)

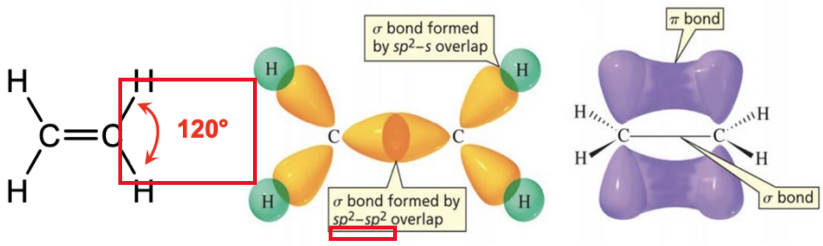
(Answer)

(a) Ethane

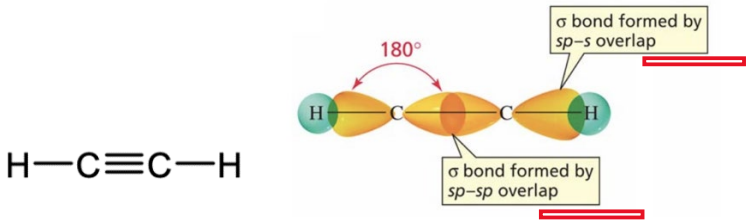




(b) Ethene



(c) Acetylene



3. (total 12 pts)

(1) Consider trans-1,3-butadiene.

(1-a) What is the total number of valence electrons? (4 pts)

How many valence electrons are involved in $\sigma -$ and $\pi -$ bonds?

(1-b) Draw a schematic diagram of HOMO and LUMO. (6 pts)

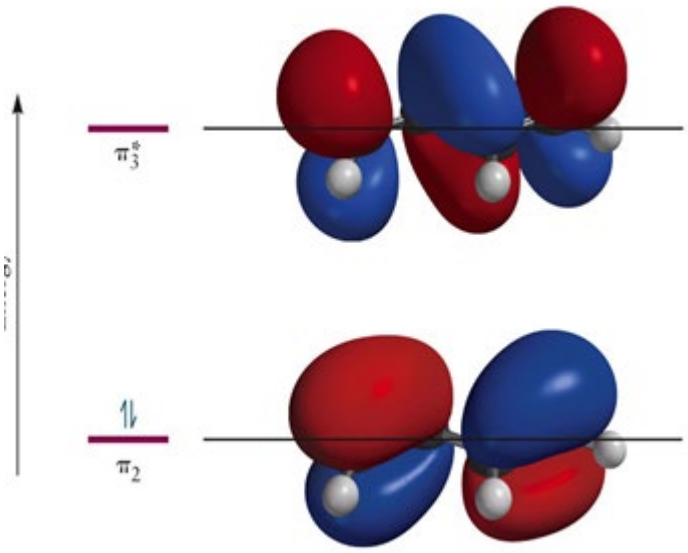
(2) Benzene exhibits greater stability than 1,3,5-hexatriene. Explain this phenomenon by identifying which molecule has the larger HOMO-LUMO energy gap. (2 pts)

Answer

(1-a) 4 pts

22 valence electrons, sigma bonds:18 electrons, pi bonds: 4 electrons

(1-b) 6 pts (3 each)



Node 표시 확실하게 해야 만점.

(2)

Benzene's pi orbitals are more delocalized than those of the linear molecule, 1,3,5-hexatriene. Thus, the bonding and antibonding interactions of benzene are greater than those of 1,3,5-hexatriene. Therefore, the HOMO-LUMO gap of benzene is greater than that of 1,3,5-hexatriene. This means that a greater energy is required to perturb the bonds of benzene than those of 1,3,5-hexatriene, and thus benzene is chemically more stable.

4. (Total 6 pts)

Complete electron configurations and fill in the blanks related to energy level structures and crystal field stabilization energies for high and low spin octahedral complexes.

Example		**(a) Mn^{2+}**	**(b) Ni^{3+}**	**(c) Ti^{2+}**
d-orbital electron configuration				
HIGH SPIN	Energy diagram	e_g —— t_{2g} ———	e_g —— t_{2g} ———	e_g —— t_{2g} ———
	CFSE			
LOW SPIN	Energy diagram	e_g —— t_{2g} ———	e_g —— t_{2g} ———	e_g —— t_{2g} ———
	CFSE			

[Solution] (1 pt each)

TABLE 8.5

Electron Configurations and Crystal Field Stabilization Energies for High- and Low-Spin Octahedral Complexes

Configuration		d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Examples		Ti^{3+}	Ti^{2+}, V^{3+}	V^{2+}, Cr^{3+}	Cr^{2+}, Mn^{3+}	Mn^{2+}, Fe^{3+}	Fe^{2+}, Co^{3+}	Co^{2+}, Ni^{3+}	Ni^{2+}, Pt^{2+}	Cu^{2+}	Zn^{2+}
HIGH SPIN	e_g	——	——	——	↑ ——	↑ ↑	↑↓ ↑	↑↓ ↑	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
	t_{2g}	↑ ——	↑ ↑ ——	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↑↓ ↑ ↑	↑↓ ↑↓ ↑	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓
	CFSE	$-\frac{2}{5}\Delta_o$	$-\frac{4}{5}\Delta_o$	$-\frac{6}{5}\Delta_o$	$-\frac{3}{5}\Delta_o$	0	$-\frac{2}{5}\Delta_o$	$-\frac{4}{5}\Delta_o$	$-\frac{6}{5}\Delta_o$	$-\frac{3}{5}\Delta_o$	0
LOW SPIN	e_g				——	——	——	↑ ——			
	t_{2g}				↑↓ ↑ ↑	↑↓ ↑↓ ↑	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓			
	CFSE	Same as high spin			$-\frac{8}{5}\Delta_o$	$-\frac{10}{5}\Delta_o$	$-\frac{12}{5}\Delta_o$	$-\frac{9}{5}\Delta_o$	Same as high spin		

CFSE, Crystal field stabilization energies.

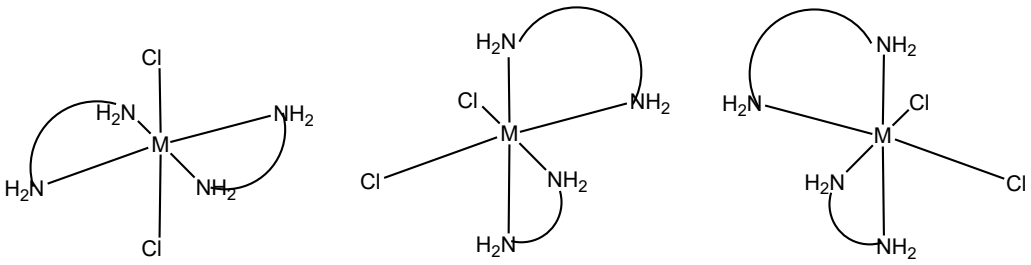
5. (Total 14 pts)

The octahedral complex $[CoCl_2(en)_2]$ Cl is a low-spin complex.

1) Name this compound
2) What is the coordination number of the complex and the oxidation state of the cobalt?
3) Determine the d-electron configuration of the cobalt.
4) Calculate the crystal field stabilization energy (CFSE) of this complex.
5) Does the complex have paramagnetic or diamagnetic properties?
6) If 3 mol of $AgNO_3$ were added to the 1 mol of the above complex, how many mol of AgCl is produced?
7) Draw all possible stereoisomers of the complex.

(Answer)

1) Dichlorobis(ethylenediamine) Cobalt (III) chloride
2) Coordination No = 6, oxidation state = +3
3) d^6 complex, 6 electrons in t_{2g}
4) CFSE = - 12/5
5) Diamagnetic
6) 1 mol
7) three isomers



6. (Total 10 pts)

The octahedral complex ions $[FeF_6]^{3-}$, $[Fe(OH_2)_6]^{3+}$, and $[Fe(CN)_6]^{3-}$ are all paramagnetic. But $[FeF_6]^{3-}$ and $[Fe(OH_2)_6]^{3+}$ are high spin and the $[Fe(CN)_6]^{3-}$ is low spin. Answer each question below.

(a) Draw an orbital energy-level diagram for each octahedral complex ion (show how to get the oxidation numbers for Fe ions in each complex). (3 pts)

(b) Predict the number of unpaired electrons for each complex. (3 pts)

(c) Place which of the complexes has the shorter absorption λ_{max} in order and explain your answer. (4 pts)

[Solution]

(a) * Electron configuration of Fe: [Ar] $3d^6\ 4s^2$

* The oxidation numbers of $[FeF_6]^{3-}$, $[Fe(OH_2)_6]^{3+}$, and $[Fe(CN)_6]^{3-}$ molecules

$[FeF_6]^{3-}$: $x + 6(-1) = -3$, $x = +3$

$[Fe(OH_2)_6]^{3+}$: $x + 6(0) = +3$, $x = +3$

$[Fe(CN)_6]^{3-}$: $x + 6(-1) = +3$, $x = +3$

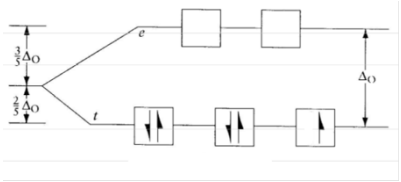
* Electron configuration of Fe^{3+}: [Ar] $3d^5$ → 5 d electrons

* The orbital energy-level diagrams of $[FeF_6]^{3-}$ and $[Fe(OH_2)_6]^{3+}$

* The configuration of *d*-electrons: $t_{2g}^3\ e_g^2$

* The orbital energy-level diagram of $[Fe(CN)_6]^{3-}$

* The configuration of *d*-electrons: t_{2g}^5

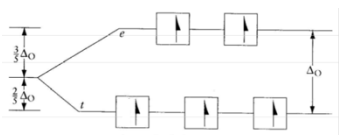


(b) The number of unpaired electrons and the magnetic property of $[FeF_6]^{3-}$, $[Fe(OH_2)_6]^{3+}$, and $[Fe(CN)_6]^{3-}$

$[FeF_6]^{3-}$: 5 unpaired electrons → paramagnetic

$[Fe(OH_2)_6]^{3+}$: 5 unpaired electrons → paramagnetic

$[Fe(CN)_6]^{3-}$: 1 unpaired electron → paramagnetic



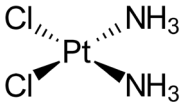
(c) $[Fe(CN)_6]^{3-}$ has the strongest field ligands of the three complexes; thus, its energy levels are split by the greatest amount. The energy of the light absorbed should be greatest, and λ_{max} should be the shortest for this ion. λ_{max} : $[FeF_6]^{3-} > [Fe(H_2O)_6]^{3-} > [Fe(CN)_6]^{3-}$

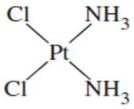
7. (Total 6 pts – 2 pts each)

Draw (i) the structure of the first member platinum-containing anti-cancer drug and (ii) the structure of its geometric isomer that does not show any anti-cancer activity. (iii) Indicate the d-orbital electron configuration of the platinum-containing anti-cancer drug.

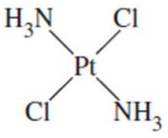
[Solution]

(i) Square planar geometry





(ii) trans isomer (name: Transplatin)



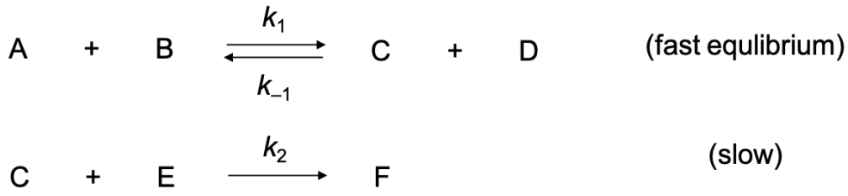
trans

(ii) d^8

8. (Total 8 pts)

Write the overall reaction and rate laws that correspond to the following reaction mechanisms. Be sure to eliminate intermediates from the answers.

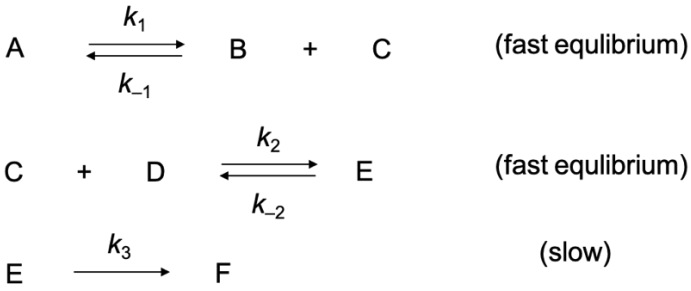
(a)



A + B + E → D + F (2 pts)

rate = k_1k_2[A][B][E] / k_{-1}[D] (2 pts)

(b)



A + D → B + F (2 pts)

rate = $k_1k_2k_3$[A][D] / $k_{-1}k_{-2}$[B] (2 pts)

9. (Total 12 pts)

The following mechanism has been proposed for the gas phase reaction of chloroform and chlorine.

step 1 $Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl(g)$ (fast)

step 2 $Cl(g) + CHCl_3(g) \xrightarrow{k_2} HCl(g) + CCl_3(g)$ (slow)

step 3 $Cl(g) + CCl_3(g) \xrightarrow{k_3} CCl_4(g)$ (fast)

1) What is the overall reaction? (2 pts)
2) What are the intermediates in the mechanism? (2 pts)
3) What is the molecularity of each of the elementary steps? (2 pts)
4) What is the rate determining step? (2 pts)
5) What is the rate law and overall order of the reaction predicted by this mechanism? (4 pts)

(Answer)

1) $Cl_2(g) + CHCl_3(g) \longrightarrow HCl(g) + CCl_4(g)$
2) $Cl(g)$, $CCl_3(g)$
3) step 1: unimolecular, step 2: bimolecular, step 3:bimolecular
4) step 2
5) Rate = $k_2[CHCl_3][Cl]$

$K_1[Cl_2] = k_{-1}[Cl]^2$, $[Cl] = \{k_1/k_{-1}\ [Cl^2]\}^{1/2}$

Rate = $k_2(k_1/k_{-1})^{1/2}\ [CHCl_3][Cl_2]^{1/2}$

Overall order is 1.5

10. (Total 10 pts)

Let's consider the following equilibrium.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C$$

Suppose the equilibrium between A and B and the equilibrium between B and C are elementary reactions. For simplicity, we assume first-order kinetics for both forward and reverse reactions. $k_1 = 10^2\ s^{-1}, k_{-1} = 10^8\ s^{-1}, k_2 = 10^9\ s^{-1}, k_{-2} = 10^4\ s^{-1}$.

(a) Calculate the equilibrium constant for the equilibrium A ⇌ C. (2 pts)

(b) Utilize the Arrhenius equation to compute ΔG_1 and ΔG_2 for the reactions A ⇌ B and B ⇌ C, respectively, while expressing these ΔG values in terms of the RT unit. Assume that the pre-exponential factors for both the forward and reverse reactions are the same. Determine which molecules A, B, C possess the highest and lowest energies. Does this energy ranking align with statement (a)? (8 pts)

Answer:

(a) Since the reaction reached the equilibrium, the forward and reverse reactions have identical rates.

$\therefore\ k_1[A] = k_{-1}[B]\ and\ k_2[B] = k_{-2}[C]$

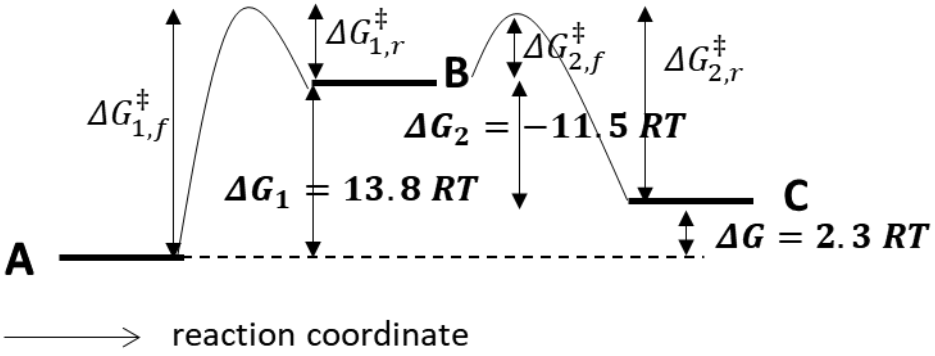
The equilibrium constant of the overall reaction $K = [C]/[A] = \frac{\frac{k_2[B]}{k_{-2}}}{\frac{k_{-1}[B]}{k_1}} = \frac{k_2}{k_{-2}}\frac{k_1}{k_{-1}} = 0.1$

(b) For A ⇌ B, $k_1 = A_1 e^{-\Delta G^{\ddagger}_{1,f}/RT}$ & $k_{-1} = A_1 e^{-\Delta G^{\ddagger}_{1,r}/RT}$ and thus $\frac{k_1}{k_{-1}} = e^{-(\Delta G^{\ddagger}_{1,f} - \Delta G^{\ddagger}_{1,r})/RT} = e^{-\Delta G_1/RT}$

Thus, $\boldsymbol{\Delta G_1 = -RT\ln(10^{-6}) = +13.8\ RT}$ **(2 pts)**

Similarly for B ⇌ C, $k_2 = A_2 e^{-\Delta G^{\ddagger}_{2,f}/RT}$ & $k_{-2} = A_2 e^{-\Delta G^{\ddagger}_{2,r}/RT}$ and thus $\frac{k_2}{k_{-2}} = e^{-(\Delta G^{\ddagger}_{2,f} - \Delta G^{\ddagger}_{2,r})/RT} = e^{-\Delta G_2/RT}$. Thus, $\boldsymbol{\Delta G_2 = -RT\ln(10^5) = -11.5\ RT}$ **(2 pts)**

Therefore, the energy profile for the overall reaction is



B has the highest energy and A has the lowest energy. (2 pt)

From (a), [C]=0.1[A] => C has a higher energy than A and thus less population of C exists in the equilibrium. Or you can also confirm ΔG = -RTlnK. (2 pt)

Physical Constants

Avogadro's number	N_A = 6.02214179 x 10^{23} mol^{-1}
Bohr radius	a_0 = 0.52917720859 Å = 5.2917720859 x 10^{-11} m
Boltzmann's constant	K_B = 1.3806504 x 10^{-23} J K^{-1}
Electronic charge	e = 1.602176487 x 10^{-19} C
Faraday constant	F = 96485.3399 C mol^{-1}
Masses of fundamental particles:	
Electron	m_e = 9.10938215 x 10^{-31} kg
Proton	m_P = 1.672621637 x 10^{-27} kg
Neutron	m_n= 1.674927211 x 10^{-27} kg
Permittivity of vacuum	ε_o = 8.854187817 x 10^{-12} C^{-2} J^{-1} m^{-1}
Planck's constant	h = 6.62606896 x 10^{-34} J s
The ratio of proton mass to electron mass	m_P / m_e = 1836.15267247
Speed of light in a vacuum	c = 2.99792458 x 10^{8} m s^{-1} (exactly)
Standard acceleration of terrestrial gravity	g = 9.80665 m s^{-2} (exactly)
Universal gas constant	R = 8.314472 J mol^{-1} K^{-1} = 0.0820574 L atm mol^{-1} K^{-1}

Values are taken from the 2006 CODATA recommended values,
as listed by the National Institute of Standards and Technology.

Conversion factors

Ångström	1 Å= 10^{-10} m
Atomic mass unit	1 u = 1.660538782 x 10^{-27} kg
	1 u = 1.492417830 x 10^{-10} J = 931.494028 MeV (energy equivalent form $E = mc^2$)
Calorie	1 cal = 4.184 J (exactly)
Electron volt	1 eV = 1.602177 x 10^{-19} J = 96.485335 kJ mol^{-1}
Foot	1 ft = 12 in = 0.3048 m (exactly)
Gallon (U. S.)	1 gallon = 4 quarts = 3.785412 L (exactly)
Liter	1 L = 10^{-3} m^{-3} = 10^3 cm^3 (exactly)
Liter-atmosphere	1 L atm = 101.325 J (exactly)
Metric ton	1 t = 1000 kg (exactly)
Pound	1 lb = 16 oz = 0.4539237 kg (exactly)
Rydberg	1 Ry = 2.17987197 x 10^{-18}J = 1312.7136 kJ mol^{-1} = 13.60569193 eV
Standard atmosphere	1 atm = 1.01325 x 10^5 Pa = 1.01325 x 10^5 kg m^{-1} s^{-2} (exactly)
Torr	1 torr = 133.3224 Pa

PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

PERIOD	GROUP 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 **H** HYDROGEN																	2 4.0026 **He** HELIUM
2	3 6.941 **Li** LITHIUM	4 9.0122 **Be** BERYLLIUM											5 10.811 **B** BORON	6 12.011 **C** CARBON	7 14.007 **N** NITROGEN	8 15.999 **O** OXYGEN	9 18.998 **F** FLUORINE	10 20.180 **Ne** NEON
3	11 22.990 **Na** SODIUM	12 24.305 **Mg** MAGNESIUM											13 26.982 **Al** ALUMINIUM	14 28.086 **Si** SILICON	15 30.974 **P** PHOSPHORUS	16 32.065 **S** SULPHUR	17 35.453 **Cl** CHLORINE	18 39.948 **Ar** ARGON
4	19 39.098 **K** POTASSIUM	20 40.078 **Ca** CALCIUM	21 44.956 **Sc** SCANDIUM	22 47.867 **Ti** TITANIUM	23 50.942 **V** VANADIUM	24 51.996 **Cr** CHROMIUM	25 54.938 **Mn** MANGANESE	26 55.845 **Fe** IRON	27 58.933 **Co** COBALT	28 58.693 **Ni** NICKEL	29 63.546 **Cu** COPPER	30 65.39 **Zn** ZINC	31 69.723 **Ga** GALLIUM	32 72.64 **Ge** GERMANIUM	33 74.922 **As** ARSENIC	34 78.96 **Se** SELENIUM	35 79.904 **Br** BROMINE	36 83.80 **Kr** KRYPTON
5	37 85.468 **Rb** RUBIDIUM	38 87.62 **Sr** STRONTIUM	39 88.906 **Y** YTTRIUM	40 91.224 **Zr** ZIRCONIUM	41 92.906 **Nb** NIOBIUM	42 95.94 **Mo** MOLYBDENUM	43 (98) **Tc** TECHNETIUM	44 101.07 **Ru** RUTHENIUM	45 102.91 **Rh** RHODIUM	46 106.42 **Pd** PALLADIUM	47 107.87 **Ag** SILVER	48 112.41 **Cd** CADMIUM	49 114.82 **In** INDIUM	50 118.71 **Sn** TIN	51 121.76 **Sb** ANTIMONY	52 127.60 **Te** TELLURIUM	53 126.90 **I** IODINE	54 131.29 **Xe** XENON
6	55 132.91 **Cs** CAESIUM	56 137.33 **Ba** BARIUM	57-71 **La-Lu** Lanthanide	72 178.49 **Hf** HAFNIUM	73 180.95 **Ta** TANTALUM	74 183.84 **W** TUNGSTEN	75 186.21 **Re** RHENIUM	76 190.23 **Os** OSMIUM	77 192.22 **Ir** IRIDIUM	78 195.08 **Pt** PLATINUM	79 196.97 **Au** GOLD	80 200.59 **Hg** MERCURY	81 204.38 **Tl** THALLIUM	82 207.2 **Pb** LEAD	83 208.98 **Bi** BISMUTH	84 (209) **Po** POLONIUM	85 (210) **At** ASTATINE	86 (222) **Rn** RADON
7	87 (223) **Fr** FRANCIUM	88 (226) **Ra** RADIUM	89-103 **Ac-Lr** Actinide	104 (261) **Rf** RUTHERFORDIUM	105 (262) **Db** DUBNIUM	106 (266) **Sg** SEABORGIUM	107 (264) **Bh** BOHRIUM	108 (277) **Hs** HASSIUM	109 (268) **Mt** MEITNERIUM	110 (281) **Uun** UNUNNILIUM	111 (272) **Uuu** UNUNUNIUM	112 (285) **Uub** UNUNBIUM		114 (289) **Uuq** UNUNQUADIUM				

GROUP NUMBERS IUPAC RECOMMENDATION (1985) — GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)

ATOMIC NUMBER — 5 — RELATIVE ATOMIC MASS (1) 10.811

SYMBOL — B

BORON — ELEMENT NAME

LANTHANIDE

6	57 138.91 **La** LANTHANUM	58 140.12 **Ce** CERIUM	59 140.91 **Pr** PRASEODYMIUM	60 144.24 **Nd** NEODYMIUM	61 (145) **Pm** PROMETHIUM	62 150.36 **Sm** SAMARIUM	63 151.96 **Eu** EUROPIUM	64 157.25 **Gd** GADOLINIUM	65 158.93 **Tb** TERBIUM	66 162.50 **Dy** DYSPROSIUM	67 164.93 **Ho** HOLMIUM	68 167.26 **Er** ERBIUM	69 168.93 **Tm** THULIUM	70 173.04 **Yb** YTTERBIUM	71 174.97 **Lu** LUTETIUM

ACTINIDE

7	89 (227) **Ac** ACTINIUM	90 232.04 **Th** THORIUM	91 231.04 **Pa** PROTACTINIUM	92 238.03 **U** URANIUM	93 (237) **Np** NEPTUNIUM	94 (244) **Pu** PLUTONIUM	95 (243) **Am** AMERICIUM	96 (247) **Cm** CURIUM	97 (247) **Bk** BERKELIUM	98 (251) **Cf** CALIFORNIUM	99 (252) **Es** EINSTEINIUM	100 (257) **Fm** FERMIUM	101 (258) **Md** MENDELEVIUM	102 (259) **No** NOBELIUM	103 (262) **Lr** LAWRENCIUM

(1) Pure Appl. Chem., **73**, No. 4, 667-683 (2001)

Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@nettlinx.com)

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