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U F m G

Registration Number:

QUESTIONS BOOKLET

TEST OF GENERAL KNOWLEDGE ON CHEMISTRY FOR APPLICANTS TO THE GRADUATE PROGRAM OF THE DEPARTMENT OF CHEMISTRY – 2nd TERM/2016

JUNE 20th, 2016

INSTRUCTIONS

- Read carefully the entire test.
- Each chosen question must be answered in the appropriate sheet of the answer booklet.
- Both question and answer booklets are required to be returned upon completion of the test.
- **Any electronic device must be turned off during the test.**

CANDIDATES FOR MASTER OF SCIENCE DEGREE
- Choose only two (02) questions in each area to answer. At the end, you will have answered eight (08) QUESTIONS.
- WARNING: If you answer THREE (03) questions of the same area, it will be evaluated only the TWO (02) formers.

CANDIDATES FOR DOCTOR OF SCIENCE DEGREE
- Choose one (01) question in each area and other two (02) questions from any area to answer. At the end, you will have answered six (06) QUESTIONS.

AREA OF KNOWLEGDE: ANALYTICAL CHEMISTRY   *AREA 1*

QUESTION 1A

An analyst prepared a 3.000 % (w/v) aqueous acetic acid (H_3CCOOH) solution and titrated 50.00 mL of this solution using sodium hydroxide 0.1000 mol L^{-1} standard solution as titrant. During the process, the pH of the medium was monitored through a pH meter with glass membrane electrode.

a) What was the pH value of the medium indicated in pH meter when the titration reached the equivalence point?

b) What should be the pH of the turning point (titration end point) of an theoretical indicator to provide a maximum error of +1.5% for the titration?

Important information: pKa (H_3CCOOH) = 4.75

AREA OF KNOWLEGDE: ANALYTICAL CHEMISTRY   *AREA 1*

QUESTION 1B

Consider a solution containing 0.05 mol L^{-1} of Ag^+ and 0.05 mol L^{-1} of Pb^{2+}, which was titrated with a potassium oxalate standard solution ($K_2C_2O_4$).

a) Which cation will precipitate first? Explain presenting calculations to prove your answer, if necessary.

b) Is it possible to precipitate these species selectively? Present all calculations that prove your answer.
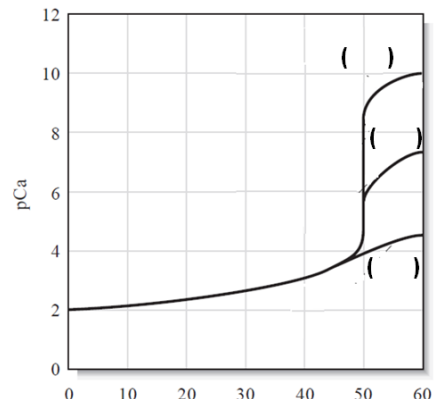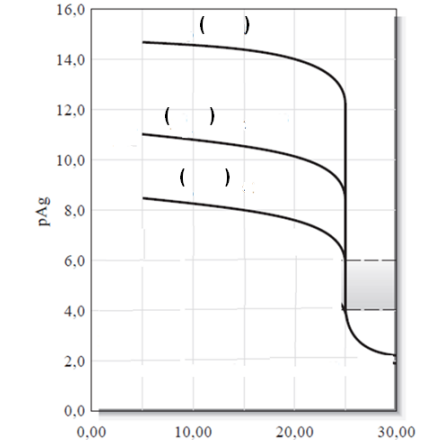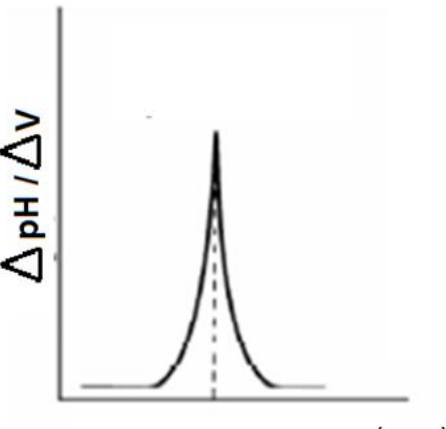
Important: To achieve an efficient separation it is necessary that the remaining concentration of the first cation precipitated does not exceed 0.1% of its analytical concentration when the precipitation of the second cation initiate.

  Important information: $K_{sp} Ag_2(C_2O_4) = 3.5 \times 10^{-11}$ $K_{sp} Pb(C_2O_4) = 8.5 \times 10^{-9}$

AREA OF KNOWLEGDE: ANALYTICAL CHEMISTRY   *AREA 1*

QUESTION 1C

Figures below present titration curves using different methodologies. Complete the parenthesis "(......)" in the graphics, using the options (letter) located at the right-side of each figure.

Volume of tritant (EDTA, 0.0100 mol L^{-1} / mL)	(A) pH of titrated solution = 8.0 (B) pOH of titrated solution = 8.0 (C) pH of titrated solution = 10.0 (D) pKa of acetic acid = 1.8×10^{-5}
Volume of tritant (AgNO$_3$, 0.100 mol L^{-1} / mL)	(E) AgCl ($K_{sp} = 1.8 \times 10^{-10}$) (F) AgBr ($K_{sp} = 5.2 \times 10^{-13}$) (G) AgI ($K_{sp} = 8.3 \times 10^{-17}$)
Volume of tritant / mL ( )	(H) EDTA (I) HCl (J) NaOH (K) AgNO$_3$

AREA OF KNOWLEGDE: ANALYTICAL CHEMISTRY   *AREA 1*

List of Equations:

$K' = \dfrac{K}{\alpha_M \alpha_L}$	$\alpha_0 = \dfrac{1}{(1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n)}$
$\alpha_1 = \beta_1 \alpha_0 [L]$	$\alpha_n = \beta_n \alpha_0 [L]^n$
$\alpha_M = [M]/c_T$	$\beta_n = \dfrac{[ML_n]}{[M][L]^n} = K_1 K_2 \ldots K_n$
$[H^+]^2 + K_a[H^+] - K_a C_a = 0$	$[H^+] = \sqrt{K_a C_a}$
$[H^+] = K_a\left(\dfrac{C_a}{C_b}\right)$	$pH = pK_a - \log\left(\dfrac{C_a}{C_b}\right)$
$K_w = K_a K_b = [H_3O^+][OH^-] = 1.0x10^{-14}$	$S = \dfrac{K_{ps}}{[M]}\left(1 + \dfrac{[H^+]}{K_{a2}} + \dfrac{[H^+]^2}{K_{a1}K_{a2}}\right)$
$\log K = \dfrac{n(E^0_{cathode} - E^0_{anode})}{0.0592}$	$E = E^0 - \dfrac{0.0592}{n}\log\dfrac{[\mathrm{Re}\,d]}{[Ox]}$

AREA OF KNOWLEGDE: INORGANIC CHEMISTRY   *AREA 2*

QUESTION 2A

Do what you are asked in each item below.

a) A mineral group has the general formula AB_2O_4, wherein the species A and B represent metal ions. Considering that the mineral is the hausmannite (Mn_3O_4), containing Mn^{2+} and Mn^{3+} ions, indicate the kind of coordination (tetrahedral or octahedral) for each cation. Justify your answer by presenting the energy diagrams and arguments of Crystal-Field Theory (CFT).

b) Consider the coordenation compounds bellow:
I. hexaamminecobalt(II) chloride
II. hexaamminecobalt(III) chloride
III. tetraaminecobalt(II) chloride

Arrange these complexes in ascending order of the ligand-field splitting parameter. Justify your answer.

AREA OF KNOWLEGDE: INORGANIC CHEMISTRY   *AREA 2*

QUESTION 2B

Crystal-Field Theory (CFT) is a model which can be used to explain thermodynamic, structural, spectroscopic and magnetic properties. The figure below contains the variation of values of the lattice energies for the third-period metal dichlorides. Consider CFT arguments and explain why:

a) VCl_2 is the compound with the greatest deviation of the line.

b) $CaCl_2$, $MnCl_2$, and $ZnCl_2$ are the compounds with the smaller deviation of the line.
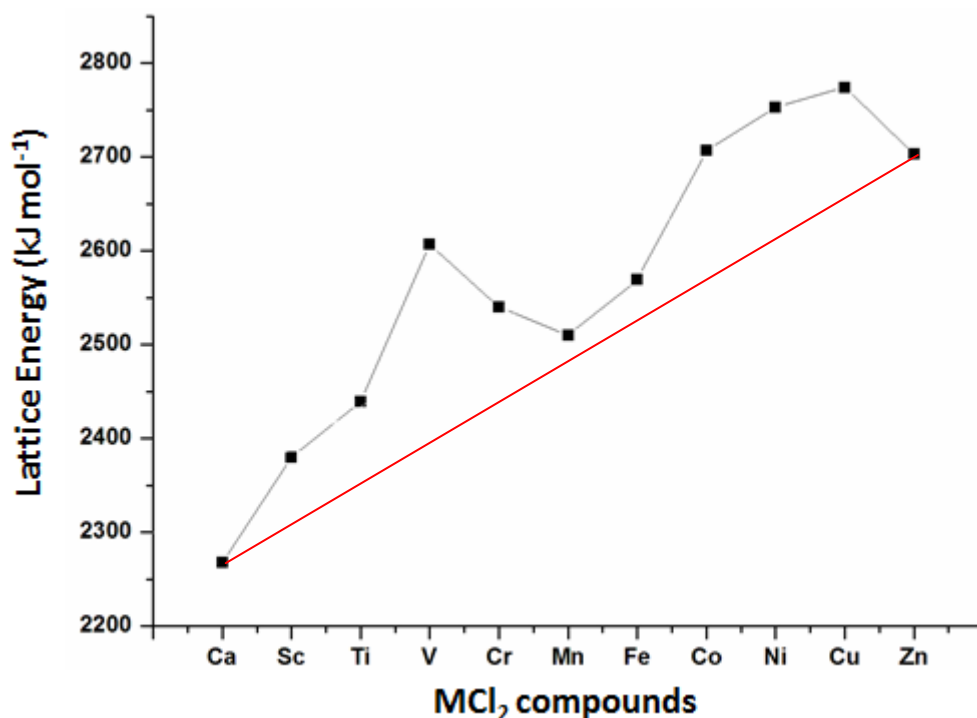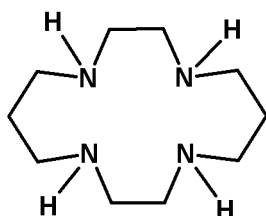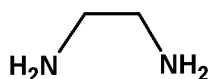
c) $ZnCl_2$ is a white solid.

Figure 1. Values of the lattice energies for the third-period metal dichlorides. The line describes the theoretical behavior for the values of Lattice Energy.

AREA OF KNOWLEGDE: INORGANIC CHEMISTRY   *AREA 2*
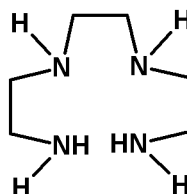
QUESTION 2C

Consider the structures of the following ligands:

(a)   (b)   (c)   (d)

a) Arrange the ligands in ascending order with respect to the capacity to form complexes with high thermodynamic stability (higher value of formation constant).

b) Indicate the ligands that favor the occurrence of the chelate effect.

c) Considering that a metal ion with electronic configuration [Kr] $4d^8$ forms a complex with the ligand shown in (a), indicate how many chelate rings are formed and the number of atoms for each of these rings.

d) Glycinate ($H_2NCH_2COO^-$) is a bidentate ligand and forms octahedral complexes when reacts with Co^{3+} ion. Write the structures of all isomers which may be formed.

QUESTION 3A

The structure of *cis*-1,3-dimethylcyclohexane is presented below.
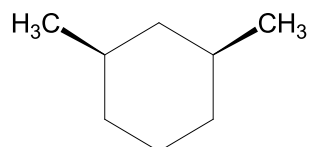
a) Represent the possible chain conformers and show explicitly all bonds between the ring carbon atoms and H atoms, as well as the bonds between the ring carbon atoms and the methyl group carbons. Explain in details the relative stability of these conformers and indicate their distribution at the conformational equilibrium.

b) Does *cis*-1,3-dimethylcyclohexane has one or more stereogenic centers? In positive case, indicate the stereogenic center(s) of the molecule, as well as the configuration of the stereogenic center(s).

c) Is *cis*-1,3-dimethylcyclohexane optically active? Explain your answer.

QUESTION 3B

Two possible conditions for acid-base reactions are presented below. The solvent used for the reactions are indicated above the arrows.

a) $CH_3CH_2CH_2CH_2$—C≡C—H   + $NaNH_2$ $\xrightarrow{\;NH_3\;(liquid)\;}$

b) $CH_3CH_2CH_2CH_2$—C≡C—H   + $NaNH_2$ $\xrightarrow{\qquad\qquad}$ ⌢⌣⌢OH
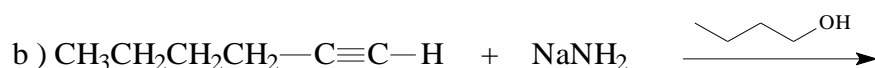
Write an equation, using the curved-arrow notation, for the forward and reverse acid-base reactions that will take place when each of the above compounds (solutions) are mixed. Indicate the equilibrium for both reactions. Indicate the valence electrons of all atoms involved in the acid-base reactions. If the atom is charged, indicate its respective charge.

To answer this question, use the table presented below, that contains the pK_a values for some compounds or the approximate pK_a values value for a few classes of compounds.

Acid	NH_3	NH_4^+	H_2O	H_3O^+	$R–OH_2^+$	$R–OH$	$R–C≡CH$
pK_a	38	9.2	15.7	-1.74	-2	16	25

QUESTION 3C

When the compound **I** is treated with sodium methoxide ($CH_3O^-Na^+$) in methanol, a mixture of compounds is obtained (**II** and **III**), being **II** the major compound. When the same compound **I** is treated with potassium *tert*-butoxide [$(CH_3)_3CO^-K^+$] in *tert*-butanol, the same mixture of compounds (**II** and **III**) is obtained, but **III** is now the major compound. When compounds **II** and **III** are treated in the same conditions *(route 3)*, alcohols **IV** and **V** are obtained, respectively. However, when both compounds (**II** and **III**) are treated in conditions of *route 4*, they provide the same compound **VI**. Based on this information answer the following questions:

a) Give the structures of compounds **I**, **II**, **III** and **VI**.

b) Explain the difference in proportion to formation of the compounds **I** and **II** in the routes **1** and **2**.

c) Explain why in the route 4, in contrary of route 3, there is the formation of just one product (compound **VI**).

AREA OF KNOWLEGDE: PHYSICAL CHEMISTRY   *AREA 4*
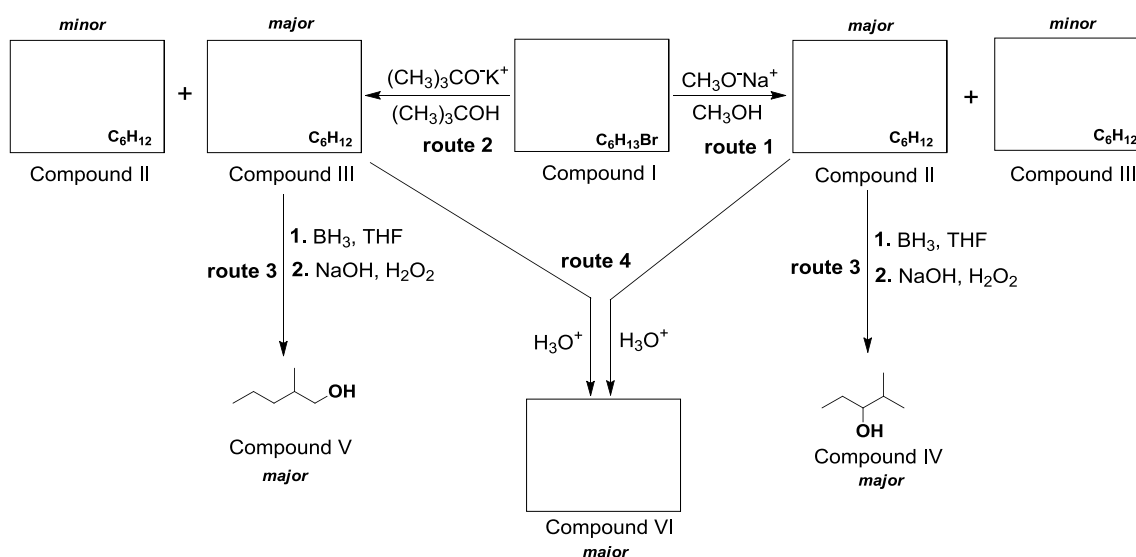
QUESTION 4A

2 mol of monoatomic ideal gas is carried through a Carnot cycle, operating between the temperatures $T_1 = 227\ ^oC$ and $T_2 = 27\ ^oC$. If $V_1 = 5\ dm^3$ and $V_2 = 10\ dm^3$, calculate the thermodynamic quantities **q**, **w** and ΔU in each step. In addition, calculate the Carnot efficiency and draw the diagram of the cycle using T and H as variables.
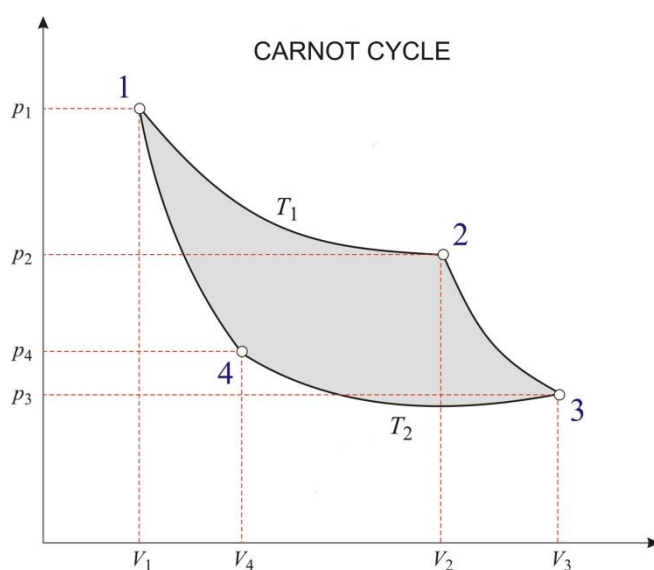
QUESTION 4B

Construct the phase diagram for a compound **A** (*i.e.* one component system) from the following data: (*i*) compound **A** exists in two solid forms, S_1 and S_2, where the densities of both the solid forms are greater than that of liquid phase, (*ii*) the melting temperature of **A** is 20.2 $^{\circ}$C under its own vapor pressure of 5.0 mmHg, (*iii*) phases S_1 and S_2 and liquid are at equilibrium at 1000 atm and 70.2 $^{\circ}$C, (*iv*) the transition temperature of solid phases increases with the increase of pressure, (*v*) the boiling temperature of liquid is 140 $^{\circ}$C (at 1 atm), and (*vi*) if the solid form S_1 is heated slowly under its own vapor pressure it is converted to S_2 at 15 $^{\circ}$C.

QUESTION 4C

The specific heat capacity of methane $CH_4(g)$ can be expressed by the equation:

$C_p = 3.422 + 17.845 \times 10^{-3}\ T - 41.65 \times 10^{-7}\ T^2$ (cal $^oC^{-1}$ mol^{-1}).

Calculate the entropy variation of 2 mol of gas when submitted to heating from 300 to 600 K at (a) constant pressure and (b) constant volume.

AREA OF KNOWLEGDE: PHYSICAL CHEMISTRY   *AREA 4*

Form

$R = 0.082057$ atm L mol^{-1} K^{-1} = 8.3143 J mol^{-1} K^{-1} = 1.98717 cal K^{-1} mol^{-1} = 2.0769 kPa m^3 kg^{-1} K^{-1}

$N_A = 6.02252$ x 10^{23} particles mol^{-1}

1 Pa = 1 N m^{-1} = 10^{-5} bar = $(1 \times 10^{-5} / 1.01325)$ atm   1atm = 760 mmHg

1 atm L = 101.325 Joule

$$Z = pV_m/RT \qquad\qquad pV_m = RT \qquad\qquad (p + a/V_m^2)(V_m - b) = RT$$

$$pV_m = RT[1 + B(T)/V_m + C(T)/V_m^2 + D(T)/V_m^3 + ...]$$

$$dU = \delta Q + \delta W \qquad\qquad H = U + pV \qquad\qquad dQ_{rev} = C_p dT$$

$$C_V = (\partial U/\partial T)_V \qquad\qquad C_P = (\partial H/\partial T)_P \qquad\qquad C_{P,m} - C_{V,m} = R$$

$$pV^{\gamma} = \text{cte} \qquad\qquad T_2 = T_1(V_1/V_2)^{nR/C_V}$$

$$\alpha = (1/V)(\partial V/\partial T)_P \qquad\qquad \kappa_T = -(1/V)(\partial V/\partial P)_T$$

$$dS = \delta Q_{rev} / T$$

$$G = H - TS \qquad\qquad A = U - TS \qquad\qquad dG = Vdp - SdT$$

$$dH = Vdp + TdS \qquad\qquad \Delta_{transition}S = \frac{\Delta_{transition}H}{T_{transition}}$$

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) = C_v \ln\left(\frac{T_f}{T_i}\right) = C_p \ln\left(\frac{T_f}{T_i}\right) \qquad \text{For solid and liquids}$$

$$\int d\ln P = \frac{\Delta H}{R}\frac{1}{T^2} dT$$

If f is a function of x and y , then:

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$\ln\left(\frac{P}{P'}\right) = -\frac{\Delta_{transition}H_m^{\Theta}}{RT} + \frac{\Delta_{transition}S_m^{\Theta}}{T} \qquad ou \qquad \ln\left(\frac{P}{P'}\right) = -\frac{\Delta_{transition}H_m^{\Theta}}{RT} + \frac{\Delta_{transition}H_m^{\Theta}}{RT'}$$

Gibbs Phase rule: F = C − P + 2   F, freedom, C, components, P, phases.

Periodic Table of the Elements

Legend:
Atomic Number | Valence Charge
Symbol
Name
Atomic Mass

Group 1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H^{+1} Hydrogen 1.008																	2 He^{0} Helium 4.003
3 Li^{+1} Lithium 6.941	4 Be^{+2} Beryllium 9.012											5 B^{+3} Boron 10.811	6 $C^{+4,-4}$ Carbon 12.011	7 $N^{+5,-3}$ Nitrogen 14.007	8 O^{-2} Oxygen 15.999	9 F^{-1} Fluorine 18.998	10 Ne^{0} Neon 20.180
11 Na^{+1} Sodium 22.990	12 Mg^{+2} Magnesium 24.305											13 Al^{+3} Aluminum 26.982	14 Si^{+4} Silicon 28.086	15 $P^{+5,+3,-3}$ Phosphorus 30.974	16 $S^{+6,-2}$ Sulfur 32.066	17 Cl^{-1} Chlorine 35.453	18 Ar^{0} Argon 39.948
19 K^{+1} Potassium 39.098	20 Ca^{+2} Calcium 40.078	21 Sc^{+3} Scandium 44.956	22 Ti^{+4} Titanium 47.88	23 $V^{+5,+4,+3}$ Vanadium 50.942	24 $Cr^{+6,+3,+2}$ Chromium 51.996	25 $Mn^{+7,+4,+2}$ Manganese 54.938	26 $Fe^{+3,+2}$ Iron 55.933	27 $Co^{+3,+2}$ Cobalt 58.933	28 Ni^{+2} Nickel 58.693	29 $Cu^{+2,+1}$ Copper 63.546	30 Zn^{+2} Zinc 65.39	31 Ga^{+3} Gallium 69.732	32 Ge^{+4} Germanium 72.61	33 $As^{+5,+3}$ Arsenic 74.922	34 $Se^{+4,-2}$ Selenium 78.972	35 $Br^{+5,-1}$ Bromine 79.904	36 Kr^{0} Krypton 84.80
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y^{+3} Yttrium 88.906	40 Zr^{+4} Zirconium 91.224	41 Nb^{+5} Niobium 92.906	42 $Mo^{+6,+4}$ Molybdenum 95.95	43 $Tc^{+7,+4}$ Technetium 98.907	44 $Ru^{+4,+3}$ Ruthenium 101.07	45 Rh^{+3} Rhodium 102.906	46 $Pd^{+4,+2}$ Palladium 106.42	47 Ag^{+1} Silver 107.868	48 Cd^{+2} Cadmium 112.411	49 In^{+3} Indium 114.818	50 $Sn^{+2,-4}$ Tin 118.71	51 Sb^{+3} Antimony 121.760	52 Te^{+4} Tellurium 127.6	53 $I^{+5,-1}$ Iodine 126.904	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba^{+2} Barium 137.327	57-71	72 Hf^{+4} Hafnium 178.49	73 Ta^{+5} Tantalum 180.948	74 $W^{+6,+4}$ Tungsten 183.85	75 $Re^{+5,+4,+3}$ Rhenium 186.207	76 Os^{+4} Osmium 190.23	77 $Ir^{+4,+3}$ Iridium 192.22	78 $Pt^{+4,+2}$ Platinum 195.08	79 Au^{+3} Gold 196.967	80 $Hg^{+2,+1}$ Mercury 200.59	81 $Tl^{+3,+1}$ Thallium 204.383	82 Pb^{+2} Lead 207.2	83 Bi^{+3} Bismuth 208.980	84 Po^{+4} Polonium [208.982]	85 At^{-1} Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra^{+2} Radium 226.025	89-103	104 Rf^{unk} Rutherfordium [261]	105 Db^{unk} Dubnium [262]	106 Sg^{unk} Seaborgium [266]	107 Bh^{unk} Bohrium [264]	108 Hs^{unk} Hassium [269]	109 Mt^{unk} Meitnerium [268]	110 Ds^{unk} Darmstadtium [269]	111 Rg^{unk} Roentgenium [272]	112 Cn^{unk} Copernicium [277]	113 Uut^{unk} Ununtrium unknown	114 Fl^{unk} Flerovium [289]	115 Uup^{unk} Ununpentium unknown	116 Lv^{unk} Livermorium [298]	117 Uus^{unk} Ununseptium unknown	118 Uuo^{unk} Ununoctium unknown

Lanthanide Series

57 La^{+3} Lanthanum 138.906	58 Ce^{+3} Cerium 140.115	59 Pr^{+3} Praseodymium 140.908	60 Nd^{+3} Neodymium 144.24	61 Pm^{+3} Promethium 144.913	62 Sm^{+3} Samarium 150.36	63 Eu^{+3} Europium 151.966	64 Gd^{+3} Gadolinium 157.25	65 Tb^{+3} Terbium 158.925	66 Dy^{+3} Dysprosium 162.50	67 Ho^{+3} Holmium 164.930	68 Er^{+3} Erbium 167.26	69 Tm^{+3} Thulium 168.934	70 Yb^{+3} Ytterbium 173.04	71 Lu^{+3} Lutetium 174.967

Actinide Series

89 Ac^{+3} Actinium 227.028	90 Th^{+4} Thorium 232.038	91 Pa^{+5} Protactinium 231.036	92 U^{+6} Uranium 238.029	93 Np^{+7} Neptunium 237.048	94 $Pu^{+7,+4}$ Plutonium 244.064	95 Am^{+3} Americium 243.061	96 Cm^{+3} Curium 247.070	97 Bk^{+3} Berkelium 247.070	98 Cf^{+3} Californium 251.080	99 Es^{+3} Einsteinium [254]	100 Fm^{+3} Fermium 257.095	101 Md^{+3} Mendelevium 258.1	102 No^{+2} Nobelium 259.101	103 Lr^{+3} Lawrencium [262]